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THE INTERNATIONAL SERIES OF MONOGRAPHS ON PHYSICS

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Already Published

- THE THEORY OF ELECTRIC AND MAGNETIC SUSCEPTIBILITIES. By J. H. VAN VLECK. 1932.
- THE THEORY OF ATOMIC COLLISIONS. By N. F. MOTT and H. S. W. MASSEY. *Second edition*. 1919.
- RELATIVITY, THERMODYNAMICS, AND COSMOLOGY. By R. C. TOLMAN. 1934.
- CHEMICAL KINETICS AND CHAIN REACTIONS. By N. SEMENOV. 1935.
- RELATIVITY, GRAVITATION, AND WORLD STRUCTURE. By E. A. MILNE. 1935.
- KINEMATIC RELATIVITY. A Sequel to *Relativity, Gravitation, and World Structure*. By E. A. MILNE. 1948.
- THE QUANTUM THEORY OF RADIATION. By W. HEITLER. *Second edition*. 1945.
- THEORETICAL ASTROPHYSICS: ATOMIC THEORY AND THE ANALYSIS OF STELLAR ATMOSPHERES AND ENVELOPES. By S. ROSSELAND. 1936.
- ECLIPSES OF THE SUN AND MOON. By SIR FRANK DYSON and R. V. D. R. WOOLLEY. 1937.
- THE PRINCIPLES OF STATISTICAL MECHANICS. By R. C. TOLMAN. 1938.
- ELECTRONIC PROCESSES IN IONIC CRYSTALS. By N. F. MOTT and R. W. GURNEY. *Second edition*. 1948.
- GEOMAGNETISM. By S. CHAPMAN and J. BARTELS. 1940. 2 vols.
- THE SEPARATION OF GASES. By M. RUHEMANN. *Second edition*. 1949.
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- THE PRINCIPLES OF QUANTUM MECHANICS. By P. A. M. DIRAC. *Third edition*. 1917.
- THEORY OF ATOMIC NUCLEUS AND NUCLEAR ENERGY SOURCES. By G. GAMOW and C. L. CRITCHFIELD. 1949. *Being the third edition of* STRUCTURE OF ATOMIC NUCLEUS AND NUCLEAR TRANSFORMATIONS.
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- THEORY OF PROBABILITY. By HAROLD JEFFREYS. *Second edition*. 1948.
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- COSMICAL ELECTRODYNAMICS. By H. ALFVÉN. 1950.
- COSMIC RAYS. By L. JÁNOSSY. *Second edition*. 1950.
- THE FRICTION AND LUBRICATION OF SOLIDS. By F. P. BOWDEN and D. TABOR. 1950.

PREFACE

THERE are very many directions in which research in physics and related subjects depends on a knowledge of the rates of collision processes which occur between electrons, ions, and neutral atoms and molecules. This has become increasingly apparent in recent times in connexion with developments involving electric discharges in gases, atmospheric physics, and astrophysics. Apart from this the subject is of great intrinsic interest, playing a leading part in the establishment of quantum theory and including many aspects of fundamental importance in the theory of atomic structure. It therefore seems appropriate to describe the present state of knowledge of the subject and this we have attempted to do in the present work.

We have set ourselves the task of describing the experimental techniques employed and the results obtained for the different kinds of collision phenomena which we have considered within the scope of the book. While no attempt has been made to provide at all times the detailed mathematical theory which may be appropriate for the interpretation of the phenomena, wherever possible the observations have been considered against the available theoretical background, results obtained by theory have been included, and a physical account of the different theories has been given. In some cases, not covered in *The Theory of Atomic Collisions*, a more detailed description for a particular theory has been provided. At all times the aim has been to give a balanced view of the subject, from both the theoretical and experimental standpoints, bringing out as clearly as possible the well-established principles which emerge and the obscurities and uncertainties, many as they are, which still remain.

It was inevitable that some rigid principles of exclusion had to be practised in selecting from the great wealth of available material. It was first decided that phenomena involving the collisions of particles with high energies would not be considered, and that other phenomena associated with the properties of atomic nuclei such as the behaviour of slow neutrons would also be excluded. It was also natural to regard work on chemical kinetics as such, although clearly involving atomic collision phenomena, as outside the scope of the book, but certain of the more fundamental aspects are included. Phenomena involving neutral atoms or molecules only have otherwise been included on an equal footing with those involving ions or electrons. A further extensive

class of phenomena have been excluded by avoiding any discussion of collision processes occurring within solids or liquids, confining the work to processes occurring in the gas phase or at a gas-solid interface. Among the latter phenomena electron diffraction at a solid surface has been rather arbitrarily excluded as it is a subject already adequately dealt with in other texts. Secondary electron emission and related effects are, however, included.

By limiting the scope of the book in this way it has just been possible to provide a fairly comprehensive account of the subjects involved. It is perhaps too much to hope that even within these limitations nothing of importance has been missed, but it is believed that the account given is fairly complete. Extensive tables of observed and theoretical data have been given throughout for reference purposes and the extent to which the data given are likely to be reliable has been indicated. Every effort has been made to provide a connected and systematic account but it is inevitable that there will be differences of opinion as to the relative weight given to the various parts of the subject and to the different contributions which have been made to it.

We are particularly indebted to Professor D. R. Bates for reading and criticizing much of the manuscript and for many valuable suggestions. Dr. R. A. Buckingham has also assisted us very much in this direction while Dr. Abdelnabi has checked some of the proofs. We also wish to express our appreciation of the remarkable way in which the Oxford University Press maintained the high standard of their work under the present difficult circumstances.

H. S. W. M.

E. H. S. B.

LONDON
August 1951

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I

THE PASSAGE OF ELECTRONS THROUGH GASES: TOTAL COLLISION CROSS-SECTION, ITS DEFINITION AND MEASUREMENT

1. Classification of collisions

A NUMBER of different effects may result from the encounter of an electron with a gas atom or molecule. These may first be distinguished as elastic, inelastic, superelastic, or radiative.

In an elastic collision no energy exchange takes place between the internal motion of the atom and the electron. The electron loses some energy in such encounters, but only because the finite ratio of the mass m of the electron to that M of the atom results in the transfer of some velocity to the centre of mass of the atom or molecule as a whole. As a result a fraction of order m/M of the initial kinetic energy of the electron is lost in an elastic collision (cf. § 5.1). This is always less than 10^{-3} so may be neglected for many purposes. Except when otherwise stated, we shall assume henceforward that an electron loses no energy in an elastic collision with an atom.

In an inelastic collision some kinetic energy is lost by the electron in exciting internal motion in the atom. Further classification of such cases may be carried out by distinguishing the state of internal motion excited. First of all the broad distinction may be made between ionizing and non-ionizing impacts, depending on whether or not sufficient energy is transferred to lead to ejection of one or more electrons from the atom. Non-ionizing inelastic collisions will involve excitation of distinct atomic states so that specification of the state excited provides still further classification. Ionizing impacts may be analysed further in terms of the number and energy of the electrons ejected from the atom.

Superelastic collisions can only occur between an electron and an excited atom and are such that the electron gains energy from the internal motion of the atom. This is clearly only possible if the energy of the internal motion of the atom before the impact is not already a minimum, i.e. the atom is excited. Important instances of collisions of this type occur between electrons and metastable atoms.

Collisions may also occur in which electromagnetic radiation is emitted. They are essentially inelastic as far as the electron is concerned, but differ in that the whole or part of the additional energy is lost as

radiation. If the loss is great enough, the electron may be captured to form a negative ion.

Provided the electron has sufficient energy to produce an inelastic collision it is roughly true that the proportion of impacts is not far from evenly divided between elastic and inelastic types (cf. Chap. III, § 3.8). Collisions involving radiation are rare compared with other types of encounter, but are of importance in certain phenomena (see Chap. VI, § 2). We must now discuss how to represent quantitatively the chance that an electron should make an encounter of any specified type.

2. The concept of collision cross-section

Consider a parallel beam of electrons of homogeneous velocity passing through a hypothetical gas consisting of solid spherical atoms of cross-sectional area Q cm.² If there are N such atoms/c.c. the chance that an electron will make a collision in moving a small distance δx cm. through the gas will be $NQ \delta x$. Regarding any such impact as removing an electron from the beam, the amount of the beam current strength lost in traversing a distance δx from a point P will be given by

$$\delta I = NQI_P \delta x,$$

where I_P is the current strength at P . Hence, on integration we have, if P is at a distance x from O ,

$$I_P = I_0 e^{-NQx}.$$

If I_P/I_0 is measured as a function of x and N , Q may thus be found.

Now we can imagine an experiment carried out in an actual gas in which similar measurements are made. A beam of electrons of homogeneous velocity is fired into the gas. In traversing a certain distance x in the gas a fraction, proportional to x , of the electrons will be deviated from their original paths and/or lose energy by collisions with the gas atoms. All electrons so affected are considered to be lost from the beam. If measurements are made of the rate at which the current remaining in the beam varies with x , it will again be found that

$$I = I_0 e^{-\alpha x},$$

where α can be regarded as an absorption coefficient of the gas for the electron beam. If p is the gas pressure in mm. Hg, then

$$N = 2.7 \times 10^{19} p / 760,$$

and we may derive from α an effective collision cross-section Q , where

$$Q = \alpha / N = 2.81 \times 10^{-17} \alpha / p \text{ cm.}^2$$

This quantity is called the total collision cross-section of the gas atoms for electrons of the beam velocity.

As far as rate of collision is concerned the actual gas behaves towards electrons of the particular velocity just as a hypothetical gas of rigid spheres of cross-section Q would do. We must be careful, however, in carrying this analogy too far. The actual gas atoms are not rigid spheres with defined boundaries—the force between an electron and an atom will fall off continuously with distance and not drop suddenly to zero at some definite separation. This raises at once an important point concerning the independence of Q , defined as above, of the nature, and particularly the angular resolving power, of the measurements involved. We have defined loss from the beam as occurring whenever an electron is deviated from its path or loses energy or both. But, on the classical theory, as long as some field exists between an electron and an atom some deviation will occur. In this case the true effective cross-section of an atom for an electron would be infinite and the observed value would depend strongly on the ability of the apparatus used to distinguish very small deviations of electrons from their original paths. In these circumstances our definition of total absorption cross-section would be theoretically meaningless. However, when allowance is made for quantum uncertainty effects it turns out that a finite value of the total effective cross-section is to be expected, provided the force between an atom and an electron falls off at large separations r faster than r^{-3} . Provided a certain minimum resolving power is achieved, this finite value can be determined in principle by experiments of the type discussed. The reason for this can be seen from the following argument due to Mott.†

To relate the classical and quantal descriptions of the scattering of an electron through a certain angle we must regard the electron as represented by a wave packet which spreads as it moves. Two conditions must be satisfied before the two descriptions of the scattering give essentially the same result. Not only must the wave-length of the electron be small compared with the closest distance of approach of the electron to the scattering atom, but the spread of the electron wave packet must not be so large as to mask a deflexion through the angle concerned.

Consider an electron wave packet travelling with velocity v_x in the x -direction so that its centre would, in the absence of deviation, pass at a distance y from the scattering centre. The classical orbit will only be

† *Proc. Roy. Soc. A*, **127** (1930), 658.

closely followed if the breadth Δy of the packet is very small compared with y . According to the uncertainty principle, this breadth Δy will be associated with an uncertainty Δv_y in the transverse velocity by the relation

$$\Delta y \Delta v_y \simeq h/m,$$

where h is Planck's constant and m the electron mass. We must therefore have

$$y \gg h/m\Delta v_y. \quad (2)$$

The existence of the uncertainty Δv_y means that the wave packet has a spreading angle $\Delta v_y/v_x$. It is a further necessary condition for the classical description of the particular collision to be valid that this spreading should be small compared with the deviation α which the electron would suffer according to classical mechanics. Thus

$$\alpha \gg \Delta v_y/v_x. \quad (3)$$

Combining (2) and (3) we must have

$$\alpha y \gg h/mv_x. \quad (4)$$

Now, except for scattering fields with potential falling off more slowly than the inverse square of the distance at large distances, αy tends to zero with α . This means that, for any wave-length h/mv of the electrons, the classical description fails at sufficiently small angles. Deviations less than this are not observable and, as it is the contribution from very small deviations which makes the classical value of Q infinite, the quantal value remains finite. In other words, increase of resolving power in an experimental apparatus does not lead to indefinite increase of the observed Q , for resolution is limited in any case by intrinsic uncertainties.

Experimental evidence in support of the quantum viewpoint can be derived, either from a study of the variation of the observed Q with experimental resolving power or of the distribution in angle of electrons scattered from atoms. The detailed discussion of such angular distributions in Chap. II, § 7.3, Fig. 50, includes a description of evidence obtained in this latter way. Agreement of measurements of Q by observers using a wide variety of apparatus also provides strong support for the correctness of the quantum viewpoint.

Although the quantity Q we have defined has a definite meaning provided the resolving power of the apparatus is sufficiently high, it is very important in making measurements to ensure that this condition is satisfied. The higher the electron velocity the higher the required re-

solving power, and in the study of the passage of positive ions through gases (see Chap. VIII, § 1.1) the requirement is very much more severe.†

There is one other important consequence of the gradual decrease of the scattering field with distance as contrasted with the rigid sphere case—the effective cross-section must be expected to vary with electron velocity.

2.1. *Analysis of the total collision cross-section*

So far we have defined the total effective cross-section for all types of collision presented by a gas atom towards electrons of a given velocity v . No attention has been paid to specifying quantities which determine separately the rate of elastic and the various kinds of inelastic, super-elastic, and radiative collisions. To do this we may assign probabilities $P_0(v)$, $P_n(v)$, etc., which represent the chance that a collision of an electron of velocity v with a gas atom should be elastic or inelastic, involving excitation of the n th state of the atom, etc., respectively. These quantities can be expected to vary with the electron velocity. The cross-section $P_0(v)Q$ is then defined as the effective cross-section for elastic collisions of electrons of velocity v with the gas atoms concerned, $P_n(v)Q$ that for inelastic collisions involving excitation of the n th state, and so on. We then have

$$Q = P_0(v)Q(v) + \sum P_n(v)Q(v) \\ = Q_0 + \sum Q_n,$$

where we have written Q_0 , Q_n , etc., respectively for the individual cross-sections. Experiments designed to measure Q_0 , Q_n , etc., respectively can be conceived in principle and have to some extent been carried out in practice. They will be discussed in some detail in Chapter II.

2.2. *Differential cross-sections*

So far we have paid no attention to the specification of the distribution in angle of electrons undergoing a particular type of collision. Consider for the moment elastic collisions. The elastic cross-section Q_0 may be further broken down as follows. Let $p(\theta)\sin\theta\,d\theta d\phi$ be the probability that, in an elastic collision, the electron is scattered into the solid angle

† As an example of the type of resolution required of an apparatus for the study of electron collisions, in order to obtain an accuracy of 1 per cent. in the measured total collision cross-section, the maximum angle of scattering that an electron may undergo without being lost to the beam must not exceed 11° for 1-volt electrons, 6.5° for 10-volt electrons, 2.3° for 100-volt electrons, 0.85° for 1,000-volt electrons, and 0.2° for 10,000-volt electrons. These figures are practically independent of the nature of the scattering material.

$d\Omega (= \sin \theta \, d\theta d\phi)$. Then $p(\theta)Q_0 \sin \theta \, d\theta d\phi$ is called the differential cross-section for elastic scattering into the solid angle $d\Omega$. It is usually written

$$I_0(\theta) \sin \theta \, d\theta d\phi,$$

so we have

$$p(\theta) = I_0(\theta)/Q_0, \quad (5)$$

and

$$Q_0 = \int_0^\pi \int_0^{2\pi} I_0(\theta) \sin \theta \, d\theta d\phi. \quad (6)$$

In the same way we may define differential cross-sections for inelastic collisions. Thus

$$I_n(\theta) \sin \theta \, d\theta d\phi$$

is the differential cross-section for scattering into the solid angle $d\Omega$ in an inelastic collision involving excitation of the n th state of the atom.

In terms of the differential cross-section the condition for the finiteness of Q_0 requires the existence of the integral in (6). This will be convergent if $I(\theta)$ does not increase as rapidly as $1/\theta^2$ for small θ . The relation of this to the law of force producing the scattering will be discussed in more detail in Chap. III, § 2.44.

2.3. Note on nomenclature

In order to avoid confusion we shall throughout this book employ the term *total collision cross-section* to mean the sum of the cross-sections for every type of collision. The term *total elastic (inelastic) cross-section* will be used for the cross-sections Q_0 (Q_n) in contradistinction to the corresponding differential cross-sections. Under certain conditions, as for example when the electron energy is insufficient to excite the atoms, the total collision cross-section will be practically equal to the total elastic cross-section, but this will not be true in general.

3. Measurement of total collision cross-sections—Ramsauer's method

The first experiments on the absorption of electrons in gases were made as long ago as 1903 by Lenard† and in 1916 Åkesson‡ obtained evidence that, in certain gases, slower electrons were more penetrating than the faster. Quantitative absolute measurements of total collision cross-sections as a function of electron velocity really dates, however, from the introduction of Ramsauer's§ method. It is a very direct method, the principle of which is illustrated in Fig. 1.

Electrons from a source F were accelerated to the desired velocity before passing through the slit S_1 . In Ramsauer's original apparatus F was a zinc plate and the electrons were ejected photo-electrically. By

† *Ann. der Physik*, **12** (1903), 714.

‡ *Lunds Årsskr.*, N.F. **12** (1916), 29.

§ *Ann. der Physik*, **64** (1921), 513 and **66** (1921), 546.

means of a magnetic field perpendicular to the plane of the paper those electrons which suffered no collision described a circular path through the slits S_1 – S_7 and entered a collector C . Electrons which were scattered from the beam failed to pass through the slits while those which suffered inelastic collisions, even without deflexion, moved in a new circular

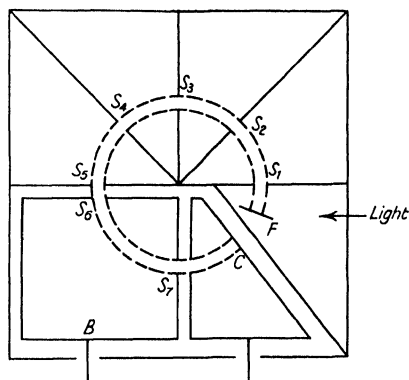


FIG. 1. Ramsauer's apparatus for measurement of total collision cross-sections.

path of smaller radius in the magnetic field and so failed to pass through the succeeding slits. In Ramsauer's apparatus the beam defined by the slit system had a mean diameter of 20 mm. and was 1 mm. wide and 8 mm. high.

The procedure adopted for this measurement was as follows. With a pressure p_1 mm. Hg in the apparatus the currents i_1 to C alone and j_1 to B and C together were measured by an electrometer. If l is the length of the path between slits S_6 and S_7 , $i_1 = j_1 e^{-\alpha p_1 l}$, where α is the absorption coefficient at a pressure of 1 mm. Hg.

If i_2, j_2 are similar currents when the pressure is p_2 mm. Hg,

$$i_2 = j_2 e^{-\alpha p_2 l},$$

so that

$$(p_1 - p_2)\alpha l = \log(j_1 i_2 / i_1 j_2).$$

α may thus be determined and hence Q from (1).

Provided the slits are narrow enough this method should give the true total collision cross-section as no type of encounter fails to be detected, except for the small number of elastic collisions through very small angles.

Ramsauer's apparatus has not only been used for measuring the total

absorption cross-section for electrons in gases and vapours but has also been adapted by Brode† for measurements in metal vapours. For this purpose the whole of the collision chamber was designed so that it could be maintained at such temperatures that the vapour pressure of the metal was of order 10^{-5} mm. Hg, convenient for the experiment. This was made possible by constructing the metal parts of tantalum and using a hot filament source for the electrons. In Brode's apparatus the beam had a mean diameter of 30 mm. and was 1 mm. wide and 10 mm. high. A single collecting chamber was used, the electron emission from the source being assumed to remain constant at the different pressures of vapour in the apparatus.

Other forms of absorption apparatus have been used. Rusch‡ used longitudinal magnetic focusing to confine the electron beam, while Mayer§ used a modification of Lenard's original apparatus in which no magnetic field was employed. These methods offer no advantage over that of Ramsauer and have received only limited application.||

An interesting method of deducing the total collision cross-section for electrons in atomic hydrogen has been applied by Kruithof and Ornstein†† in the course of measurements on the dissociation of molecular hydrogen by electron impact (Chap. IV, § 5.2). An electron beam of energy between 17.0 and 28.0 eV was passed through hydrogen gas at a pressure of a few hundredths of a mm. of Hg and the total intensity of the radiation emitted across a number of sections of the beam was determined photometrically. As the beam proceeded it became broader due to elastic scattering and the relative number of electrons scattered out of the beam at different points along its length could be determined from the photometric measurements. From this the total collision cross-sections could be estimated for the mixture of atomic and molecular hydrogen in the tube. Knowing then the degree of dissociation and the total collision cross-section for molecular hydrogen, that for atomic hydrogen could be calculated.

4. Observed total collision cross-sections of atoms||

It has been customary in describing experimental results to give the observed value of α at 1 mm. Hg pressure, usually called the 'probability of collision'.

To obtain Q in units of πa_0^2 (where $a_0 = 0.53 \times 10^{-8}$ cm. is the radius

† *Phys. Rev.* **34** (1929), 673. .

‡ *Ann. der Physik*, **80** (1926), 707.

§ *Ibid.* **64** (1921), 451.

|| See the summary by Kollath, *Phys. Zeits.* **31** (1930), 985.

†† *Physica*, **2** (1935), 611.

of the first Bohr orbit of the hydrogen atom, usually taken as the atomic unit of length), we have

$$Q \text{ (in units of } \pi a_0^2) = 0.325\alpha.$$

In Fig. 2 the variation of Q , in units of πa_0^2 , with electron velocity expressed in $\sqrt{\text{volts}}$, as observed for the three rare gases argon, krypton, and xenon is illustrated.

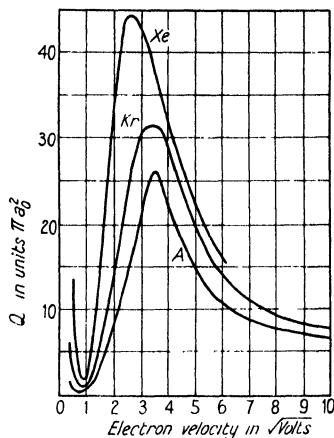


FIG. 2. Observed total collision cross-sections of A, Kr, Xe.

and xenon is illustrated. It is immediately obvious that the observed variation is not what would be expected on classical ideas. The slower the electrons the more effectively should they be scattered by the atomic field. On the contrary, a pronounced maximum is observed for each of the three gases for electrons with energy in the neighbourhood 8–15 eV. The gases are practically transparent to electrons of about 1 eV energy. For even slower electrons the cross-section rises again, the increase being more pronounced the heavier the rare gas atom.

The remarkable transparency of the heavier rare gases atoms towards electrons of energy 1 eV or so was discovered independently by Ramsauer† and by Townsend and Bailey‡ using a more indirect method (described in §§ 6–8) so will be referred to as the Ramsauer-Townsend effect. The measurements illustrated in Fig. 2 represent the average of those obtained by several observers.§ Over most of the electron energy

† *Ann. der Physik*, **64** (1921), 513; **66** (1921), 546.

‡ *Phil. Mag.* **43** (1922), 593.

§ Ramsauer, *Ann. der Physik*, **72** (1923), 345; Brode, *Phys. Rev.* **25** (1925), 636; Rusch, *Ann. der Physik*, **80** (1926), 707; Bruche, *ibid.* **84** (1927), 279; Ramsauer and Kollath, *ibid.* **3** (1929), 536; Normand, *Phys. Rev.* **35** (1930), 1217.

range the agreement between the different observers is within 10 per cent., indicating that the true total collision cross-section has been measured.

The total cross-section-velocity curves illustrated in Fig. 2 are by no means typical of other atoms. Thus in Fig. 3 the observed curves

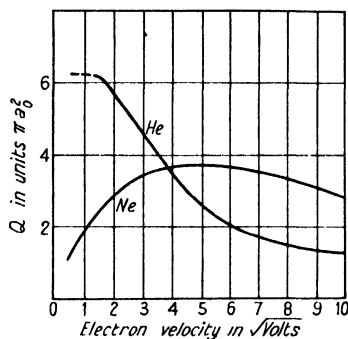


FIG. 3. Observed total collision cross-sections of He and Ne.

obtained for helium† and for neon‡ are illustrated. It will be noticed that the cross-sections are very much smaller on the whole than for the other rare gases and do not exhibit such marked variations with electron velocity.

Fig. 4 illustrates Brode's§ measurements for zinc, cadmium, and mercury. Apart from some differences in detail, the behaviour of the cross-section-velocity curves is generally similar for all three of these chemically similar atoms. It will be noticed that the cross-section increases rapidly at low electron velocities to values considerably in excess of those observed for the rare gases. The greatest cross-sections observed, however, are those for the alkali metals. The results of Brode's|| measurements for these are illustrated in Fig. 5. Again the behaviour of the chemically similar set of atoms is much the same, both as regards variation with velocity and the huge magnitude which is attained at certain electron energies. It is noteworthy also that, for each atom, the cross-section attains a sharp maximum for electrons with energy of order 2–3 eV, falls sharply for a small range of reduced energy, and then

† Ramsauer, *Ann. der Physik*, **66** (1921), 546; Brüche, *ibid.* **84** (1927), 279; Ramsauer and Kollath, *ibid.* **3** (1929), 536; Normand, *Phys. Rev.* **35** (1930), 1217.

‡ Ramsauer, *Ann. der Physik*, **66** (1921), 546; Rusch, *Phys. Zeits.* **26** (1925), 748; Brüche, *Ann. der Physik*, **84** (1927), 279; Ramsauer and Kollath, *ibid.* **3** (1929), 536; Normand, *Phys. Rev.* **35** (1930), 1217.

§ *Proc. Roy. Soc. A*, **125** (1929), 134; *Phys. Rev.* **35** (1930), 504.

|| *Ibid.* **34** (1929), 673.

appears, from the observations in sodium and caesium, to begin rising again. Once more we have here a complicated velocity variation. The

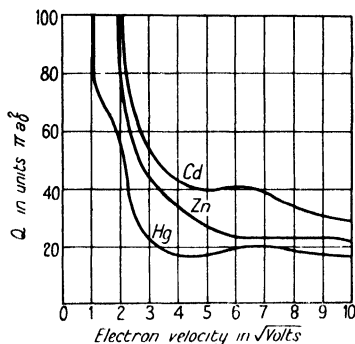


FIG. 4

FIG. 4. Observed total collision cross-sections of Cd, Zn, Hg.

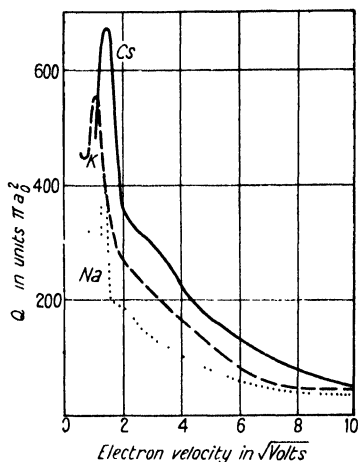


FIG. 5

FIG. 5. Observed total collision cross-sections of Na, K, Cs.

only other monatomic substance which has been investigated is thallium, and Brode's measurements† for this atom are illustrated in Fig. 6.

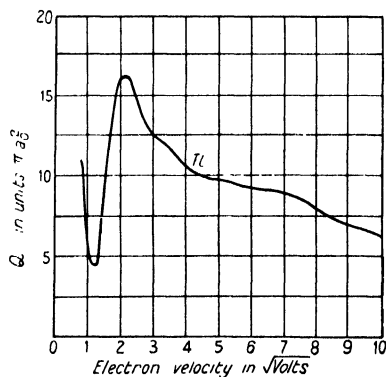


FIG. 6. Observed total collision cross-sections of Tl.

† Ibid. **37** (1931), 570.

Fig. 7 shows the results obtained for atomic hydrogen by Kruithof and Ornstein,[†] using the indirect method described above.[‡]

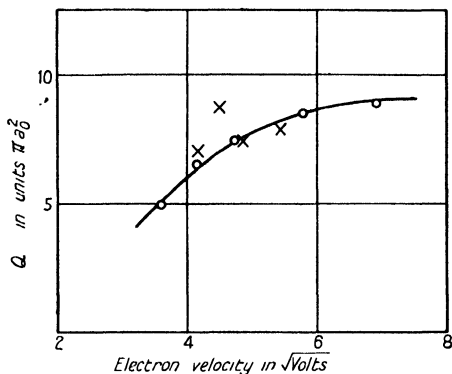


FIG. 7. Observed total collision cross-sections of atomic hydrogen.
 × Kruithof and Ornstein; ○ Lindeman (quoted by Kruithof and Ornstein).

Summarizing, the most striking feature of the measurements for atoms is the wide range of variation in the magnitude and velocity variation of the total collision cross-section from one chemically similar group of atoms to another. On the other hand, within a chemically similar group there is a very close similarity of behaviour. In many cases the total cross-section does not vary monotonically with electron velocity, but exhibits a marked maximum and minimum. The theoretical interpretation of these and other features will be given in Chap. III, § 2.3.

5. Diffusion of electrons through gases

We now consider the diffusion of a swarm of electrons through a gas at pressure p under the influence of a constant electric field of strength F . This is of interest, not only from its application to electric discharge and other phenomena, but also because it can provide valuable information about the collision cross-sections of atoms and molecules towards slow electrons. It is particularly useful in determining the mean energy loss suffered by a slow electron on collision with a gas molecule. The electrons concerned may have too small an energy to produce any electronic excitation within the molecule but may excite vibration or rotation. In an atomic gas the only loss will occur in so-called elastic collisions and may be calculated from a knowledge of the atomic weight

[†] Loc. cit.

[‡] In Fig. 7, which is taken from Kruithof and Ornstein's paper, a comparison is made with the results of a direct determination made by Lindeman. No reference is given, however, to Lindeman's work and no indication of his experimental method.

of the gas. Nevertheless, it is of importance to study diffusion in such cases to show that the method is on a sure foundation. We therefore discuss first the experimental and theoretical researches which have been carried out concerning the diffusion of slow electrons through the rare gases. These studies are of historical interest also inasmuch as Townsend and Bailey† observed in this way the anomalous behaviour of slow electrons in argon as long ago as 1921 independently of Ramsauer's investigations.‡ It will be shown that the two sets of results are entirely compatible. In Chapter IV the application of the diffusion method to the study of energy losses due to excitation of molecular vibration and rotation (§ 7) and to negative ion formation (§ 6.222) will be described.

The principle of the method which may be used to determine the mean free path and mean energy loss for collision is as follows. As the electrons diffuse they gain energy from the field but, in the steady state, this is balanced by the energy lost in collision with the gas atoms. In this steady state the swarm will possess a definite mean drift velocity u in the direction of the field and also a definite mean kinetic energy ϵ . A very simple approximate argument shows how these quantities are related to the collision properties of the gas atoms towards the electrons.

We suppose that the mean free path of the electrons in the gas has a constant value l and that the fraction of its energy which an electron loses in a collision with a gas atom is also constant and equal to a small quantity λ . Then, if c is the mean velocity of the random motion of the electron, the number of collisions made in traversing a distance x in the direction of the field will be cx/ul since the actual length of path will be xc/u . The energy lost in these collisions will be $\lambda\epsilon cx/ul$. Hence, for a steady state,

$$\lambda\epsilon cx/ul = Fex,$$

the energy gained from the field. As $\epsilon = \frac{1}{2}mc^2$ approximately, where m is the mass of an electron, we have

$$\lambda c^3/u = 2Fel/m. \quad (7)$$

A second relation follows by considering the mean distance traversed in the direction of the field in the interval δt between collisions. Assuming all directions of motion after the collision to be equally probable, then this distance will be $u \delta t$, so that

$$\frac{1}{2}Fe \delta t^2/m = u \delta t.$$

Apart from a numerical factor of order unity, δt may be taken as l/c , giving

$$2uc = Fel/m. \quad (8)$$

† Loc. cit.

Since l is inversely proportional to the gas pressure p , both c and u are functions of F/p . Also, if c and u are measured for a fixed value of F/p , then l and λ can be obtained.

In practice l will not be a constant and the measurements of c and u will give certain mean values of l and λ over the velocity distribution of the electrons. We cannot, therefore, hope to derive, from experiments on electron swarms, any information as definite about collision cross-sections as may be obtained from experiments of the Ramsauer type. It is possible, however, to work with electrons of lower energy than in the more direct experiments and to obtain information about the energy losses of electrons on collision with molecules which cannot be got in any other way.

To analyse the diffusion phenomena in more detail in relation to collision cross-sections, we shall consider a swarm of such small mean energy that inelastic collisions with the gas atoms do not occur. The only loss of energy in elastic collisions therefore arises from the finite value of the ratio of the mass m of an electron to that M of a gas molecule. On the other hand, we shall suppose that the mean energy of the molecules is very much smaller than that of the electrons. We also suppose that the electron concentration in the stream is so small that interaction between the electrons can be ignored. Under these conditions it becomes possible, given the results of Ramsauer's experiments and also of measurements on the angular distribution of elastically scattered electrons, to compute both the drift velocity and the mean kinetic energy as functions of F/p . These may then be compared with values observed by methods described in §§ 6, 7 and good agreement will be found. This enables one to apply the technique with confidence to molecular gases in which the mean energy loss λ is not known beforehand and in which attachment may occur.

5.1. *Momentum transfer (diffusion) cross-section*

With the assumptions made, the fraction of its energy lost per impact by an electron which is scattered through an angle θ is given by

$$2(1 - \cos \theta)m/M, \quad (9)$$

if $(m/M)^2$ is ignored.

If $p(\theta)\sin \theta \, d\theta d\phi$ is the probability that, on collision, the electron be scattered into the solid angle $d\Omega$ about θ , the mean fractional energy loss per collision will be

$$2(m/M) \int_0^\pi \int_0^{2\pi} (1 - \cos \theta) p(\theta) \sin \theta \, d\theta d\phi. \quad (10)$$

Referring to §§ 2.1, 2.2 we have, in terms of the total and differential cross-sections Q_0 and $I_0 d\Omega$ for elastic scattering,

$$p(\theta) = I_0(\theta)/Q_0,$$

so the mean fractional energy loss per collision becomes

$$2(m/M)Q_d/Q_0,$$

where

$$Q_d = \int_0^\pi \int_0^{2\pi} I_0(\theta)(1 - \cos \theta) \sin \theta \, d\theta d\phi, \quad (11)$$

and is usually referred to as the momentum transfer cross-section.† Thus the fractional amount of energy lost by an electron in traversing a distance x in a gas containing N atoms/c.c. is $2(m/M)NQ_d x$, just as if the total elastic cross-section Q_0 were replaced by Q_d and the fractional energy lost per collision by $2m/M$. Thus, for purely elastic collisions, we should take $l = 1/NQ_d$ and $\lambda = 2m/M$ in (7) and (8). It must be remembered, however, that in general Q_d will be a function of electron energy.

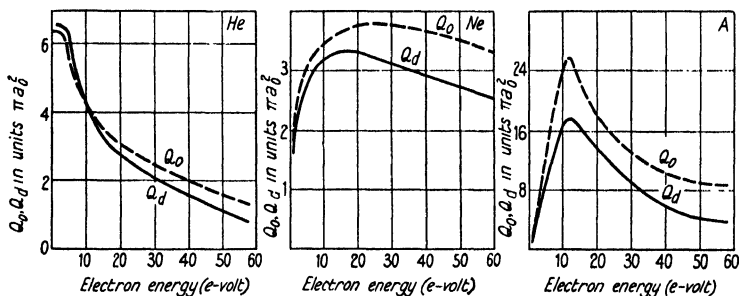


FIG. 8. Comparison of momentum transfer (diffusion) cross-sections with total collision cross-sections for He, Ne, Ar.

Observed total collision cross-section, — — —.

Derived momentum transfer cross-section, — — — —.

Q_d differs appreciably from Q_0 only when there is a pronounced concentration of scattering in either the backward or forward directions. If $I_0(\theta)$ is a constant, independent of θ , then Q_d and Q_0 are equal. It will be shown in Chap. III, § 2.41, that, for sufficiently slow electrons, the scattering is independent of angle so, in such cases, Q_d need not be distinguished from Q_0 . At higher energies there is an appreciable difference, as may be seen by reference to Fig. 8, in which Q_d and Q_0 are compared for argon, neon, and helium. In obtaining Q_d the observed angular distributions, described in Chap. III, § 2.42, have been used.

† Q_d is sometimes referred to as the diffusion cross-section on account of its importance in the discussion of diffusion phenomena (see Chap. VII, § 3.1).

If the mean energy ϵ of the gas molecules cannot be ignored the expression (10) for the mean fractional energy loss per collision must be modified by multiplication by the factor $1 - \frac{2}{3}\epsilon_0/\epsilon$. If the electrons themselves have a Maxwellian distribution of mean energy $\bar{\epsilon}$ the corresponding factor becomes modified to $\frac{2}{3}(1 - \epsilon_0/\bar{\epsilon})$.

5.2. The electron velocity distribution, drift and random velocity

Consider the steady state of a swarm of electrons diffusing through a gas containing N atoms/c.c., of mass M , with momentum transfer cross-section Q_d , under the action of a uniform electric field F in the direction of the x -axis. Let $f(\xi, \eta, \zeta) d\xi d\eta d\zeta$ be the fraction of electrons with velocities lying between $\xi, \xi + d\xi; \eta, \eta + d\eta; \zeta, \zeta + d\zeta$. Then it may be shown that,† ignoring $(m/M)^2$,

$$f(\xi, \eta, \zeta) = f_0(v) + (\xi/v)f_1(v),$$

where

$$v^2 = \xi^2 + \eta^2 + \zeta^2 = 2\epsilon/m,$$

$$\left. \begin{aligned} f_0(v) &= A \exp \left[- (6m/M) \int_0^\epsilon \epsilon d\epsilon / \epsilon_l^2 \right], \\ f_1(v) &= - (\epsilon_l / mv) df_0/dv, \end{aligned} \right\} \quad (12)$$

and A is such that $4\pi \int_0^\infty f_0(v) v^2 dv = 1$.

ϵ_l is given by $Fe/NQ_d = Fel$, the energy gained in falling through a free path in the direction of the field, and is in general a function of ϵ . If, however, Q_d is effectively constant for all electron energies of importance, then

$$\left. \begin{aligned} \pi \Gamma(\frac{3}{2}) f_0(v) &= (3m/M)^{\frac{1}{2}} (m/2\epsilon_0)^{\frac{1}{2}} \exp \{ - (3m/M) (\epsilon/\epsilon_0)^2 \}, \\ f_1(v) &= 6(m\epsilon/M\epsilon_0) f_0(v), \end{aligned} \right\} \quad (13)$$

where ϵ_0 is written for the now constant value of Fel .

The effect of the variability of Q_d on the distribution function is illustrated in Fig. 9. Here four distributions are given, all with the same mean energy. One is simply the form (13) while the other three are those for helium, neon, and argon using the general result (12) and the cross-sections Q_d illustrated in Fig. 8. It will be seen that the Ramsauer-Townsend effect in argon leads to quite a pronounced deficiency of the higher energy electrons.

† Druyvesteyn, *Physica*, **10** (1930), 61; **1** (1934), 1003; Davydov, *Phys. Zeits. Sowj.* **8** (1935), 59; Morse, Allis, and Lamar, *Phys. Rev.* **48** (1935), 412.

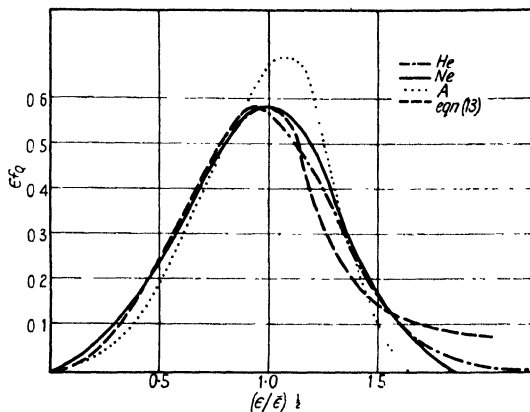


FIG. 9. Electron velocity distribution in a diffusing electron swarm, inelastic collisions being ignored.

The function ϵf_0 , where f_0 is defined in (12) and ϵ is the electron energy, is plotted as a function of $(\epsilon/\bar{\epsilon})^{1/2}$ where $\bar{\epsilon}$ is the mean energy. The curves for He, Ne, and A have been obtained using the diffusion cross-sections illustrated in Fig. 8. The curve (— · —) has been obtained from (13) using a constant diffusion cross-section.

5.21. Proof of velocity distribution formula. We follow the method of Morse, Allis, and Lamar.[†] Consider an element $d\gamma = d\xi d\eta d\zeta$, of the velocity space. The representative points of the electrons in this space are given by their velocity components. In the steady state the number of representative points which leave this element per second due to the applied field must be equal to the net number entering it due to collisions.

The number c $d\gamma$ leaving per second will be given by

$$\frac{d\xi}{dt} \frac{\partial f}{\partial \xi} d\gamma = - \frac{eF}{m} \frac{\partial f}{\partial \xi} d\gamma. \quad (14)$$

The number a leaving the element per second due to collisions will be given simply by

$$a d\gamma = N Q_0 v f d\gamma,$$

where N is the number of gas molecules/c.c. and Q_0 is the total elastic cross-section. This must be subtracted from the number b entering the element due to collisions to give

$$c = b - a.$$

The calculation of b involves the momentum transfer cross-section. Since in a collision electrons lose a fraction $2(m/M)(1 - \cos\theta)$ of their initial velocity, those which, after collision, find their representative points in the element $d\gamma$ must, before collision, have had a velocity

$$v' = v\{1 + (1 - \cos\theta)(m/M)\},$$

$(m/M)^2$ being ignored. These representative points must have come from an element

$$d\gamma' = d\gamma(v'/v)^3.$$

[†] Loc. cit

Hence

$$b \, d\gamma = Nv' \int_0^{2\pi} \int_0^{\pi} I_0(v', \theta) f(v', \xi') \sin \theta \, d\theta d\phi d\gamma,$$

$$- N(v'^4/v^3) \int_0^{2\pi} \int_0^{\pi} I_0(v', \theta) f(v', \xi') \sin \theta \, d\theta d\phi d\gamma.$$

We may therefore write

$$b - a = (N/v^3) \int_0^{2\pi} \int_0^{\pi} [v'^4 f(v', \xi') I_0(v', \theta) - v^4 f(v, \xi) I_0(v, \theta)] \sin \theta \, d\theta d\phi.$$

To simplify this, we expand in powers of m/M , retaining only the first two terms, to give

$$b - a = (N/v^3) \int_0^{2\pi} \int_0^{\pi} \left[v^4 \{f(v, \xi') - f(v, \xi)\} I_0(v, \theta) + (m/M)(1 - \cos \theta) v \frac{\partial}{\partial v} \{v^4 f(v, \xi') I_0(v, \theta)\} \right] \sin \theta \, d\theta d\phi. \quad (15)$$

At this stage we must make some assumption as to the form of $f(v, \xi)$. We expand it as

$$f(v, \xi) = f_0(v) + (\xi/v) f_1(v), \quad (16)$$

ignoring higher order harmonics in ξ/v . In doing this, it is supposed that the effect of the electric field on the distribution function is small, a result which will be justified at the end.

We have then

$$\int_0^{2\pi} \int_0^{\pi} [f(v, \xi') - f(v, \xi)] I_0(v, \theta) \sin \theta \, d\theta d\phi = f_1(v) \int_0^{2\pi} \int_0^{\pi} [\cos \omega' - \cos \omega] I_0(v, \theta) \sin \theta \, d\theta d\phi, \quad (17)$$

where $\cos \omega = \xi/v$, $\cos \omega' = \xi'/v$. From the geometry of the collision

$$\cos \omega' = \cos \omega \cos \theta + \sin \omega \sin \theta \cos(\phi - \chi),$$

so that the integral (17) becomes

$$-f_1(v) Q_d(v) \cos \omega.$$

Again, treating $f_1(v)$ as small,

$$\left(\frac{m}{M}\right) \int_0^{2\pi} \int_0^{\pi} (1 - \cos \theta) v \frac{\partial}{\partial v} [v^4 f(v, \xi') I_0(v, \theta)] \sin \theta \, d\theta d\phi$$

becomes

$$\left(\frac{m}{M}\right) \frac{d}{dv} [v^4 f_0(v) Q_d].$$

Thus we have

$$b - a = -N Q_d v f_1 \cos \omega + (mN/Mv^2) \frac{d}{dv} (v^4 Q_d f_0). \quad (18)$$

Returning now to c we have, using the form (16) for f ,

$$c = \left(\frac{eF}{m}\right) \left\{ \frac{\partial f_0}{\partial \xi} + \frac{f_1}{v} + \xi \frac{\partial}{\partial \xi} \left(\frac{f_1}{v} \right) \right\}.$$

Now

$$\frac{\partial f}{\partial \xi} = \frac{\xi}{v} \frac{df}{dv}$$

so

$$c = \left(\frac{eF}{m} \right) \left\{ \frac{\xi}{v} \frac{df_0}{dv} + \frac{f_1}{v} + \frac{\xi^2}{v} \frac{d}{dv} \left(\frac{f_1}{v} \right) \right\}.$$

Since we are ignoring the effect of all harmonics beyond the first we replace ξ^2 in this expression by its spherical average $v^2/3$ and obtain

$$c = \left(\frac{eF}{m} \right) \left\{ \cos \omega \frac{df_0}{dv} + \frac{1}{3v^2} \frac{d(v^2 f_1)}{dv} \right\}. \quad (19)$$

Equating separately the terms in c and $b-a$ with and without $\cos \omega$ gives now

$$\left(\frac{eF}{m} \right) \frac{df_0}{dv} = -NQ_d v f_1, \quad (20)$$

$$\left(\frac{eF}{3m} \right) \frac{d(v^2 f_1)}{dv} = (mN/M) \frac{d}{dv} (v^4 Q_d f_0). \quad (21)$$

Integrating (21) gives

$$\frac{1}{2} e F f_1 = 2(m/M) N \epsilon Q_d f_0 + \text{const.}/v^2, \quad (22)$$

where $\epsilon = \frac{1}{2} m v^2$. This equation represents the energy balance, the term on the left-hand side being proportional to the energy gained from the field, the term involving Q_d to that lost by collision. In a steady state the constant should be taken equal to zero.

Writing now

$$\epsilon_l = e F / N Q_d$$

we have

$$f_1 = 6(m\epsilon/M\epsilon_l) f_0.$$

Substitution in (20) gives

$$\frac{df_0}{dv} = -3(m^3 v^3 / M \epsilon_l^2) f_0.$$

This can be integrated to give

$$f_0 = A \exp \left[- (6m/M) \int_0^\epsilon \epsilon d\epsilon / \epsilon_l^2 \right], \quad (23)$$

A being a normalizing constant, which is given by

$$\int f_0 d\gamma = 1.$$

5.3. The mean energy and drift velocity

We have for the mean energy $\bar{\epsilon}$

$$\begin{aligned} \bar{\epsilon} &= \frac{1}{2} m \iiint (\xi^2 + \eta^2 + \zeta^2) f(\xi, \eta, \zeta) d\xi d\eta d\zeta \\ &= 2\pi m \int_0^\infty v^4 f_0(v) dv \end{aligned} \quad (24)$$

$$= 0.427 (M/m)^{1/2} \epsilon_0, \text{ when } Q_d \text{ is constant.} \quad (25)$$

The root mean square velocity c is therefore given by

$$c = 0.924 (M \epsilon_0^2 / m^3)^{1/2}. \quad (26)$$

Similarly we have, for the drift velocity u ,

$$\begin{aligned} u &= \iiint \xi f(\xi, \eta, \zeta) d\xi d\eta d\zeta \\ &= \frac{4}{3}\pi \int_0^{\infty} v^3 f_1(v) dv \end{aligned} \quad (27)$$

$$= 0.634_5 (m/M)^{\frac{1}{2}} (2\epsilon_0/m)^{\frac{1}{2}}, \text{ when } Q_d \text{ is constant.} \quad (28)$$

It is of interest now to compare the formulae for c^3/u and cu with those we obtained by very crude arguments. From (26) and (28) we have, treating Q_d as constant,

$$c^3/u = 0.880 M \epsilon_0 / m^2, \quad (29)$$

$$2cu = 1.658 \epsilon_0 / m. \quad (30)$$

As λ is to be taken as $2m/M$ and $\epsilon_0 = Fel$, we see that the more refined treatment introduces factors 0.880 and 1.658 on the right-hand sides of the equations.

After describing the methods used to measure c and u we shall discuss the comparison of the observed values for the rare gases with the predictions of the above formulae, using the cross-sections Q_d of Fig. 8.

6. Measurement of the mean energy of a diffusing swarm of electrons

The mean energy is best measured by observing the lateral spread of the swarm as it diffuses under the action of a uniform field, a method introduced by Townsend.†

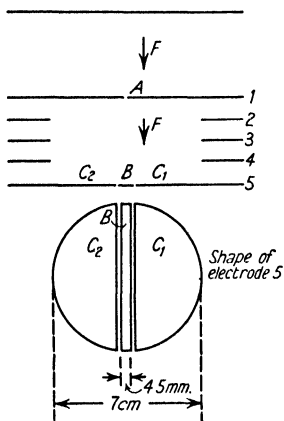


FIG. 10. Townsend's apparatus for measurement of drift velocity and mean energy of a diffusing swarm of electrons.

The principle of the method is illustrated in Fig. 10. An electron stream which has already acquired a steady drift motion through a gas at pressure p in a uniform electric field of strength F , enters the diffusion chamber through an orifice A in the upper electrode 1. It continues to diffuse through this chamber under the same uniform field and is collected on a receiving electrode 5. This electrode consists of an inner portion B and outer portions C_1 , C_2 so that the currents reaching B and C_1 , C_2 may be separately measured. From the ratio of these currents the mean energy of the swarm may be derived as follows.

We define first a diffusion coefficient D for the swarm. This is such

† *Motion of Electrons in Gases* (Clarendon Press, 1925); *J. Frank. Inst.* **200** (1925), 563.

that, in the absence of any electric field, the local velocity $\mathbf{v}$ of flow at any point within the swarm is given by

$$n\mathbf{v} = -D \text{grad } n, \quad (31)$$

where n is the number of electrons/c.c. at that point. In doing this we assume that the electron-energy distribution is not appreciably affected by the sideways diffusion. The effect of the electric field will now be to superpose the drift velocity $\mathbf{u}$ so that

$$n\mathbf{v} = -D \text{grad } n + n\mathbf{u}. \quad (32)$$

The motion must also satisfy the equation of continuity

$$\text{div } n\mathbf{v} = 0,$$

so that

$$\text{div}(-D \text{grad } n + n\mathbf{u}) = 0,$$

or

$$\nabla^2 n = (1/D)\mathbf{u} \cdot \text{grad } n. \quad (33)$$

In our case the field is taken along the x -direction so

$$\nabla^2 n = \frac{u}{D} \frac{\partial n}{\partial x}. \quad (34)$$

By solving this equation with the appropriate boundary conditions the value of n at each point of the receiving electrode may be determined. The fraction R of the current received on the inner portion B , as a function of u/D and the geometry of the apparatus, may now be obtained by integration. It remains to relate u/D to the mean energy.

The equation (32) may be interpreted dynamically if we remember that the electron pressure p is proportional to the concentration n so that

$$p\mathbf{v}/D = -\text{grad } p + p\mathbf{u}/D. \quad (35)$$

The term $-\text{grad } p$ represents the momentum transferred per unit volume by the flow of electrons across its surface. $p\mathbf{v}/D$ is the momentum lost per unit volume in collisions with gas atoms. It is clear then that if $p\mathbf{u}/D$ is taken as the momentum communicated per unit volume by the electric field $\mathbf{F}$, the equation expresses the conservation of momentum. But this momentum is $ne\mathbf{F}$, so that

$$p\mathbf{u}/D = ne\mathbf{F},$$

or, for our case

$$u/D = neF/p.$$

Since $p = \frac{2}{3}n\bar{\epsilon}$ we have

$$\bar{\epsilon} = \frac{2}{3}eFD/u. \quad (36)$$

In the experiments of Townsend† the distance between the electrodes 1 and 5 was 4 cm. Guard rings such as 2, 3, 4 in Fig. 10 were included to ensure uniformity of the applied electric field. The orifice A consisted

† Loc. cit.

of a rectangular slot 1.5 cm. long and 2 mm. wide. The shape and dimensions of the electrodes B , C_1 , and C_2 are illustrated in Fig. 10. Very small currents of the order 10^{-12} amps. were received on electrode 4 and a special induction balance was devised to measure them with accuracy. No precautions were taken to ensure good vacuum conditions, the apparatus not being constructed of materials which would permit of outgassing by heating. It is likely, however, that no important error has been introduced thereby. In support of this three reasons may be adduced:

- (a) The same apparatus has been used to measure drift velocities (§ 7.1). These agree quite closely with those obtained by a different method (§ 7.2) using high vacuum technique.
- (b) The mean energies observed for diffusion in the rare gases agree quite closely with those calculated from the formula (24), the total cross-section measurements of Ramsauer, and the observed differential cross-sections (Chap. II, § 7.3; III, § 2.4) as may be seen by reference to § 8 and Fig. 12.
- (c) An apparatus operating on the Townsend principle but in which the vacuum conditions are very good has been constructed by Huxley and Zaazou.† It gives results for the drift velocity of air which do not differ by more than a factor of 2 from those obtained with the Townsend apparatus.

In Huxley and Zaazou's apparatus (Fig. 11), constructed of nichrome, the orifice A was a circular hole of 1 mm. diameter. The inner receiving electrode B consisted of two semicircular disks of radius 5 mm., as shown in Fig. 11(b), but these were connected together in the measurement of the mean electron energy. The outer electrode C was a concentric ring of outer radius 1.5 cm. It too was split into two parts which were connected together for the mean energy measurement. The electrons were generated in a brush discharge from a fine tungsten wire W enclosed in a pyrex sheath S . Electrons entered the space between the plates E and D through a hole H about 1 mm. in diameter in the side of S . An axial electric field of about 50 volt/cm. impelled them through the mesh of fine holes at the centre of electrode D and they then drifted through the orifice A under the influence of a similar field applied between electrodes D and F . The electrode assembly was rigidly mounted on three pillars consisting of a nichrome rod sheathed in a pyrex glass tube. Finally, the whole was enclosed within a pyrex glass tube which could be evacuated to a low pressure and thoroughly outgassed. The measurements for air

† *Proc. Roy. Soc. A*, **196** (1949), 402.

made with this apparatus are the most precise yet carried out. They will be discussed in Chap. IV, § 7, as they are particularly relevant to the determination of mean energy loss in molecular gases.

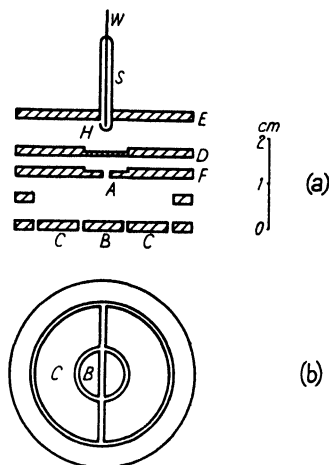


FIG. 11. Huxley and Zaazou's apparatus.

7. Measurement of drift velocity

We shall describe here two methods which have been used extensively for the measurement of u —the magnetic deflexion method of Townsend and the electrical shutter method of Bradbury and Nielsen.

7.1. The magnetic deflexion method

If a uniform magnetic field H is applied in a direction perpendicular to the electric field F the stream is deviated, in the steady state, through an angle $\theta = \arctan(1.06Hu/F)$. Hence, by measuring θ for given H and F , u may be determined.

The full theory of this result has been given by Allis and Allen.[†] It merely introduced the factor 1.06 into the formula previously given by Townsend.[‡]

Their derivation follows on very similar lines to that involved in the determination of the energy distribution function. Using the same notation as in § 5.21 and taking the magnetic field along the z -axis, we have

$$e = \frac{d\xi}{dt} \frac{df}{d\xi} + \frac{d\eta}{dt} \frac{df}{d\eta} \quad (37)$$

[†] *Phys. Rev.* **52** (1937), 703.

[‡] *Electricity in Gases* (Oxford 1914), p. 100.

with

$$\frac{d\xi}{dt} = eF/m + (eH/m)\eta,$$

$$\frac{d\eta}{dt} = -(eH/m)\xi.$$

Following (16) we now write

$$f(v, \xi, \eta) = f_0(v) + (\xi/v)f_1(v) + (\eta/v)f_2(v). \quad (38)$$

Carrying out the same procedure as before gives

$$c = \frac{eF}{m} \left\{ \xi \frac{df_0}{dv} + \frac{1}{3v^2} \frac{d(v^2 f_1)}{dv} \right\} + \frac{eH}{m} \left\{ \eta f_1 - \frac{\xi}{v} f_2 \right\}, \quad (39)$$

$$b - a = -NQ_d(f_1 \xi + f_2 \eta) + (mN/Mv^2) \frac{d}{dv} (v^4 Q_d f_0). \quad (40)$$

Equating separately to zero those terms in $c - b + a$ which are independent of, and those which are proportional to, ξ, η respectively, gives

$$(eF/mv^2) \frac{d}{dv} (v^2 f_1) - (3m/Mv^2) \frac{d}{dv} (v^4 f_0/l), \quad (41)$$

$$(eF/mv) \frac{df_0}{dv} - (eH/mv) f_2 = -f_1/l, \quad (42)$$

$$(eH/mv) f_1 = -f_2/l, \quad (43)$$

where l is $1/NQ_d$ as before.

These equations may be easily integrated to give

$$\log f_0 = -(3m/M) \left(2 \int \epsilon d\epsilon/\epsilon_l^2 + \epsilon H^2/m F^2 \right) + \log A, \quad (44)$$

$$f_1 = (6m\epsilon/M\epsilon_l) f_0, \quad (45)$$

$$f_2 = -(3mvH/MF) f_0. \quad (46)$$

As before the constant A is to be chosen so that $\iiint f d\xi d\eta d\zeta = 1$.

The components u_x, u_y of the drift velocity are now given by

$$u_x = \frac{4}{3}\pi \int_0^\infty v^3 f_1(v) dv, \quad u_y = \frac{4}{3}\pi \int_0^\infty v^3 f_2(v) dv.$$

These integrals may be expanded in a power series in $(2eH^2/F)(3/Mm)^{1/2}$ to give

$$u_y/u_x = 3Hu/2^{\frac{1}{2}}F = 1.06Hu/F, \quad (47)$$

u being the drift velocity in the absence of the magnetic field and terms of higher order in H being neglected.

This relation has been used extensively by Townsend and Bailey† and their collaborators to measure drift velocities in a number of gases. The apparatus was the same as that used for the measurement of mean energies. In addition to the uniform electric field, a uniform magnetic field of strength H was applied in a direction perpendicular to the electric field and parallel to the straight sides of the electrode B (Fig. 10). The

† See § 8 of this chapter and §§ 6, 7 of Chap. IV. A comprehensive set of tables of observed drift velocities is given in *The Behaviour of Slow Electrons in Gases* by Healey and Reed (Amalg. Wireless (Aust.) Ltd., 1941), Chap. IV.

magnetic force was adjusted so that the current arriving on the electrode C_1 was equal to that arriving on B and C_2 . In this case the centre of the stream fell on the narrow slot between C_1 and B . If d is the distance between the plane of the slit A and the plane of B and $2b$ is the width of B , we then have

$$u = 0.94 Fb/Hd. \quad (48)$$

Huxley and Zaazou† employed a modification to this procedure. The two semicircular portions of their receiving electrode (Fig. 11 (b)) were disconnected. With a given magnetic field H applied parallel to the common diameter the currents received on the two halves are unequal. The ratio R_1 is a function of $\tan \theta$ and $Fd/\bar{\epsilon}$ which may be calculated. Having measured $\bar{\epsilon}$ by the method described in § 6, it follows that $\tan \theta$ may be obtained from R_1 .

7.2. The electrical shutter method of Bradbury and Nielsen‡

This is one of the most recent methods which has been used for the measurement of drift velocities. It operates on the shutter principle, which is as follows.

Let S_1, S_2 be two shutters placed at different levels in the diffusing electron swarm. At regular intervals these shutters open for a short interval of time so that electrons may pass through. They are synchronized in phase so that both are open at the same time. Electrons will only succeed in passing through both shutters if they traverse the distance between them in an integral number of cycles. By observing the variation of the current passing through S_2 as a function of the frequency of shutter operation the drift velocity may be determined.

In the adaptation of this method by Bradbury and Nielsen to the measurement of electron drift velocities the shutters consisted of an electron filter of the type introduced by Loeb, Lusk, and Cravath§ (see Chap. VII, § 6.2, for an alternative shutter used for measuring positive ion mobilities). This is a grid of copper between alternate wires of which a high-frequency potential difference may be applied to sweep electrons, passing through the grid, to one or other set of wires. If the magnitude of the alternating potential difference is reduced all the electrons arriving at the grid are not collected by it—those which reach the grid at a time when the alternating field is nearly zero will pass through it. Two such devices with synchronized alternating fields functioned as the shutters S_1, S_2 . Electrons which travelled between the filters in a whole number

† *Proc. Roy. Soc. A*, **196** (1949), 402.

‡ *Phys. Rev.* **49** (1936), 388; **50** (1936), 950; **51** (1937), 69.

§ *Ibid.* **33** (1929), 605; **48** (1935), 684.

of half-cycles were able to pass through the second filter. In practice the frequency was fixed and F/p varied to give the value appropriate to this drift velocity, this being repeated for various frequencies.

The grids used by Bradbury and Nielsen were made of copper wires of 0.08 mm. diameter mounted 1.0 mm. apart on mica frames and were maintained at a distance 5.93 cm. apart. The alternating potential applied to the grids by a radio-frequency oscillator could be varied between 0 and 200 volts and the frequency between 10^4 and 10^7 cycles/sec. Six guard rings maintained a uniform field in the space through which the electrons diffused. The whole apparatus was sealed in a pyrex glass tube with a graded quartz seal. This was to admit ultra-violet light for the production of electrons by photo-emission. The apparatus could be baked out and pumped down to a very low pressure (10^{-7} mm. Hg) before admitting the gas under investigation. There can be no doubt that effects due to impurities were negligible in this work. The fact that the results agree well with those obtained by the Townsend method makes it probable that impurities were unimportant in that work also.

A number of other methods have been devised for the study of electronic and ionic mobility. These are mainly of historical interest now and will not be discussed here.†

8. Mean energies and drift velocities in the rare gases—comparison with single collision data and diffusion theory

A detailed comparison of the measured mean energies and drift velocities of electrons in helium, neon, and argon with those calculated from the formulae (24) and (27) using the full expressions (12) for the velocity distribution functions and the momentum loss cross-sections illustrated in Fig. 8, has been made by Allen.

The results are illustrated in Fig. 12. In all cases the observed energy has been measured by Townsend's method, while drift velocities observed by both the magnetic deflexion and electrical shutter method are included. It will be seen that these two methods give substantially the same results.

For low values of the ratio F/p good agreement is found between the observed and calculated values for all three gases. At the higher values of F/p allowance must be made for inelastic collisions involving excitation of the atoms. An approximate method of doing this has been

† See, for example, Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, 1939), Chap. 1.

worked out by Allen, and the calculated curves at higher F/p include this correction.

Similar calculations have been carried out by Druyvesteyn† for the mean energy in neon and by Smit‡ in helium in which accurate allowance is made for inelastic collisions by a method discussed in Chap. III, § 4.3. Their results are also included in Fig. 12. They agree with those of Allen for low F/p , but give slightly higher mean energies at higher F/p .

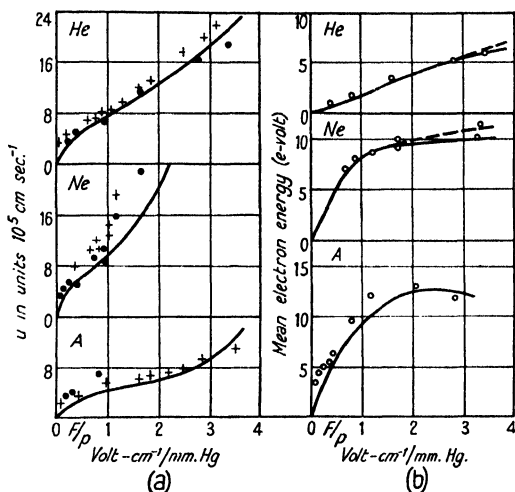


FIG. 12. Comparison of observed and calculated drift velocity and mean energy of a diffusing electron swarm in He, Ne, and A.

(a) Drift velocity for different values of F/p . ● measurements by Townsend method (magnetic deflexion); + Nielsen's measurements (electrical shutter method); — curve calculated by Allen.

(b) Mean energy for different values of F/p . ○ measurements by Townsend's method; — curve calculated by Allen allowing for elastic collisions only; --- curve calculated by Smit for He and by Druyvesteyn for Ne allowing for inelastic collisions.

It is important to remember that the distribution laws given in § 5.2 are not valid for high electron concentrations in which electronic interaction is important. In such cases, which frequently arise in discharge plasmas, the distribution is more nearly Maxwellian.§ Assuming this, Mierdel|| has calculated $\bar{\epsilon}$ for He, Ne, and A allowing for inelastic as well

† Druyvesteyn and Penning, *Rev. Mod. Phys.* **12** (1940), 87, § 8.

‡ *Physica*, **3** (1936), 543.

§ Davydov, *Phys. Zeits. Sowj.* **12** (1937), 269; Haseltine, *J. Math. Phys.* **18** (1939), 174; Druyvesteyn and Penning, *op. cit.*, § 7.

|| *Wiss. Ver. Siemens Konz.* **17** (1938), 71.

as elastic collisions.† The results are very different from those obtained with the distribution (12), especially for large F/p . They agree well with probe measurements made in the positive columns of discharges through $\text{Ne}^\ddagger$ and $\text{A}^\S$.

It appears that no important discrepancy exists and that the diffusion technique can be employed with confidence to obtain information about attachment and loss of energy by rotational and vibrational excitation in collisions between slow electrons and gas molecules.

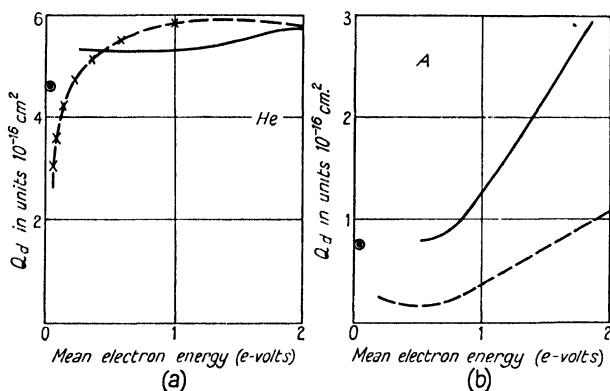


FIG. 13. Comparison of cross-sections measured directly and by electron swarm methods for low-energy electrons.

- (a) He electron swarm { $-x-x-$ Townsend and Bailey.
 (•) Wahlin.
 Ramsauer method ——— (see Fig. 3).
 (b) A electron swarm { ——— (given by Healey and Read).
 (•) Wahlin.
 Ramsauer method ——— (see Fig. 2).

It is also possible to obtain information about the behaviour of the total collision cross-section at lower electron velocities than can be employed in a direct measurement by a method such as Ramsauer's. At these low energies the diffusion and total elastic cross-section are equal. If it is assumed that they vary slowly with electron velocity, the formulae (29) and (30) may be employed to obtain them from measurements either of drift velocity or of mean energy. In this way mean cross-sections for the collisions of electrons with mean energy as low as $1/15 \text{ eV}$ in helium||

† See also Cahn, *Phys. Rev.* **75** (1949), 293.

‡ Seeliger and Hirschert, *Ann. der Physik*, **11** (1931), 817.

§ Ibid.; Groos, *Zeits. f. Phys.*

|| Townsend and Bailey, *Phil. Mag.* **46** (1923), 657; Wahlin, *Phys. Rev.* **37** (1931), 260.

and 1/30 eV in argon† have been obtained. These results are given in Fig. 13, in which the variation of mean cross-section with mean electron energy is illustrated. The corresponding total collision cross-sections observed by Ramsauer's method (see Figs. 2 and 3) are also illustrated as functions of the electron energy in the same diagram. It will be seen that for each gas the two sets of curves are as similar over the common energy range as would be expected from the fact that one set refers to mean values over a range of energies and the other to values at a definite energy. The diffusion method may therefore be regarded as an important means of extending information about total collision cross-sections down to very low electron energies. Further data obtained for molecular gases by this method in the low energy range are given in Chap. IV, § 3.1.

† Ibid.; Healey and Reed, *The Behaviour of Slow Electrons in Gases* (Amalg. Wireless (Aust.) Ltd. 1941), p. 87.

II

THE EXPERIMENTAL ANALYSIS OF THE CROSS-SECTIONS FOR IMPACT OF ELECTRONS WITH ATOMS

1. Introduction

IN Chapter I we have described the methods which have been used for measuring the total collision cross-sections of atoms towards electrons. For electron energies less than $E_1 - E_0$ —the difference in energy between the lowest excited state and the ground state of the atom—the total cross-section is equal to the elastic cross-section, contributions from radiative encounters being negligible (see Chap. VI, § 2). At higher energies, however, excitation and ionization of the atoms can occur and the total collision cross-section includes the sum of the cross-sections for all these processes in addition to the elastic cross-section, i.e.

$$Q = Q_0 + \sum_s Q_s + \int_0^{\epsilon_{\max}} Q_\epsilon d\epsilon. \quad (1)$$

The cross-section Q_s is that for excitation of the s th state of the atom and $Q_\epsilon d\epsilon$ that for an ionizing collision in which the energy of the ejected electron lies between ϵ and $\epsilon + d\epsilon$.

We are concerned now with the analysis, by suitable experiments, of the total cross-section into individual cross-sections. Furthermore, an individual cross-section such as Q_s may be analysed further in the form

$$Q_s = 2\pi \int_0^\pi I_s(\theta) \sin \theta d\theta, \quad (2)$$

where $I_s(\theta) d\omega$, the differential cross-section (see Chap. I, § 2.2), defines the angular distribution of the electrons which are scattered in producing collision excitation of an atom to the s th state.

For various reasons which will be given below, it is not possible to make a really complete analysis which would involve knowledge, for a given atom, of $I_s(\theta)$ for all s , θ , and electron energies. The measurements which have been made may be summarized as follows:

(a) Measurements of the absolute magnitude of

$$\int_0^{\epsilon_{\max}} Q_\epsilon d\epsilon = Q_i, \quad (3)$$

the cross-section for ionization, as a function of electron energy.

- (b) Analysis of the ionization cross-section Q_i into contributions from single, double, etc., ionization processes.
- (c) Determination of the absolute magnitude of the cross-section for inner-shell ionization of certain metallic atoms, as a function of energy, obtained from the measurement of the intensity of characteristic X-radiation emitted on electron bombardment of a thin target.
- (d) Determination by optical methods of the variation with electron energy of the cross-sections Q_s for excitation. It is possible to obtain information also about the absolute magnitude of the Q_s from these measurements, but the accuracy attainable in this respect is much lower than in the measurements of Q_i (see (a)).
- (e) Determination of the angular distribution function $I_s(\theta)$ for elastic collisions ($s = 0$) and the most probable inelastic collisions (those involving excitation of the first, and possibly the second, excited states which combine optically with the ground state, or ionization).

It is not possible to measure the absolute value of $I_s(\theta)$ for given s , θ , and electron energy except in special circumstances and then only roughly. For given s the relative magnitudes for different θ and electron energy may be obtained. In certain experiments the measurements are restricted to observation of $I_s(\theta)$ as a function of electron energy for different s at a fixed θ .

- (f) Use of electrical methods to obtain information about the absolute magnitudes of the strongest excitation cross-sections.

Although the information obtained from these experiments is not complete it nevertheless provides, when taken as a whole, a fairly clear picture of the way the different cross-sections vary. In the next chapter we shall discuss the theoretical interpretation of the data obtained and also the extent to which theory can fill up the gaps still left in our knowledge of the cross-sections.

2. The electrical measurement of ionization cross-sections

The chance that an electron of energy E , in passing a small distance δl through a gas, will undergo an ionizing collision with a gas atom is $NQ_i\delta l$, where N is the number of gas atoms/c.c. and Q_i is the total cross-section for ionization

$$Q_i = \int_0^{\epsilon_{\max}} Q_{\epsilon} d\epsilon.$$

These ionizing collisions give rise to a positive ion current. The ratio of the strength of this current to that of the incident beam will be $NQ_i\delta l$, provided that only one atomic electron is ejected in each collision. As

this ratio may be measured directly, it follows that Q_i may readily be determined. It is, of course, important to remember that the ratio of collected positive ion current to incident electron current will only be equal to $NQ_i \delta l$ when the ratio is small.

If an electron is sufficiently energetic there will be a finite chance that it will knock off more than one electron from an atom in an ionizing collision. Thus if $Q_i^{(1)}$, $Q_i^{(2)}$, ... are the cross-sections for single, double, ... ionization, the observed positive ion current will be given by

$$N \delta l (Q_i^{(1)} + 2Q_i^{(2)} + \dots),$$

as doubly charged ions give a double contribution to the collected current. To determine the separate cross-sections it is now necessary to measure further the relative values $Q_i^{(2)}/Q_i^{(1)}$, $Q_i^{(3)}/Q_i^{(1)}$, ..., etc. This may be done by a charge to mass ratio analysis of the positive ion current arriving at the collector G . We shall call the sum $Q_i^{(1)} + 2Q_i^{(2)} + \dots$ the apparent cross-section Q_i^{app} for ionization. It will equal the true cross-section only at electron energies below the threshold for double ionization (usually several times the energy for single ionization), but as single ionization is usually much more probable than multiple ionization, the difference between the apparent and true cross-sections is rarely very great.

Many writers express their results in terms of quantities other than the ionization cross-section. Sometimes the 'probability of ionization', P_i , is used, and this is defined as the fraction of the total number of electron collisions with the gas molecules being studied that give rise to ionization, i.e. $P_i = Q_i/Q$. Since the calculation of P_i requires a knowledge of the total collision cross-section, or alternatively of the mean free path of the electrons in the gas being studied, it is a quantity less directly associated with the actual experimental observations than Q_i .

Another quantity that has been used by many authors to express their results is the number, α_i , of positive ions formed by each electron in traversing 1 cm. of path at a pressure of 1 mm. Hg. This is equal to nQ_i^{app} , where n is the number of gas molecules per c.c. at a pressure of 1 mm. Hg. Just as in Chap. I, § 4, we have

$$Q_i^{\text{app}} = 2.81 \times 10^{-17} \alpha_i \text{ cm.}^2$$

2.1. Measurement of the apparent total ionization cross-section

Fig. 14(a) illustrates a typical experimental arrangement for the direct measurement of the positive ion current produced in a gas by an electron beam. It was used by Compton and van Voorhis† for the measurement of Q_i for H_2 , He, Ne, A, N_2 , Hg, and HCl.

† *Phys. Rev.* **26** (1925), 436.

Electrons from the cathode K were accelerated through the narrow tube T into the cylindrical collision chamber B where they underwent ionizing collisions with the gas under investigation. Surrounding the electron beam was a grid G consisting of five 20-mil. wires supported by a ring of the same size wire. This grid was maintained at a negative potential relative to the electron beam so as to attract to it the positive ions formed by the beam in the collision chamber.

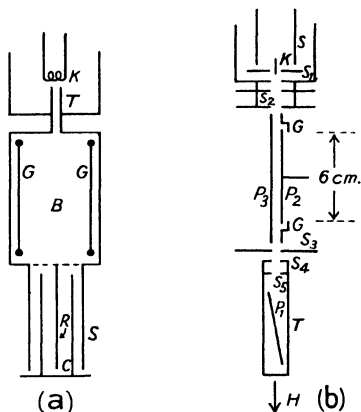


FIG. 14. Apparatus for measurement of ionization cross-sections. (a) Compton and van Voorhis; (b) Smith.

The use of a collector grid instead of a solid electrode box has some advantages. It reduces both the photo-electric current, and that arising from impact of metastable atoms on the collectors (see Chap. IX, § 6.1).

After passing through the collision chamber the electron beam was collected by an ion trap S , constructed as shown in the figure. A potential difference was applied between the central rod R of the trap and the cylinder C co-axial with it. The electrons were collected by R , and positive ions produced in S were collected by C .

The length of path of the beam in the collision chamber was 2.8 cm. and the gas pressure was from $1-5 \times 10^{-3}$ mm. Hg. Under these conditions $NQ_i \delta l$ was about 0.05 and the requirement that the chance of an electron undergoing an ionizing collision should be small was well fulfilled. As a further check that the observed positive ion current really did arise from single collisions the linearity of its variation with beam current and gas pressure could be tested.

The main disadvantage of the method of Compton and van Voorhis lay

in the fact that the collecting potential applied to the grid G had to be made high in order to prevent electrons scattered from the main beam reaching the collector. As a result, the collector field penetrated to the region of the primary beam so that the energy of the beam at the centre of the chamber was only about 0.6 times its energy when entering and leaving the chamber. Correction had to be made for this, but effectively the actual experimental curves obtained correspond to ionization by electrons of a considerable range of energies.

To overcome this difficulty a modification has been introduced by Jones† in which a uniform magnetic field of a few hundred gauss is applied in a direction parallel to the electron beam. This field confines all scattered electrons to a region close to the beam so they cannot reach the collector G . It also prevents secondary electrons from escaping from the main beam collector. On the other hand, there is the disadvantage that the average path length of the beam electrons in the gas now depends on the magnetic field. This is because the path of an electron becomes a helix of radius determined by the angle the initial direction of motion of the electron, when leaving the filament, makes with the magnetic field. The maximum such angle is, of course, limited by the defining hole. If l is the length of the collision chamber, d the diameter of the defining hole in mm., H the magnetic field strength in gauss, and V the energy of the electrons in electron volts, the maximum path length of a beam electron is

$$l\{1 + 1 \cdot 10 \times 10^{-4} d^2 H^2 / V\}.$$

Thus for $d = 1$ mm., $H = 1,000$ gauss, and $V = 100$ volts, the maximum path length of some of the electrons is more than doubled by this effect.

The collimation of the electron beam by a magnetic field has been applied extensively by Tate and his co-workers‡ in the study of ionization cross-sections. A typical arrangement, due to Smith, is shown in Fig. 14 (*b*). Electrons from the filament K produced ionization in the collision chamber between the plates P_2 and P_3 . A small potential was applied to attract positive ions to P_2 , a rectangular plate, 6 cm. by 2 cm., surrounded by a guard-ring device G . The electron current was measured by the collecting electrode P_1 , which could be held at a positive potential of 400 volts relative to the cage, T . Owing to the use of a magnetic field for collimation of the electron beam it was only necessary to keep P_2 a

† *Phys. Rev.* **29** (1927), 822.

‡ Smith, *ibid.* **36** (1930), 1293; **37** (1931), 808; Tate and Smith, *ibid.* **39** (1932), 270; Bleakney, *ibid.* **34** (1929), 157; **35** (1930), 1180; **36** (1930), 1303; Bleakney and Smith, *ibid.* **49** (1936), 402.

few volts negative relative to P_3 . Care had to be taken, however, to ensure that this potential was sufficiently high to collect all the ions produced by the electron beam.

No correction seems to have been made in these measurements for the increase in electron path due to the magnetic field and, except at the lower voltages, this correction would have been negligible. A correction should have been applied when the beam energy was not much above the threshold for ionization.

The measurements of Smith have been extended by Liska† up to energies 450 times the ionization potential in He and 1,000 times in Hg.

2.11. The atomic beam method. A somewhat different method has been applied‡ to determine the apparent ionization cross-sections of mercury, sodium, and potassium. In this method a homogeneous electron beam is fired at right angles across an atomic beam and the ions so formed collected by a Faraday cage in which the atomic beam is itself condensed.

Fig. 15 illustrates the arrangement used by Funk.§ A beam B of sodium or potassium atoms produced in the oven O was defined by the hole H and passed into the Faraday cylinder F on which it condensed. F was cooled by contact with the liquid-air trap, T . Electrons from the source K , especially designed to produce a homogeneous beam, passed at right angles to the atomic beam into the collector C . Atoms of the beam, ionized by electron impact, entered F and gave rise to a current which was measured by an electrometer. To measure the current entering F arising from ionization of the residual gas, the beam B could be interrupted by means of a screen S , attached to a ground-glass joint.

If i_1 , i_0 are respectively the currents collected by F and C , d the length of the electron path across the atomic beam, and n the number of atoms

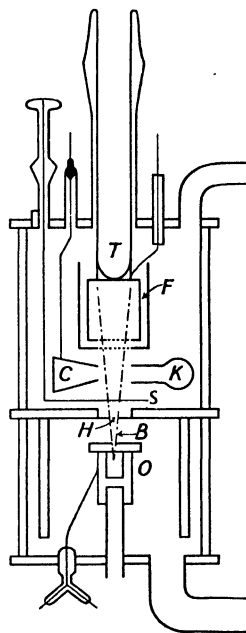


FIG. 15. Funk's apparatus for measuring the ionization cross-sections of Na and K by the atomic beam method.

† Ibid. **46** (1934), 169.

‡ Smyth, *Proc. Roy. Soc. A*, **102** (1922), 283; Hippel, *Ann. der Physik*, **87** (1928), 1035; Ditchburn and Arnot, *Proc. Roy. Soc. A*, **123** (1929), 516; Funk, *Ann. der Physik*, **4** (1930), 149.

§ Loc. cit.

per c.c. in the beam, then the apparent ionization cross-section is given by

$$Q_i^{\text{app}} = i_1 / n i_0 d.$$

n could be calculated from the oven temperature and the vapour pressure of the material being studied.

In practice a correction always had to be made for ions formed in the residual gas in the apparatus, some of which could enter F . As this correction was usually comparable with the effect due to the atomic beam, the accuracy of the measurement was low except at potentials below the threshold for ionization of the residual gas.

2.2. Analysis of positive ion current

To complete the determination of the true cross-section for single, double,... ionization it is necessary to perform a charge to mass ratio analysis of the positive ions produced. The most systematic study of the relative probabilities of multiple ionization processes has been made by Bleakney† using the apparatus illustrated schematically in Fig. 16.

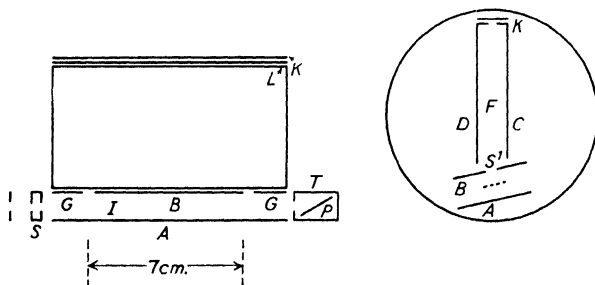


FIG. 16. Apparatus of Bleakney for measuring charge-mass ratio of ions produced by electron impact.

Just as in Smith's apparatus, electrons were collimated by a magnetic field and the ions produced in the chamber I were attracted to the plate B by means of a small potential difference between A and B .

In Bleakney's work the first slit S had dimensions 1×4 mm. and a tungsten filament was stretched lengthwise behind it. This ensured that the collimated electron beam was in the form of a ribbon having dimensions approximately defined by the first slit.

A slit S' having dimensions 0.25×60 mm. was cut in the plate B , parallel to the direction of the electron beam. A sample of ions attracted to B passed through this slit into the analysing chamber F . The charge

† Loc. cit.

to mass ratio of the ions emerging from the slit S' was measured by passing them between the condenser plates C and D , maintained at different potentials. Under the action of crossed electric and magnetic fields ions describe trochoids. In Fig. 16 let y refer to a direction parallel to the condenser plates and x perpendicular to them. If a particle of charge e and mass M passes through S' moving in the y -direction with velocity v_0 at time $t = 0$, the equation of its path in the condenser will be

$$\begin{aligned}x &= (Mc/eH)(v_0 - Fc/H)\{1 - \cos(eHt/Mc)\}, \\y &= (Fct/H) + (Mc/eH)(v_0 - Fc/H)\sin(eHt/Mc),\end{aligned}\quad (4)$$

where F and H are the electric and magnetic field strengths respectively and c is the velocity of light.

For a particular ion to be collected by the electrode K , x must vanish identically, the condition for which can be written $e/M = F^2c^2/2VH^2$, where V is the potential through which the ion has fallen before entering the analyser.

Thus by measuring the current to K as the ratio F/H was changed, the relative numbers of singly, doubly,... charged ions produced in I could be determined.

The plates A and B in Bleakney's apparatus were set at a slight angle to the x -direction to allow for the curvature of the ion path before reaching the slit S' .

Analysis of the positive ions formed, both as regards charge and mass, is of special interest when the ionization of molecules is studied. This subject is discussed in Chap. IV, §§ 5.4 and 6. In those sections apparatus is described which was primarily designed for the study of molecular ionization but which could be used equally well for the investigation of the multiple ionization of atoms.

2.3. Observed results

Measurements of the absolute magnitude of the apparent ionization cross-section as a function of electron energy have been made for helium, neon, argon, and mercury. Bleakney† has analysed the positive ions produced in each case so that by combining his results with those of the apparent cross-section the absolute values of the individual cross-sections are obtained. These are tabulated in Table I, and in Fig. 17 the way in which the cross-sections for multiple ionization of mercury vary with electron energy is illustrated. Further data are available for ionization of molecules, but these are discussed in Chap. IV, §§ 5.4 and 6.

† Loc. cit. The values given in Table I are obtained by combining the results of Bleakney, Smith, and Laska.

TABLE I
Ionization Cross-sections and Apparent Ionization Cross-sections

E_i = ionization threshold energy; $E_{\max}$ = electron energy when Q_i is a maximum ($= Q_i(E_{\max})$).
 $Q_i(E)$ = ionization cross-section for electrons of energy E .
 $Q_i^{\text{app}}(E)$ = apparent ionization cross-section.

Atom	Ion	E_i (eV)	$E_{\max}$ (eV)	$Q(E_{\max})$ $\times 10^{-16} \text{ cm}^2$	$Q(2E_i)$ $\times 10^{-16} \text{ cm}^2$	$Q(3E_i)$ $\times 10^{-16} \text{ cm}^2$	$Q(5E_i)$ $\times 10^{-16} \text{ cm}^2$	$Q(10E_i)$ $\times 10^{-16} \text{ cm}^2$	$Q(20E_i)$ $\times 10^{-16} \text{ cm}^2$
He	He ⁺	24.46	110	0.352	0.236	0.318	0.351	0.297	0.205
	He ⁺⁺	75	300	0.0015	0.0009	0.00135	0.0014	..	..
	Total (Q_{app})	24.46	110	0.353	0.236	0.318	0.352	0.301	0.208
Ne	Ne ⁺	21.5	150	0.782	0.320	0.551	0.733	0.744	0.551
	Ne ⁺⁺	63.0	250	0.045	0.025	0.043	0.039	0.028	..
	Ne ⁺⁺⁺	125.0	..	..	0.0020	0.0023	0.0020	..	..
A	Total (Q_{app})	21.5	170	0.845	0.320	0.551	0.771	0.830	0.633
	A ⁺	15.7	50	3.21	2.53	3.26	3.09	2.36	1.94
	A ⁺⁺	44.0	115	0.308	0.282	0.296	0.239	0.113	..
Hg	A ⁺⁺⁺	88	300	0.011	0.010	0.011	0.011	..	..
	A ⁺⁺⁺⁺	258	..	..	0.0014	..	..	..	..
	Total (Q_{app})	15.7	90	3.65	2.53	3.26	3.54	3.27	2.36
Hg	Hg ⁺	10.4	50	5.85	3.37	5.06	5.87	4.92	3.51
	Hg ⁺⁺	30	115	0.900	0.562	0.871	0.843	0.59	..
	Hg ⁺⁺⁺	71	210	0.201	0.146	0.197	0.146	..	..
Hg	Hg ⁺⁺⁺⁺	120	410	0.048	0.048	..	..	..	..
	Hg ⁺⁺⁺⁺⁺	225	..	..	0.014	..	..	..	..
	Total (Q_{app})	10.4	75	7.05	3.37	5.06	6.60	6.80	5.61

TABLE I (cont.)

Atom	Ion	$Q(40E_i) \times 10^{-16} \text{ cm.}^2$	$Q(70E_i) \times 10^{-16} \text{ cm.}^2$	$Q(150E_i) \times 10^{-16} \text{ cm.}^2$	$Q(300E_i) \times 10^{-16} \text{ cm.}^2$	$Q(450E_i) \times 10^{-16} \text{ cm.}^2$	$Q(600E_i) \times 10^{-16} \text{ cm.}^2$	$Q(800E_i) \times 10^{-16} \text{ cm.}^2$	$Q(1,000E_i) \times 10^{-16} \text{ cm.}^2$
He	He ⁺	..	..	..	..	..	..	..	..
	He ⁺⁺	..	..	..	..	..	..	..	..
	Total (Q_{app})	0.128	0.085	0.043	0.021	0.013	..	..	..
Ne	Ne ⁺	..	..	..	..	..	..	..	..
	Ne ⁺⁺	..	..	..	..	..	..	..	..
	Ne ⁺⁺⁺	..	..	..	..	..	..	..	..
	Total (Q_{app})	0.405	0.267	0.152	..	..	..	..	..
A	A ⁺	..	..	..	..	..	..	..	..
	A ⁺⁺	..	..	..	..	..	..	..	..
	A ⁺⁺⁺	..	..	..	..	..	..	..	..
	Total (Q_{app})	1.38	0.97	0.53	0.28	..	..	..	..
Hg	Hg ⁺	2.25	..	..	..	..	..	..	..
	Hg ⁺⁺	..	..	..	..	..	..	..	..
	Hg ⁺⁺⁺	..	..	..	..	..	..	..	..
	Hg ⁺⁺⁺⁺	..	..	..	..	..	..	..	..
	Hg ⁺⁺⁺⁺⁺	..	..	..	..	..	..	..	..
	Total (Q_{app})	3.79	2.0	1.2	0.75	0.49	0.38	0.25	0.22

It will be seen that the cross-section increases with the electron energy from a zero value at the ionization threshold E_i , up to a maximum at about $5E_i$, after which it falls off gradually at higher energies. The energy variation of Q_i will be discussed further in connexion with the theory in Chap. III, §§ 3.5, 3.7.†

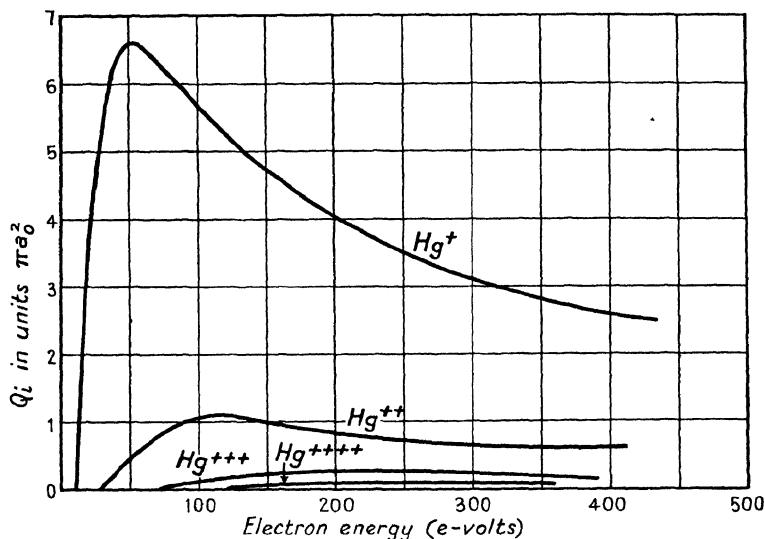


FIG. 17. Cross-section for different degrees of ionization of mercury by electron impact (Bleakney, Smith).

2.4. Variation with electron energy of the cross-section near the threshold

The study of the way the cross-section varies with energy in the neighbourhood of the threshold is important for the accurate determination of ionization potentials. For this purpose special precautions must be taken to ensure that the incident electron beam is homogeneous in energy. This is also necessary to examine whether the cross-section energy curve is smooth or exhibits a 'fine' structure.

The first experiments of this kind were those of Lawrence,‡ who carried out his measurements in a magnetic field which provided a velocity analysis of the incident electrons. Fig. 18 shows the principle of the apparatus used by Nottingham§

† Absolute ionization cross-sections have also been estimated by Funk (loc. cit.) for Na and K using the atomic beam method (see § 2.11). The values he obtained varied widely between different experiments. He observed a maximum cross-section at about twice the ionization potential of approximately 3×10^{-16} cm.² for K and 7×10^{-16} cm.² for Na. Owing to the large correction for ionization of the residual gas in his experiments, these results should be regarded as orders of magnitude only. A similar maximum cross-section at twice the ionization threshold was also obtained by Hippel for Hg (loc. cit.) using the atomic beam method.

‡ *Phys. Rev.* **28** (1926), 947.

§ *Ibid.* **55** (1939), 203.

which is a development of that used earlier by Lawrence. Electrons emitted from the filament F were accelerated through the slit S_1 into the analyser A where they were separated in velocity. Between the slits S_2 and S_3 the electrons were accelerated again and passed through the ionization chamber I containing the gas under investigation (in this case mercury vapour). The electrons were collected in the hollow collecting electrode E . The ion collector was a wire P at negative potential but surrounded by two grids G_1 and G_2 which shielded the space through which the electron beam passed from the effects of the ion collector field.

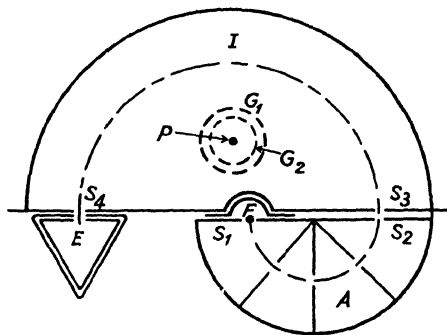


FIG. 18. Nottingham's apparatus for studying ionization of mercury near the threshold.

In practice a very small positive potential was applied to the outer grid G_1 which completely neutralized the effects of the potential of P on the path of the electron beam. The ionization current measured was that due to the ions which drifted through the outer grid G_1 .

In the experiments of Lawrence and Nottingham the incident electron beam was made homogeneous in energy by analysis in a magnetic field. The homogeneity of the beam may be improved by using an oxide-coated cathode rather than a tungsten cathode as a source of electrons, since the energy spread of the electrons from a hot cathode is proportional to the absolute temperature of emission. Further, the oxide-coated cathode may be heated indirectly and can be made an equipotential surface, thus avoiding the lack of homogeneity arising from the effect of the potential drop along the filament. Nottingham's apparatus was sealed off from the pumps and a getter used to obtain a high vacuum. Freshly distilled mercury was contained in a sealed pellet which could be broken after sealing off, thus ensuring a clean mercury surface during the experiment.

In accurate experiments care has also to be taken to allow for contact potentials between different surfaces in a vacuum. These contact potentials may be of the order of a volt or two, and may vary with time if the nature of the surfaces changes during an experiment. To correct for them the apparatus can be calibrated in terms of the critical potentials of helium which are known accurately from spectroscopic data. On the other hand, Nottingham determined the contact potentials by applying known accelerating potentials to the electrons and then measuring their actual energy from the radius of their path in the magnetic field.

Hughes and van Atta† in a detailed study of the ionization of mercury and potassium vapour employed the space-charge method for measuring the ionization. The method was developed in 1923 by Hertz.‡ It is not very suitable for the study of absolute ionization cross-sections. Hughes and van Atta used it to study the variation of the ionization cross-section with incident electron energy near the ionization potential. The principle of the method is illustrated in Fig. 19.

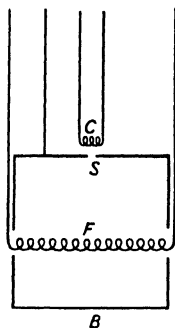


FIG. 19. Hughes and van Atta's adaptation of the space-charge method for the study of ionization near the threshold.

A filament F emitted electrons inside a box B containing the gas under investigation. These electrons were attracted to the walls of the box by means of a potential V_2 below the ionization potential of the gas. F was run sufficiently hot so that the electron current from it was space-charge limited. Another filament C was mounted outside the box opposite a slit, S , and by means of a potential V_1 electrons were accelerated into the box. As V_1 was increased it eventually passed through the ionization potential of the gas in the box. When this happened positive ions produced inside the box moved towards the filament F under the influence of V_2 . These ions neutralized the space-charge in the neighbourhood of F , thus causing an increase in the electron current from F to the walls. This increased electron current was much greater than the positive ion current which entered the box. Langmuir§ has shown that for plane parallel electrodes, when ions are injected at one of the electrodes, a single ion emitted with negligible velocity will permit $0.378(M/m)^{1/2}$ additional electrons to pass, where M , m are respectively the masses of the ions and the electrons.

2.5. Observed results of the measurements of ionization cross-section near the ionization potential—Ultra-ionization potentials

The form of the ionization curve for mercury has been studied in detail by many investigators|| at potentials near the ionization potential. Lawrence, taking great care to obtain a very homogeneous beam of electrons, found that the ionization cross-section energy curve was not smooth in this region but contained a number of subsidiary maxima, leading him to postulate the existence of a series of 'ultra-ionization' potentials of Hg. These occur within a volt or two of the ionization potential. Lawrence's observations have been confirmed by several other investigators and similar 'ultra-ionization' potentials have been observed for potassium.†† They were not observed, however, for the inert gases.‡‡

Nottingham's§§ measurements with mercury vapour confirm the existence of the phenomena reported by Lawrence. He found ionization to set in at an electron energy of 10.4 volts and to rise to a distinct maximum at 10.8 volts, followed by a minimum at 11.05 volts, while definite structural details were observed up to about 16 volts.

† *Phys. Rev.* **36** (1930), 214.

‡ *Zeits. f. Phys.* **18** (1923), 307. See also Kingdon, *Phys. Rev.* **21** (1923), 408.

§ *Ibid.* **33** (1929), 954.

|| Lawrence, loc. cit.; Haupt, *Phys. Rev.* **38** (1931), 282; Nielsen, *ibid.* **37** (1931), 87; McFadden, *ibid.* **55** (1939), 797.

†† Hughes and van Atta, loc. cit.

‡‡ Womer, *Phys. Rev.* **38** (1931), 454.

§§ Loc. cit.

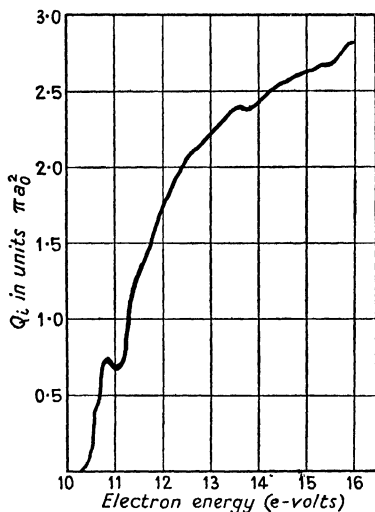


FIG. 20. Cross-section for ionization of mercury near the ionization potential.

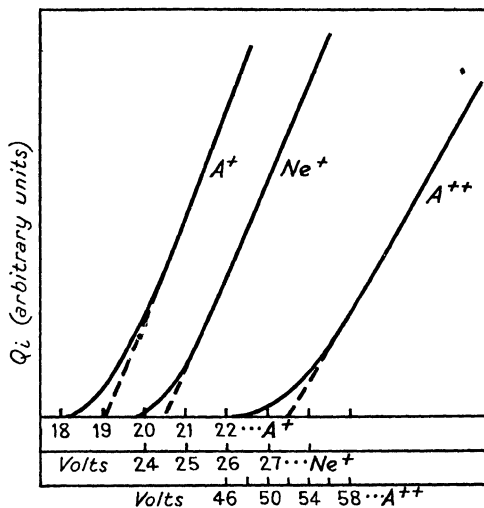


FIG. 21. Cross-section for ionization of argon (A^+ and A^{++}) and neon near the ionization potential.

Fig. 20 shows the curve obtained by Nottingham for the ionization cross-section of mercury vapour near the ionization potential.

Quite apart from the ultra-ionization potentials there may be other interesting

details of the ionization curve near the ionization potential. The actual form of the ionization curve appears to be characteristic of the particular ionization. Thus Fig. 21 shows the curve obtained near the ionization potential for A^+ , Ne^+ , and A^{++} by Stevenson and Hipple.† The 'tail' of the curve is much greater, on the voltage scale, for A^{++} than for A^+ and different again for Ne^+ , although in each case the same apparatus was used, making it unlikely that the effect could be accounted for by inhomogeneity of the incident electron beam.

3. Inner-shell ionization of atoms by electron impact

3.1. Variation with electron energy of inner-shell ionization cross-section

In the ionizing collisions discussed so far we have only considered ionization by ejection of one or more of the outer electrons from an atom. A considerable body of data is available, however, on the ionization of an atom in an inner shell, from a study of the efficiency of excitation of characteristic X-radiation by electron impact.

The vacant state in the inner shell can be filled either by a radiative transition from a higher shell or by a radiationless reorganization (Auger effect). The ratios of the intensities of the X-radiation arising from transitions between different outer levels and a given inner level have been thoroughly explored for many elements.‡ The probability that the vacant state will be filled by a radiative transition, the fluorescence yield, has also been measured for the innermost shells of many elements.‡ In principle, therefore, to determine the cross-section for a given inner-shell ionization it is only necessary to measure the intensity of one of the X-ray lines which results from the filling of the vacancy. The practical application of these principles, however, encounters many difficulties. As might be expected, the measurement of the absolute value of the cross-section is even more difficult than that of the relative values at different electron energies.

Owing to the complicated nature of the processes occurring at the target of an ordinary X-ray tube, most of the X-ray data available using ordinary thick targets are too complex to allow even of an estimate of the way the cross-section for inner-shell ionization of the atoms concerned varies with electron energy (the K ionization function). However, a series of very careful investigations have been carried out by Webster and his colleagues§ in which the intensity of the X-radiation from targets of thickness a few hundred Å was studied as a function of electron energy. Similar measurements have been made by McCue.|| Under the conditions

† *Phys. Rev.* **62** (1942), 237.

‡ See, for instance, Compton and Allison (1933), *X-rays in Theory and Experiment*.

§ Webster, Hansen, and Duvoneck, *Phys. Rev.* **43** (1933), 839; Pockman, Webster, Kirkpatrick, and Harworth, *ibid.* **71** (1947), 330.

|| *Ibid.* **65** (1944), 168.

of their experiments the corrections to be made for secondary modes of inner shell ionization were not large and could be estimated. It has thus been possible to obtain data on the inner-shell ionization cross-sections for the K shell of silver and nickel of accuracy comparable with that obtained in the experiments described above for ionization of outer electrons.

The thin targets used by Webster and his colleagues were either in the form of thin foils or of very thin layers deposited by vacuum evaporation on a beryllium base. An element of low atomic number such as beryllium was chosen as the underlying metal in order to reduce the contribution to the silver $K\alpha$ radiation (in the case of the measurements in silver) due to fluorescent excitation by primary X-radiation produced in the backing material (see Chap. VI, § 3.3). Great care was taken to obtain uniform films and it was found that uniformity could be achieved by carrying out the evaporation sufficiently rapidly.

It was necessary to go to some trouble to avoid effects which are usual with hot cathode X-ray tubes, viz. the deposition of layers of tungsten and carbon on the target. Such deposition was avoided by using a carefully designed vacuum line and set of cold traps. Also, since the physical dimensions of the focal spot in such an X-ray tube vary with tube potential, it was necessary to design the geometry of the slit system leading to the X-ray spectrometer, used to isolate the silver $K\alpha$ radiation, so as to ensure that radiation from the whole of the focal spot entered the spectrometer system and was measured.

The X-ray intensities in these experiments were measured by means of an ionization chamber. This chamber was made with two compartments connected with opposing potentials so that the currents due to natural ionization cancelled out. Only one compartment was exposed to the X-rays.†

Having measured the intensity of silver $K\alpha$ radiation emitted per unit current as a function of the incident electron energy, the following corrections to the data were necessary to obtain the form of the variation with incident electron energy of the K ionization cross-section for silver.

(i) *Diffusion of the electron stream in the thin target.* This makes the actual mean length of electron path in the target greater than the target thickness. To correct for diffusion, Webster, Clark, and Hansen‡ used an empirical expression for the multiple scattering of electrons given by Bothe,§ viz.

$$\theta = \frac{8.0}{1} \cdot \frac{V + 511}{V + 1022} Z \left(\frac{\rho x}{A} \right)^{\frac{1}{2}},$$

† Further discussion of the technique of experiments of this kind is given in Chap. VI, § 3.3.

‡ *Phys. Rev.* **37** (1931), 115.

§ *Handbuch der Physik*, **24** (1927), Chap. 1.

where θ is the most probable deflexion by multiple scattering of an electron of energy V keV in a thickness x microns of an element of atomic number Z , atomic weight A , and density ρ gm. cm.⁻³

(ii) '*Back-diffusion*' of the electrons through the thin target. Owing to multiple scattering of the electrons in the backing material (beryllium), many of the incident electrons will be scattered through an angle greater than 90° and 'rediffuse' through the thin silver target. To estimate the effect of such rediffused electrons in exciting silver $K\alpha$ radiation in the thin target it was necessary to know:

- (a) the ratio of the number of electrons deflected by multiple scattering through angles greater than 90° to the number incident on the beryllium,
- (b) the distribution in angle of these 'back-diffused' electrons, and
- (c) their distribution in energy.

Experimental data were available on all these points. From experiments by Neher† for beta rays of energy 10 to 100 keV Webster, Clark, and Hansen estimated, for (a), the value 0.025. On the basis of old measurements by Kovarik and McKeehan,‡ the distribution in angle of the back-diffused electrons was taken to be such as to give a mean path length of the back-diffused electrons through the thin target equal to approximately twice the target thickness. The distribution in energy of the 'back-diffused' electrons was even harder to assess, but some experimental evidence on this was available from the measurements of Wagner§ for layers of Al, Cu, Ag, and Au. The distributions assumed, based on these measurements, were confirmed by later measurements of Chylinski.||

(iii) *Retardation of the electrons in passing through the thin target.* Owing to the loss in energy of the electrons in passing through the thin silver target, a correction has to be made for the fact that all the measured silver $K\alpha$ radiation is not produced by electrons homogeneous in energy. To calculate this correction, Webster, Hansen, and Duveneck used the equation found empirically by E. J. Williams†† for light elements

$$\frac{dV}{dx} = -a\rho\beta^{-1.4},$$

where a is a nearly constant factor of about 1.1, V is the electron energy in eV, x is the thickness traversed in cm., ρ is the density of the material in gm./c.c., and β is the ratio of the electron velocity to that of light.

(iv) *Fluorescent K radiation of the silver film produced by continuous X-radiation from the beryllium backing material.* The intensity of this fluorescent radiation is given by the integral

$$\frac{1}{2} \int_{\nu_K}^{\nu_0} \int_0^{\frac{1}{2}\pi} I(\nu_0, \nu) \{1 - \exp(-\mu d \sec \theta)\} \frac{\mu_K}{\mu} \frac{\nu_K}{\nu} u_K \sin \theta \, d\theta d\nu,$$

where $I(\nu_0, \nu)$ is the intensity of the continuous X-ray spectrum, emitted by the beryllium in the frequency range $d\nu$, ν_0 is the high-frequency limit, ν_K the K limit of silver, μ the absorption coefficient of silver at frequency ν , and μ_K the part of it due to K electrons. d is the thickness of the silver target, θ the angle made by any ray with the normal to the target, and u_K the K fluorescence yield of silver. Sufficient experimental data are available to enable this integral to be calculated.

† *Phys. Rev.* **37** (1931), 655.

§ *Ibid.* **35** (1930), 98.

†† *Proc. Roy. Soc. A*, **130** (1930), 310.

‡ *Ibid.* **6** (1915), 426.

|| *Ibid.* **42** (1932), 393.

It is clear from the uncertainty of the experimental data available to make the necessary corrections that there is little possibility of calculating the inner-shell ionization function from measurements made using thick targets where the corrections outlined above will all be large.

For the conditions met with in the thin target measurements, these corrections are sufficiently small to enable the K ionization function to be obtained. As an example of the magnitude of the corrections, Table II shows how they vary with incident electron energy for one of the thin silver targets deposited on beryllium. The particular target used in this comparison was 450 Å thick. The quantity U expresses the ratio of the incident electron energy to the ionization energy (for silver the ionization potential is 24.9 kV). For each correction the intensity at twice the excitation potential is taken as a standard and the corrections at the other potentials made relative to the correction at $U = 2$. The various corrections are expressed in percentages and show by what percentage the observed values have to be corrected in order to give the correct form of the ionization function.

TABLE II

Magnitude of Corrections to Silver $K\alpha$ Intensity Measurements to obtain the K Ionization Function for Silver

(Film thickness 450 Å.)

U	Correction (i) per cent.	Correction (ii) per cent.	Correction (iii) per cent.	Correction (iv) per cent.
1.2	-4.7	+1.6	+1.6	+2.7
1.5	-2.3	+1.0	+0.3	+1.7
2.0	0	0	0	0
2.5	+1.0	-0.7	-0.1	-1.2
3.0	1.6	1.2	-0.1	-2.5
3.5	2.0	-1.6	..	-3.7
4.0	2.2	-1.9	..	-5.0
5.0	2.5	-2.2	-0.1	(-7)
6.0	2.7	-2.4	..	(-9)
7.0	2.8	-2.6	-0.1	(-11)

It is seen that the corrections are all small except for the fluorescent excitation (iv) which becomes appreciable for high-energy electrons. With this exception the estimated values of the corrections are probably sufficiently accurate to enable the form of the ionization function to be obtained within a few per cent. In order to overcome the uncertainty in correction (iv) Webster, Hansen, and Duveneck carried out measurements at high voltages using free silver foils as targets, thus making correction (iv) very small. In order to get sufficient mechanical strength these foils were about 1,800 Å thick so that they would not be expected to give the correct form of the ionization curve at low potentials. Nevertheless, by combining the data on beryllium-backed silver films at low potentials with that on free silver foils at high potentials, the final results

given by these workers for the K ionization function of silver is probably accurate to within a few per cent. up to incident electron energies of seven times the ionization potential. The measurements of Pockman, Webster, Kirkpatrick, and Harworth on nickel up to 22 times the ionization potential are of the same order of accuracy.

3.2. *Absolute magnitude of the cross-section*

The absolute value of the cross-section for K shell ionization by electron impact has been measured for silver by Clark† and for nickel by Smick and Kirkpatrick.‡ In these measurements the method of balanced filters developed by Ross§ was employed. This has the advantage of separating out monochromatic X-radiation of much greater intensity than is possible by means of the X-ray crystal spectrometer. In this method two filters, composed of materials which are adjacent elements in the periodic system, are used in turn. The thickness of these two filters may be adjusted so that the spectrum of an incident continuous beam of X-radiation after transmission through either filter coincides at all wave-lengths except in the region between the respective K limits. The difference in ionization produced by the X-radiation passing through these filters must therefore arise from radiation of wave-lengths between the two K limits.

In the experiments of Smick and Kirkpatrick,|| balanced filters of iron and cobalt were used to isolate the nickel K radiation. As finally adjusted, the cobalt filter passed 63.9 per cent. of the Ni $K\alpha$ radiation, the iron filter passed 6.8 per cent. The transmission of the two filters was appreciably the same except for a region 0.13 Å wide around the wave-length of the Ni $K\alpha$ radiation.

In the measurements of the absolute cross-section of ionization by electron impact it is necessary, in addition to the corrections described above, to correct for the absorption of the Ni $K\alpha$ radiation in the nickel target, and to know accurately the mean thickness of the nickel film. Other constants required in the determination are the transmission coefficients of the various absorbers through which the X-radiation must pass, the mean X-ray energy expended per ion pair produced in the gas of the ionization chamber (air), the K fluorescence yield of nickel and the ratio of the number of emitted nickel $K\alpha$ quanta to the total number of emitted quanta in all lines of the K series.

Of all these, Smick and Kirkpatrick consider the greatest uncertainty

† *Phys. Rev.* **48** (1935), 30.

§ *Ibid.* **28** (1926), 425.

‡ *Ibid.* **67** (1945), 153.

|| *Loc. cit.*

lies in the assumed value of the X-ray energy required to produce an ion pair. In their final result they claim an absolute accuracy of about 5 per cent.

3.3. *Results of the measurements*

The measured absolute values of the cross-section for silver for potentials up to 7 times the ionization potential are shown in Fig. 80 (e) of Chap. III, where a comparison is also made with the theory. This experimental curve is obtained by combining the measurements of Clark† with those of Webster, Hansen, and Duveneck.† Similarly Fig. 80 (f) (Chap. III) shows the corresponding experimental curve for nickel, obtained by a similar combination of the measurements of Pockman, Webster, Kirkpatrick, and Harworth† with those of Smick and Kirkpatrick.†

Webster, Pockman, and Kirkpatrick† have also studied the L -shell ionization function for gold by measuring the variation with electron energy of the intensity of Au $L\alpha$ and Au $L\beta_1$ lines which are produced by atoms ionized in the L_{III} and L_{II} levels respectively.

Using thin targets of tungsten deposited on beryllium Huizinga§ has studied the relative intensity of W $L\beta_1$, W $L\beta_2$, and W $L\beta_3$, lines, arising from ionization of the L_{II} , L_{III} , and L_I levels respectively, for electron energies ranging from 25 to 40 keV. He found that as the electron energy increased in this range the probability of excitation of the L_I level increased by about 20 per cent. relative to that of the L_{II} and L_{III} levels.

No determinations of absolute cross-sections have been made for L -shell ionization.

McCue† has measured the variation of intensity of the $L\alpha$ doublet of silver with electron energy for thin targets of silver on beryllium, thus obtaining the form of variation of the ionization cross-section of the Ag L_{III} state. His results are shown in Fig. 80 (e) of Chap. III.

A quantity of some interest would be the relative ionization cross-sections for the same atom in the L and K shells. The measurement of this quantity, however, is fraught with considerable difficulty because it involves the comparison of the intensities of X-ray beams of widely different wave-length, and no direct measurements of it have yet been made.

3.4. *Double inner-shell ionization*

The cross-section for double inner-shell ionization of an atom can be studied and compared with that for a single ionization. Consider a

† Loc. cit.

3595.47

‡ *Phys. Rev.* **44** (1933), 130.

§ *Physica*, **4** (1937), 317.

doubly ionized atom which has lost an electron from both the K and the L shell. If such an atom undergoes a transition $LL \rightarrow KL$, the X-radiation emitted will be a satellite line of the $K\alpha$ radiation.

Parratt† and Shaw and Parratt‡ have measured the relative intensity of $K\alpha$ satellites as compared with that of the $K\alpha$ lines for elements of atomic number 11 to 46. These experiments were not carried out with truly thin targets and so they need correction for the effect of fluorescent excitation by the general radiation produced in the target. Since one might expect the double inner-shell photo-ionization of an atom to be very improbable, the effect of the fluorescent excitation would be expected to give too small a value for the relative intensity of the satellites to the parent line.

Fig. 89 (chap. III) shows how the observed relative intensity decreases with increasing atomic number. The decrease appears fairly regular up to an atomic number about 38, but for higher atomic number there is a sharp decrease in relative intensity. In these experiments the potential applied to the X-ray tube was in each case roughly twice the K ionization potential or a little greater. The curves show therefore the form of variation with atomic number of the relative probability of a double KL ionization to that of a single K ionization.

4. Optical measurement of cross-sections for excitation

4.1. Principle of the method

The passage of an electron beam of sufficient energy through a gas produces excited atoms. These atoms dispose of their surplus energy by radiation, and it is possible, in principle, to determine the cross-sections for excitation of the different levels by measurement of the absolute intensities of the emitted spectral lines for a given electron beam current.

Let n_j be the number of excited atoms produced per c.c. by the beam. The current strength in the beam is supposed so small that collisions between excited atoms and a beam electron may be neglected. In the same way the gas pressure is supposed so low that collisions between excited and normal atoms, which may lead to transfer of excitation, may also be ignored. We then have

$$\frac{dn_j}{dt} = -A_j n_j + N Q_j v n_e + \sum A_{ij} n_i. \quad (5)$$

In this equation A_{ij} is the probability/sec. of the radiative transition from the i th to the j th level, $A_j = \sum A_{jk}$, the suffix k referring to levels

† *Phys. Rev.* **50** (1936), 1.

‡ *Ibid.* 1006.

of lower energy than that specified by j . Q_j is the cross-section for excitation of the j th level, v is the electron velocity, and n_e, N are the respective numbers of electrons and gas atoms/c.c. In equilibrium we have

$$n_j = (NQ_j v n_e + \sum A_{ij} n_i) / A_j. \quad (6)$$

The total number of quanta of the radiation emitted, per unit length of the electron beam, with frequency corresponding to the transition $j \rightarrow k$ is

$$J_{jk} = A_{jk} n_j S, \quad (7)$$

where S is the cross-sectional area of the beam. From (6) we have finally

$$J_{jk} = \frac{A_{jk}}{A_j} \left(N Q_j \frac{i}{e} + \sum_i J_{ij} \right), \quad (8)$$

where

$$A_{jk}/A_j = J_{jk} / \sum_k J_{jk}$$

and $i = v S n_e$ is the current strength in the beam. It follows that, if measurements are made of the absolute intensities of the radiation emitted in transitions both to and from the j th state of the atom, then the cross-section Q_j may be derived. Similarly, if relative intensity measurements are made for these lines at different electron energies, the form of the variation of Q_j with energy may be derived. Relative magnitudes of the Q_j for different j may also be obtained from the relative intensities of all the lines involved.

What is usually measured in optical experiments of this kind is the relative variation with energy of the intensity of a number of chosen spectral lines. This is called the optical excitation function of the particular line concerned. It gives the relative variation with energy of J_{jk} which is *not* the same as that of Q_j unless the contribution due to transitions from upper levels can be ignored. If sufficient lines have been measured these cascade contributions can be allowed for as described above, but in most experiments this has not been so and resort has had to be made to theoretical estimates of the A_{jk} . Similarly, absolute measurements are usually given in terms of an effective cross-section Q_{jk} which is defined by $J_{jk} = N Q_{jk} i/e$, so that, in terms of (8),

$$Q_{jk} \left[1 - \frac{\sum J_{ij}}{\sum J_{jk}} \right] = \frac{A_{jk}}{A_j} Q_j. \quad (9)$$

Again, Q_j can only be deduced if the ratios of the quantities J_{ij}, J_{jk} are obtainable from the observed data either directly or with assistance from theory.

The method is incapable of giving information about the cross-section

for excitation of metastable levels. Atoms in such states lose their excitation without emission of radiation. Milatz and Ornstein† have used a method in which the number of metastable atoms present in the collision chamber is measured by means of the absorption they produce in a light beam of suitable wave-length (see § 4.41). In this way they were able to determine how the concentration of metastable atoms varies with electron energy. To allow for the population of the metastable state by cascade it is necessary to measure, not only the absolute intensity of the different spectral lines ending on the metastable state, but also the lifetime of the metastable state (see Chap. VII, § 9).

4.2. The measurement of optical excitation functions

The apparatus used is simple in principle. Fig. 22 shows the arrangement used by Hanle and Schaffernicht.‡ Electrons from an oxide-coated cathode K , after acceleration through 80 volts, passed through

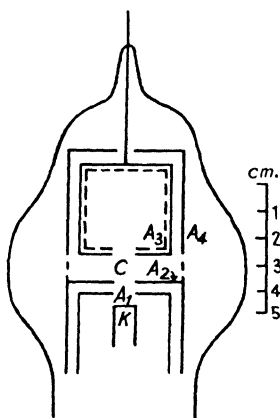


FIG. 22. Hanle and Schaffernicht's apparatus for the study of optical excitation cross-sections.

the slit A_1 and were then retarded to the required energy by a suitable potential on A_2 . After suffering collisions in the collision chamber C , they were collected by the Faraday cylinder A_3 at the same potential as A_2 , and about 1 cm. from it. Atoms within C were excited and emitted radiation in their subsequent reorganization.

The electrode A_2 was electrically connected with the cylinder A_4 which surrounded the whole of the collision space C , thus ensuring that it was free of electrical fields. The inside of the Faraday cylinder was screened by a fine wire mesh to prevent secondary or reflected electrons from entering the collision space. Radiation from this space was passed through the glass envelope of the tube and

its intensity measured.

Hanle and Schaffernicht carried out an absolute intensity measurement. After leaving the tube the light was incident on a lens, which brought it to a focus on a photo-cell after passage through a suitable monochromatic filter. In this way a measure could be obtained of the intensity of a single line excited in the collision space C . A mercury

† *Physica*, **2** (1935), 355. See also Woudenberg and Milatz, *Physica*, **8** (1941), 871.

‡ *Ann. der Physik*, **6** (1930), 905.

lamp whose intensity could be compared with that of a standard Hefner lamp by means of a thermo-element was used to make the measurement absolute. Light from the lamp was focused on the photo-cell after passing through a neutral filter, the known transmission of which was of suitable magnitude to make the intensity from the mercury lamp comparable with that of the monochromatic radiation reaching the photo-cell from the collision space C . Care had, of course, to be taken to exclude reflected radiation from entering the photo-cell.

Hanle and Schaffernicht's measurements were made on a number of mercury lines in the visible region. For such lines no errors were encountered due to the resonance absorption of the radiation before leaving the tube. Absolute intensity measurements had previously been carried out by Bricout† for the mercury line $\lambda 2537$ ($6^1S_0-6^3P_1$), in the ultraviolet, but since this line arises from a transition to the ground state of the mercury atom, the possibility of resonance absorption before leaving the tube is high and Hanle and Schaffernicht considered that Bricout's measurements were invalidated by this effect.

A general arrangement similar to that described above has been employed by many investigators, except that a spectrograph has been used to isolate the various spectral lines emitted.

An independent measurement of the absolute intensity of the mercury line $\lambda 4358$ ($6^3P_1-7^3S_1$) was made by Fischer.‡ He used an electron tube of similar design to that of Hanle and Schaffernicht, but isolated the mercury line by means of a spectrograph and compared its intensity photometrically with that in a narrow band of the continuous spectrum around this wave-length emitted from a tungsten incandescent lamp at a temperature of $1,700^\circ \text{C}$. From Wien's law he calculated the energy in the given wave-length band incident on the spectrograph slit from the tungsten lamp and, knowing the dispersive power of the spectrograph, was able to calculate from the photometric data the absolute intensity of the $\lambda 4358$ line emitted from the electron tube. For electrons of energy 60 eV Fischer obtained a cross-section for emission of this line of $8.04 \times 10^{-18} \text{ cm}^2$ in very good agreement with the independent value of $8.25 \times 10^{-18} \text{ cm}^2$ obtained earlier by Hanle and Schaffernicht.

A considerable amount of data on absolute excitation cross-sections has been obtained by Hanle and his collaborators§ using the absolute intensity of this line of mercury as a standard. The gases studied were present, mixed with mercury vapour, in an apparatus of the type

† *J. Phys. Rad.* **9** (1928), 88.

‡ *Zeits. f. Phys.* **86** (1933), 646.

§ Thieme, *ibid.* **78** (1932), 412; Haft, *ibid.* **82** (1933), 73.

described above (Fig. 22). Knowing the partial pressure of the mercury vapour, an intensity measurement of the lines being investigated relative to the $\lambda 4358$ line of mercury sufficed to determine their absolute cross-section for excitation.

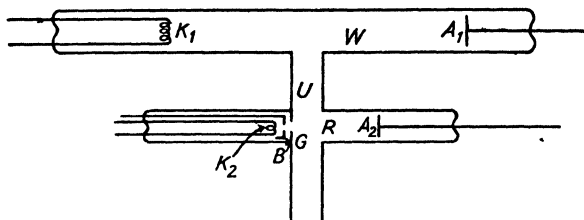


FIG. 23. Apparatus for studying excitation cross-section of the Balmer lines.

When a spectrograph is employed for intensity measurements, however, it is necessary that light from the whole cross-section of the electron beam in the collision space should enter the spectrometer slit. This is because, in general, this cross-section will change with electron velocity. The observed intensity of a given line excited at different energies will therefore correspond to different current densities unless this precaution is taken. It is not clear how serious this effect may have been in the work of Hanle's associates.

In some very careful measurements of the absolute excitation cross-sections of helium, Lees† overcame this difficulty by using a wide spectrograph slit at right angles to the electron beam so that a complete cross-section of the beam could be photographed and the integrated intensity across the whole beam measured photometrically.

In addition to investigations on a number of monatomic gases and vapours, measurements have been made of the excitation functions of atomic hydrogen by Ornstein and Lindeman‡ using an apparatus illustrated in Fig. 23. Hydrogen was passed through the hot cathode discharge tube W in which dissociation took place (see Chap. IV, § 5.2). The atomic hydrogen passed out of the discharge through the tube U , and in a time short compared with its lifetime in the atomic form ($\frac{1}{5}$ second) reached the tube R . Electrons from the cathode K_2 , accelerated through slits in electrodes B and G , passed down the tube R to the anode A_2 . The slit G was a glass diaphragm which, by shielding the atomic hydrogen from the metal surface S of the electron gun, prevented recom-

† *Proc. Roy. Soc. A*, **137** (1932), 173.

‡ *Zeits. f. Phys.* **80** (1933), 525. See also Ornstein, Lindeman, and Vreesswijk, *Physica*, **2** (1935), 540.

bination at this surface. The hydrogen atomic spectrum was excited by electron collision and the intensity of the radiation excited just outside the slit G measured as a function of electron energy. No attempt, however, was made to measure the absolute cross-section.

In the measurement of excitation cross-sections care has to be taken to ensure that the observed effects do not arise from multiple processes. To be certain on this point it is necessary to carry out measurements of the intensity of the lines excited by electrons of a given energy for a wide range of current and pressure. Cross-sections for excitation must be estimated for values of current and pressure in the range of linearity of the intensity-current and intensity-pressure curves.

4.3. Observed results of measurements of optical excitation cross-sections

Measurements of the cross-section for excitation of spectral lines by electron impact have been carried out for H, He, Ne, A, Na, Zn, Cd, Hg, Tl, Ag, Pb.†

4.31. Results of measurements in helium—derivation of excitation cross-sections. Lees‡ and Thieme§ have not measured the absolute values of the effective cross-sections Q_{jk} (defined by (8)) for a sufficient number of lines to enable the cross-sections Q_j (for excitation of the j th excited state) to be derived from (9) without appeal to theory. Nevertheless they have investigated sufficient lines for the Q_j to be derived with

† H—Ornstein and Lindeman, *Zeits. f. Phys.* **63** (1930), 8; *ibid.* **80** (1933), 532; Ornstein, Lindeman, and Vreeswijk, *Physica*, **2** (1935), 541.

He—Elenbaas, *Zeits. f. Phys.* **59** (1930), 289; Hanle, *ibid.* **56** (1929), 94; Lees, *Proc. Roy. Soc. A*, **137** (1932), 173; Lees and Skinner, *ibid.* 186; Michels, *Phys. Rev.* **36** (1930), 1362; Thieme, *Zeits. f. Phys.* **78** (1932), 412.

Ne—Hanle, *Zeits. f. Phys.* **65** (1930), 512; Herrmann, *Ann. der Physik*, **25** (1936), 143; Milatz and Woudenberg, *Physica*, **7** (1940), 697.

A—Fischer, *Zeits. f. Phys.* **86** (1933), 646; Herrmann, *Ann. der Physik*, **25** (1936), 143.

Na—Christoph, *ibid.* **23** (1935), 51; Haft, *Zeits. f. Phys.* **82** (1933), 73; Loveridge, Thesis, Univ. of California (1931) quoted by Brode, *Rev. Mod. Phys.* **5** (1933), 257; Michels, *Phys. Rev.* **38** (1931), 712; Ornstein and Baars, *Proc. Amst. Acad.* **34** (1931), 1259.

Zn—Larché, *Zeits. f. Phys.* **67** (1931), 440.

Cd—Ibid.

Hg—Bricout, *J. Phys. Radium*, **9** (1928), 88; Crozier, *Phys. Rev.* **31** (1928), 800; Fischer, *Zeits. f. Phys.* **86** (1933), 646; Hanle, *ibid.* **54** (1929), 848; Hanle and Schaffernicht, *Ann. der Physik*, **6** (1930), 905; Ornstein, Lindeman, and Oldeman, *Zeits. f. Phys.* **83** (1933), 171; Ostensen, *Phys. Rev.* **34** (1929), 1352; Schaffernicht, *Zeits. f. Phys.* **62** (1930), 106; Thieme, *ibid.* **78** (1932), 412; White, *Phys. Rev.* **28** (1926), 1124.

Tl—Strohmeier, *Zeits. f. Phys.* **107** (1937), 409; Fuhrmann, *Ann. der Physik*, **34** (1939), 625.

Ag—Fuhrmann, loc. cit.

Pb—Ibid.

‡ *Proc. Roy. Soc. A*, **137** (1932), 173.

§ *Zeits. f. Phys.* **78** (1932), 412.

reasonable accuracy using calculated values of the transition probabilities A_{jk} . These give immediately the ratio A_{jk}/A_j on the right-hand side of (9). The measurements do not give all the J_{ij} or J_{jk} on the left-hand side. However, some transition from each state i which contributes appreciably to $\sum J_{ij}$ will have been studied so that J_{ii} , say, will be known. J_{ij} is then given from $J_{ij} = J_{ii} A_{ij}/A_{ii}$. The same applies to $\sum J_{jk}$.

Table III gives for four electron energies effective cross-sections Q_{jk} for various helium lines, measured by Lees and by Thieme, while the derived cross-sections Q_j with and without allowance for the cascade correction $(1 - \sum J_{ij}/\sum J_{jk})$ of (9) are given in Table IV.

There is a very wide discrepancy between the two sets of observed intensities for the 3^3P-2^3S line, but for other lines they differ by a factor of about two or three only, which does not seem excessive in view of the difficulty of the measurements. It will be noted that in most cases the cascade effect is small and it is usually a good approximation to ignore it.

The excitation functions (Q_{jk} as a function of electron energy) for various lines, obtained from Lees's results, are illustrated in Fig. 24. Apart from cascade effects which are generally small (see Table IV), these excitation functions have the same form as those for the excitation of the j th level (Q_j as a function of electron energy.)

For terms of the same series (Fig. 24 (a)) the excitation functions are of very similar form but marked differences exist between terms of different series. It is found that three clearly marked types of excitation function occur.

The first type is characteristic of terms which combine optically with the initial (ground) state and is exemplified by the curves of Fig. 24 (a) for n^1P terms. The excitation function resembles that which represents the ionization cross-section as a function of electron energy. There is a rise to a broad maximum at an electron energy 4 or 5 times the excitation threshold followed by a slow decrease for further increase of electron energy.

The second type is characteristic of terms which have a different multiplicity from that of the ground state, i.e. for helium, the triplet terms. Fig. 24 (b) exemplifies this type as displayed by the 4^3S and 3^3P terms. The excitation function rises to a sharp maximum for an electron energy only slightly above the threshold and then decreases very rapidly to very small values at electron energies 3 or 4 times larger. It would seem, by reference to Fig. 24 (b), that the 4^3D term represents an exception. Although at low excitation energies its excitation function has the characteristic form for a triplet state it behaves like that for a 1P term (Fig.

24 (a)) at higher energies. It has been shown, however, that this anomalous behaviour, which is found for other 3D terms, is due to excitation of helium atoms to 3D levels by impact with other helium atoms which

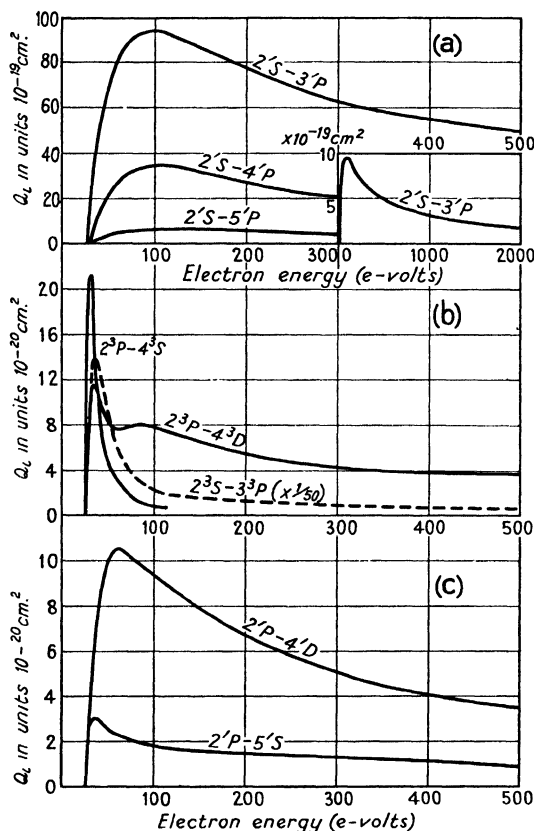


FIG. 24. Observed excitation functions obtained by Lees for Ho lines.

- (a) Three lines of the same series, $\lambda 5015$ (2^1S-3^1P), $\lambda 3964$ (2^1S-4^1P), $\lambda 3614$ (2^1S-5^1P).
 (b) $\lambda 3888$ (2^3S-3^3P), $\lambda 4713$ (2^3P-4^3S), $\lambda 4472$ (2^3P-4^3D).
 (c) $\lambda 4922$ (2^1P-4^1D), $\lambda 4438$ (2^1P-5^1S).

have been excited by electron impact to 1P states. This is discussed in detail in Chap. VII, § 8.2. The true electron excitation function for the 3D terms resembles that for other triplet levels.

A form of excitation function intermediate between the above two types is found for the 5^1S and 4^1D terms (Fig. 24 (c)), which, while not combining optically with the ground state, nevertheless have the same

TABLE III
Observed Cross-section Q_{jk} (in units 10^{-20} cm.²) for Excitation of Helium Lines

Electron energy	Line	Wave-length	60 eV		100 eV		200 eV		400 eV		$Q_{jk}(\text{max})$		$E_0(\text{max})$ (eV)	
			Lees	Thieme	Lees	Thieme	Lees	Thieme	Lees	Thieme	Lees	Thieme	Lees	Thieme
2^1S-3^1P		3,015	80.0	72.1	94.2	83.0	80.0	68.1	55.1	43.8	100.0	84.0	100	100
2^1S-4^1P		3,964	26.4	24.5	29.4	28.8	24.1	22.9	17.0	12.2	34.0	29.0	100	100
2^1S-5^1P		3,614	4.0	..	5.1	..	3.8	..	2.9	..	5.7	..	10	..
2^1P-4^1S		5,047	..	11.4	..	8.15	..	5.3	..	3.31	..	16.5	..	40
2^1P-5^1S		4,437	2.3	6.5	1.8	4.8	1.3	2.9	0.76	1.71	2.8	8.1	36	37
2^1P-6^1S		4,168	1.1	2.6	0.87	1.6	0.45	0.83	..	0.58	1.2	4.0	36	35
2^1P-4^1D		4,921	9.7	18.9	8.6	13.5	6.0	7.7	4.0	7.5	11.0	23.0	74	50
2^1P-5^1D		4,387	5.2	10.1	5.3	7.8	3.8	4.1	2.5	2.4	6.0	12.0	74	50
2^1P-6^1D		4,143	..	4.8	..	3.4	..	2.05	..	1.2	..	6.0	..	50
2^1P-7^1D		4,009	..	2.0	..	..	..	..	..	..	..	2.5	..	50
2^3S-3^3P		3,888	27.0	503.0	11.4	167.0	4.6	46.2	2.9	20.3	72.0	1700.0	32	30
2^3P-4^3S		4,713	2.7	6.8	1.01	2.6	..	0.5	..	0.3	21.0	38.0	30	30
2^3P-5^3S		4,121	0.9	3.9	0.29	1.4	..	0.36	..	0.17	4.5	19.0	30	30
2^3P-6^3S		3,867	..	1.4	..	0.47	..	0.05	..	..	..	9.0	..	30
2^3P-3^3D		5,875	..	18.5	..	9.5	..	4.9	..	3.6	..	42.0	..	30
2^3P-4^3D		4,471	7.7	7.5	7.0	4.2	5.3	2.1	3.5	1.2	12.0	18.0	34	30

$Q_{jk}(\text{max})$ is the maximum observed cross-section for excitation for each line and $E_0(\text{max})$ the energy at which the maximum occurs.

TABLE IV

Cross-sections Q_j (in units 10^{-20} cm^2) for Excitation of Helium Levels derived from the Cross-sections for Line Excitations given in Table III

Electron energy	60 eV				100 eV				200 eV				400 eV			
	Lees		Thieme		Lees		Thieme		Lees		Thieme		Lees		Thieme	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
3 ¹ P	3.500	3.500	3.130	3.130	4.100	4.100	3.610	3.610	3.460	3.460	2.960	2.960	2.360	2.360	1.900	1.900
4 ¹ P	730	..	675	..	780	..	795	..	660	..	630	..	470	..	335	..
5 ¹ P	120	..	..	..	155	..	..	..	114	..	..	..	87	..	..	..
4 ¹ S	..	..	23.3	20.4	..	..	16.6	14.1	..	..	10.9	9.3	..	..	6.75	6.0
5 ¹ S	4.75	..	13.4	..	3.7	..	9.9	..	2.7	..	6.0	..	1.6	..	3.5	..
6 ¹ S	2.9	..	6.9	..	2.3	..	4.3	..	1.2	..	2.2	..	..	..	1.5	..
4 ¹ D	13.2	13.2	25.8	25.8	11.7	11.7	18.4	18.4	8.2	8.2	10.5	10.5	5.5	..	10.2	10.2
5 ¹ D	7.9	..	15.4	..	8.1	..	11.8	..	5.8	..	6.2	..	3.8	..	3.6	..
6 ¹ D	..	..	8.2	..	..	..	5.8	..	..	..	3.4	..	..	..	2.0	..
3 ³ P	27.0	16.5	503	503	11.4	4.0	167	155	4.6	..	46.2	..	2.9	..	20.3	..
4 ³ S	4.6	..	11.5	3.3	1.7	..	4.4	1.4	..	..	0.8	0.2	..	..	0.5	0.1
5 ³ S	1.9	..	8.2	..	0.6	..	2.9	..	..	..	0.7	..	..	..	0.4	..
6 ³ S	..	..	2.9	..	..	..	1.0	..	..	..	0.1	..	..	..	..	..
3 ³ D	..	..	18.5	13.8	..	..	9.5	8.5	..	..	4.9	4.6	..	..	3.6	3.6
4 ³ D	9.8	..	9.6	..	9.0	..	5.4	..	6.8	..	2.7	..	4.5	..	1.5	..

(a) Cross-section estimated without allowance for cascade effects.

(b) Cross-section estimated allowing for cascade effects.

multiplicity. In these cases, the excitation rises to a maximum at a smaller electron energy than for the optically allowed excitations of Fig. 24 (a), but falls off much more slowly at high electron energies than for the intercombination transitions of Fig. 24 (b). It is also noteworthy that, for the 5^1S level, the maximum occurs at a smaller energy than for the 4^1D level. This result, which holds for other S and D levels, may be correlated with the fact that a transition 1^1S-n^1S is optically forbidden to a much greater degree than 1^1S-n^1D which is associated with a quadrupole moment.

The above classification of excitation functions in terms of the optical relation of the excited states to the initial state is of wide generality (see §§ 4.32, 4.44, 5.2, and Chap. IV, § 5.2). There is still some doubt, however, as to whether the distinction is so apparent at electron energies close to the threshold as would appear from the optical measurements (see § 5.2).

It will be noted that none of the measurements concern lines in which the final state is the ground 1^1S state. This is because the wave-lengths of such lines lie in the neighbourhood of 1,000 Å, the most difficult region of the spectrum to investigate. Information concerning the electronic excitation of the 2^1P and 2^3P levels is therefore not available from these experiments. Some data concerning these levels may be obtained by the electrical methods discussed in § 5.

A further discussion and analysis of the helium data is given in Chap. III, § 3.5.

4.32. Results of measurements in mercury. In contrast to helium a number of measurements have been made of the excitation function of the mercury resonance line $\lambda 2537$ ($6^1S_0-6^3P_1$). These measurements are rendered difficult by the resonance character of the line because absorption and re-radiation of the line occurs in the vapour away from the electron beam (see also Chap. VII, § 7.21). This is reflected in the poor agreement between the results obtained by different investigators, manifest by reference to Fig. 25.

Ornstein, Lindeman, and Oldeman† have measured the relative excitation functions for the lines $\lambda 3131$ ($6^3P_1-6^3D_1$), $\lambda 3125$ ($6^3P_1-6^3D_2$), $\lambda 4078$ ($6^3P_1-7^1S_0$) and $\lambda 4358$ ($6^3P_1-7^3S_1$). These results, which agree reasonably well with those of Hanle and Schaffernicht,‡ make it possible to determine the contribution from cascade processes to the population of the 6^3P_1 level and hence to obtain the excitation cross-section of the level from the observed excitation function of the $\lambda 2537$ line. The procedure is illustrated in Fig. 26, in which the excitation functions for the

† *Zeits. f. Phys.* **83** (1933), 171.

‡ Loc. cit.

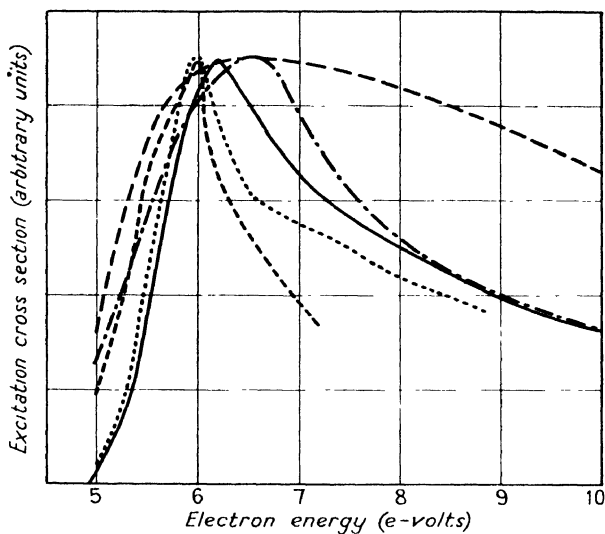


FIG. 25. Excitation function for the Hg resonance line $\lambda 2537$ ($6^1S_0-6^3P_1$) near the excitation potential.

— — — — — Bricout; · · · · · Hanle; White; - - - - - Ostensen;
— · · · — Ornstein, Lindeman, and Oldeman.

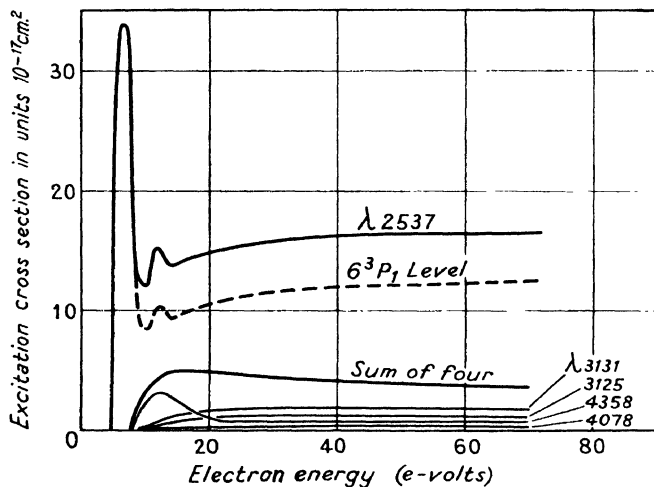


FIG. 26. Excitation function of 6^3P_1 level of mercury allowing for all important modes of population of the level.

different lines and the final derived result for the 6^3P_1 level are illustrated as functions of the electron energy.

The $\lambda 2537$ line arises from a level which is of different multiplicity from that of the ground state, so we should at first sight expect the excitation function for the 2^3P_1 level to resemble that for the helium triplets (Fig. 24 (b)). For electron energies close to the threshold it does so, but at higher energies it assumes the form characteristic of the excitation of an optically allowed level (Fig. 24 (a)). The explanation of this anomaly does not lie in the existence of any secondary mode of excitation (as for the n^3D levels of helium) but in the fact that for a heavy atom, such as mercury, spin-orbit coupling is not negligible and the 3P_1 level is not a pure triplet state. This is clear from the fact that the resonance line $\lambda 2537$ is one involving an apparent change of multiplicity. The singlet component of the level is responsible for the form of the excitation

TABLE V
Excitation Cross-sections Q_{jk} for Mercury Lines

$V_{\max}$ = electron energy when Q_{jk} is a maximum ($= Q_{jk}(\max.)$). Q_{jk} (60 eV) is the cross-section for 60 eV electrons.

Line	Wave-length λ	$V_{\max}$ (eV)	$Q_{jk}(\max.)$ $\times 10^{-20} \text{ cm}^2$	$Q_{jk}(60 \text{ eV})$ $\times 10^{-20} \text{ cm}^2$	Observer†
$6^1S_0-6^3P_1$	2,537	6.5	{ 32,000	11,000	1
		6.5	{ 17,000	..	2
$6^3P_0-7^3S_1$	4,047	11	{ 1,320	386	3
			{ 1,725	315	4
$6^3P_1-7^3S_1$	4,358	12	{ 2,790	822	3
			{ 1,070	804	5
$6^3P_2-7^3S_1$	5,461	12	{ 2,290	671	3
			{ 3,150	569	4
$6^3P_1-6^3D_1$	3,131	50	2,000	2,000	1
$6^3P_1-6^1D_2$	3,125	50	1,500	1,500	1
$6^3P_1-6^3D_2$	4,078	25	720	564	4
$6^3P_1-7^1S_0$	5,769	25	{ 590	519	3
$6^1P_1-6^3D_2$			{ 700	575	4
$6^1P_1-6^3D_1$	5,789	20	{ 1,168	1,015	3
$6^1P_1-6^1D_2$			{ 1,350	925	4
$6^1P_1-7^1D_2$	4,347	20	{ 457	406	3
			{ 811	650	4
$6^1P_1-8^1D_2$	3,906	20	500	330	4
$6^1P_1-8^1S_0$	4,916	35	305	205	4
$6^1P_1-9^1S_0$	4,108	35	152	94.5	4
$7^1S_0-9^1P_1$	6,234	35	260	247	4
$7^3S_1-8^1P_1$	6,072	30	193	183	4
$7^3S_1-9^1P_1$	5,675	..	142	132	3

† 1. Ornstein, Lindeman, and Oldeman, *Zeits. f. Phys.* **83** (1933), 171. 2. Bricout, *J. Phys. Rad.* **9** (1928), 88. 3. Hanle and Schaffernicht, *Ann. der Physik*, **6** (1930), 905. 4. Thieme, *Zeits. f. Phys.* **78** (1932), 412. 5. Fischer, *ibid.* **86** (1933), 646.

function at electron energies greater than 2 or 3 times the threshold energy. This matter is discussed further in Chap. III, § 3.53.

Table V gives absolute data on the excitation cross-sections for a number of mercury lines obtained from the measurements of different investigators. No attempt has been made to allow for secondary excitation which was probably important for several of the lines.

4.33. Results of measurements on Balmer lines. Fig. 27 shows the form of the excitation functions obtained by Ornstein and Lindeman† for the $H\alpha$, $H\beta$, and $H\gamma$ lines of atomic hydrogen. It is seen that

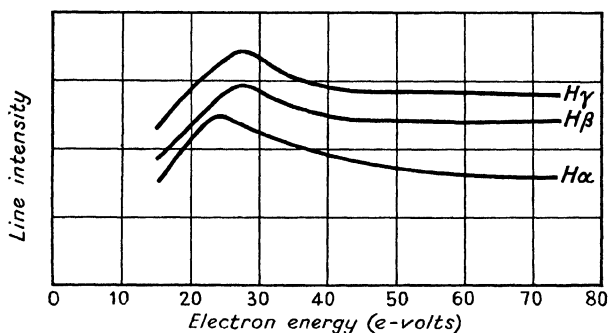


FIG. 27. Excitation functions of $H\alpha$, $H\beta$, and $H\gamma$ lines.

the general form of these curves resembles those corresponding to optically allowed excitations of He and Hg.

4.4. Measurement of the excitation function of metastable states by optical methods

The methods outlined in § 4.2 are not available for the measurement of excitation functions of metastable states since radiative transitions from such states do not in general occur. Two optical methods are in principle available for the determination of the concentration of metastable atoms — the absorption method and the anomalous dispersion method.‡ Then if the concentration is proportional to the rate of production, excitation functions for the production of the metastable state may be obtained.

Only the absorption method has actually been applied to the determination of excitation functions for metastable states under conditions of excitation of such low current density and pressure that multiple

† Ibid. **80** (1933), 525.

‡ The applicability of these methods is not of course limited to the study of metastable states. They can be used to study the concentration of atoms in any excited state. In practice, however, the lifetime of non-metastable excited states is so short that the concentration of such excited atoms will generally be so small as to make application of the methods difficult except in the case of gas discharges of high current density.

processes are improbable (see § 4.2). The anomalous dispersion method has, however, been applied to study the concentration of atoms in metastable states in a glow discharge from which information about excitation functions can be obtained indirectly (see § 4.5).

4.41. The optical absorption method. The optical absorption method has been applied by Milatz and Ornstein† to measure the rate of production of metastable neon atoms by electron impact and a similar method has been applied to He by Woudenberg and Milatz.‡ Their apparatus is illustrated in Fig. 28.

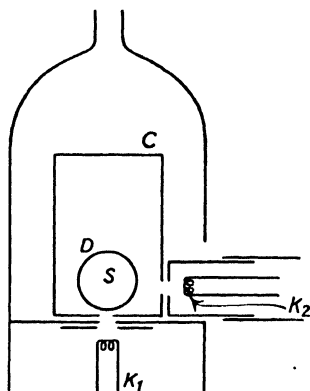


FIG. 28. Apparatus for studying excitation of metastable levels of Ne and He.

Electrons from an oxide-coated cathode K_1 were accelerated through a slit system into a cage C where they were collected. Two holes, D , were cut opposite each other in the sides of the cage. Light from the positive column of a neon discharge tube passed through these holes and then fell on the slit of a spectrograph. The plate holder of the spectrograph was replaced by a curved slit in a position to receive light of wave-length 6,402 Å. This line corresponds to the transition p_9-s_5 and it is absorbed strongly by neon atoms excited

to the s_5 state. Behind the slit was placed a photo-cell. On varying the potential difference between K_1 and C the intensity of the $\lambda 6402$ radiation reaching the photo-cell varied. The absorption of this radiation on passing through the electron tube was then a measure of the number of metastable atoms present.

Let $\Delta I/I$ be the fractional reduction of intensity of the radiation over the absorption line due to the presence of atoms in an excited state. Then

$$\Delta I/I = l \int k_\nu d\nu/\Delta\nu,$$

where $\Delta\nu$ is the width of the absorption line, k_ν the absorption coefficient of the radiation in the frequency range between ν and $\nu+d\nu$, and l the path length of the beam in the space containing the excited atoms.

Then§

$$\int k_\nu d\nu = \pi e^2 N_j f_{kj}/mc,$$

where f_{kj} is the oscillator strength associated with the transition giving

† *Physica*, **2** (1935), 355.

‡ *Ibid.* **8** (1941), 871.

§ See Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, p. 96 (Cambridge).

rise to the absorption and N_j the number of excited atoms per unit volume. Thus

$$N_j = (mc/\pi e^2)(\Delta\nu/l f_{kj})(\Delta I/I). \quad (10)$$

The excitation function for the j state will then be obtained by measuring the variation of $\Delta I/I$ with the energy of the electrons entering C .

Owing to space charge effects the potential at the point where the electron beam passed opposite to the window D was not equal to the potential of C . To determine the true potential of S a subsidiary cathode K_2 was introduced and its potential varied. At a certain stage the beam from this cathode just became visible at the point S . Under these conditions the potential difference between K_2 and S was just equal to the excitation potential of the first level from which visible lines commenced (18.4 volt). Thus the energy at S of the electrons emitted from A could be calculated to within about 1 eV.

In the experiments of Woudenberg and Milatz the concentration of neon atoms in the s_5 state was about 5×10^8 per c.c. and the ratio $\Delta I/I$ was about 0.015.

4.42. The anomalous dispersion method. The refractive index μ of a rarefied gas in the neighbourhood of a critical frequency is given by

$$\mu - 1 = \frac{e^2}{2\pi m} \frac{F_{kj}}{v_{kj}^2 - \nu^2},$$

where

$$F_{kj} = N_j f_{kj} (1 - G_{kj}),$$

$$G_{kj} = N_k g_j / N_j g_k,$$

$$f_{kj} = mc^3 A_{kj} (g_k / g_j) / 8\pi^2 e^2 \nu_{kj}^2.$$

In these expressions j, k refer to the lower and upper levels of the absorption line in question, N_j, N_k, g_j, g_k respectively to the corresponding number of atoms per c.c. and the statistical weights of the levels. ν_{kj} is the frequency of the line and A_{kj}, f_{kj} are respectively the Einstein A coefficient and the oscillator strength for the transition. In many cases N_k/N_j is small and G_{kj} , the negative dispersion term, can be taken as small compared with unity. If this is the case

$$F_{kj} = N_j f_{kj}. \quad (11)$$

If excited atoms in the state j are present in a gas a measurement of the anomalous dispersion in the neighbourhood of a critical frequency ν_{kj} will enable F_{kj} to be determined. Then, if the conditions of excitation are altered, the variation in the concentration of the excited atoms can be investigated.

The usual experimental arrangement was developed by Roschdestwensky† and has been applied to the study of excited atoms in gas discharges by Ladenburg and his colleagues (see § 4.51).

Light from an arc lamp S (Fig. 29) is divided into two beams by the first plate P_1 of a Jamin interferometer. One beam passes along the tube T_1 (50–80 cm. long and about 1 cm. in diameter) containing the gas under investigation at a pressure

† *Ann. der Physik*, **39** (1912), 307; *Trans. Opt. Inst., Leningrad*, **2** (1921), No. 13.

of about 1 mm. Hg. The other beam passes along a similar evacuated tube T_2 , the two coherent beams being united by the second plate P_2 of the interferometer.

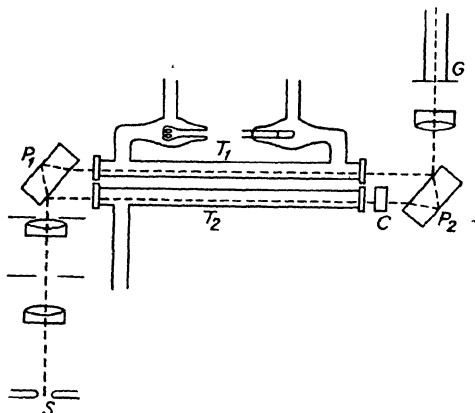


FIG. 29. Apparatus for determination of density of excited atoms in a gas discharge tube by measurement of anomalous dispersion.

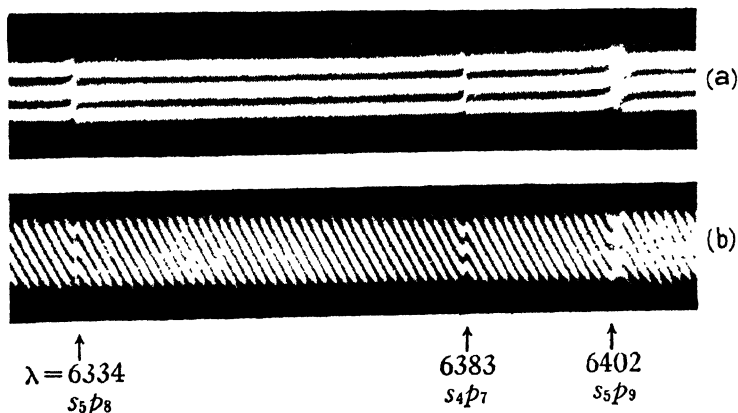


FIG. 30. Anomalous dispersion in a neon discharge; (a) without plate K ; (b) with plate K .

The interference fringes are focused on to the slit of a grating spectrograph G of high dispersion. The spectrum produced is traversed by interference fringes which are almost horizontal owing to the high dispersion of the spectrograph. On both sides of the spectral lines, however, the horizontal fringes are bent in a characteristic way owing to the rapid variation of refractive index with wave-length in the neighbourhood of a critical frequency. Fig. 30 (a) shows the appearance of a portion of the spectrum from a neon tube obtained by Ladenburg.†

† *Rev. Mod. Phys.* **5** (1933), 243.

In most of the work the plane parallel compensating plate C was placed in the path of the second beam. This has the effect of rotating the fringes relative to the length of the spectrum. The fringes in the neighbourhood of a critical frequency then have a characteristic hooked appearance as shown in Fig. 30(b).

From the positions of the maxima and minima in the fringe system on either side of the critical frequency F_{kj} can be calculated from the relation

$$F_{kj} = (K\pi m\nu_{jk}^3 A^2)/e^2 c l, \quad (12)$$

where l is the thickness of the gas layer, A the wave-length separation of the two hooks symmetrically placed with regard to the critical frequency, and K a constant which can be measured for a given apparatus.†

4.43. Determination of absolute excitation cross-sections for metastable atoms. In the methods described in §§ 4.41, 4.42, N_j can be calculated

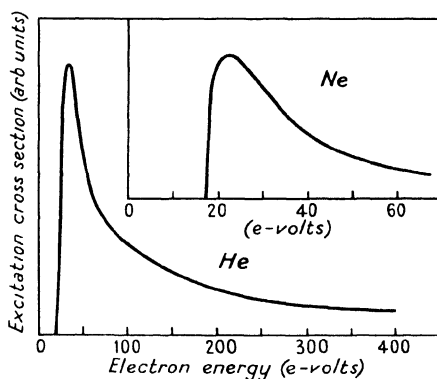


FIG. 31. Observed excitation functions for metastable levels obtained by the absorption method: He (Woudenberg and Milatz); Ne (Milatz and Ornstein).

explicitly if f_{kj} is known. These oscillator strengths have been calculated theoretically in a number of cases.‡ Knowing N_j an estimate can often be made of the rate of production of the excited atoms from geometrical considerations. For example, in the measurements of Milatz and Ornstein on neon§ it was assumed that metastable atoms were produced along the axis of a cylindrical volume and moved radially to the wall with velocity v determined by the gas temperature. If n_j is the rate of production of metastable atoms per unit length of the incident electron beam, the concentration $N_j(r)$ at distance r from the axis is

$$N_j(r) = n_j/(2\pi vr). \quad (13)$$

† If $\Delta\lambda$ is the wave-length separation of a convenient number p of fringes in the neighbourhood of λ_{jk} , then $K = -p\lambda_{jk}/\Delta\lambda$.

‡ Hylleraas, *Zeits. f. Phys.* **106** (1937), 395; Bates and Damgaard, *Phil. Trans. Roy. Soc. A*, **242** (1949), 101.

§ Loc. cit.

The measured N_j was the average value of $N_j(r)$ over the cross-section of the beam of radiation. Knowing this average, n_j could be calculated from the geometry of the arrangement.

4.44. Results of measurements of excitation function of metastable states. The results of the experiments of Woudenberg and Milatz† on the electronic excitation function of metastable helium and of Milatz and Ornstein‡ for metastable neon are shown in Fig. 31. It is seen that both functions are of characteristic form for an excitation involving change of multiplicity (cf. Fig. 24(b)).

4.5. Estimation of cross-sections for excitation from studies of gas discharges

Some evidence concerning the magnitude of cross-sections for excitation can be obtained from an analysis of electron concentration, electron temperature, and excited atom concentrations in the positive column of a glow discharge. Measurements of this kind do not, of course, give such detailed information as that obtainable by more direct methods. The calculated cross-sections refer to a mean electron energy averaged over the electron energy distribution of the discharge plasma. Nevertheless, the method can sometimes give information that is very difficult to obtain in other ways. Thus Fabrikant§ and his collaborators have used it to obtain cross-sections for excitation of mercury by electron impact from an initial excited state, while Mohler|| has deduced cross-sections for superelastic collisions with excited atoms. These processes may assume great importance in the discharge plasma.

Let n_j be the concentration of atoms in the j th excited state in a discharge plasma and n_e the electron concentration. The number of atoms per unit volume of the plasma which are brought to this state per second from lower states by electron impact will be

$$\alpha_j n_0 n_e + \sum \alpha_{kj} n_k n_e.$$

The first term arises from direct excitation from the ground state, the second by further excitation to the j th state of atoms already excited to the k th state. If Q_{0j} is the cross-section for the former process

$$\alpha_j = \int_{E_j}^{\infty} f(E) Q_{0j}(E) (2E/m)^{\frac{1}{2}} dE, \quad (14)$$

where $f(E) dE$ is the fraction of electrons with energy between E and

† *Physica*, **8** (1941), 871.

‡ *Ibid.* **2** (1935), 355.

§ Fabrikant and Cirg, *C.R. (Doklady) U.R.S.S.* **16** (1937), 263.

|| *Bureau of Standards J. Res.* **9** (1932), 493.

$E + dE$ and E_j is the excitation energy. A similar expression holds for α_{kj} with Q_{0j} and E_j replaced by Q_{kj} and E_{kj} respectively.

The number of atoms per unit volume of the plasma which leave the j th state per second will be

$$n_j(\sum \alpha_{ji} n_e + \beta_j n_e + \gamma_j n + 1/\tau_j).$$

The term $1/\tau_j$ represents the loss due to radiation, τ_j being the radiative lifetime, $\sum \alpha_{ji} n_e$ is the rate at which atoms in the j th level are raised to an upper i th level by inelastic collisions with electrons. $\beta_j n_e$ is the loss due to superelastic collisions with electrons and $\gamma_j n$ that due to deactivation in collision with other atoms. This last term is usually small in a pure gas (see Chap. VII, § 7.23) and will be neglected henceforward.

For equilibrium we have then

$$\alpha_j n_0 n_e + \sum \alpha_{kj} n_k n_e + \delta_j = n_j(\sum \alpha_{ji} n_e + \beta_j n_e + 1/\tau_j), \quad (15)$$

where δ_j is the rate at which the j th level is populated by radiative transitions, and by superelastic collisions from upper states.

In spite of the complicated nature of this relation, it is possible to obtain information about individual collision cross-sections from a study of certain special cases:

(a) At low current densities both n_e and n_k will be small compared with n_0 . Also, for the more highly excited states the term δ_j will be relatively small. We have then, approximately,

$$\alpha_j = n_j/n_0 n_e \tau_j. \quad (16)$$

If the usual assumption is made that $f(E)$ has the Maxwellian form corresponding to an electron temperature T_e , i.e.

$$f(E) = 2(E/\pi k^3 T_e^3)^{1/2} e^{-E/kT_e},$$

it follows that the cross-section $\bar{Q}_{0j}$, averaged over the Maxwellian energy distribution, may be obtained from measurements of n_e , T_e , n_j , and τ_j under the conditions assumed. As a partial check the derived values of $\bar{Q}_{0j}$ should not vary rapidly with increase of the current density in the discharge.

(b) If j refers to the first excited state, $\alpha_{kj} = 0$ on the left-hand side of (15) and on the right-hand side $\beta_j n_e$ is usually much larger than $\sum \alpha_{ji} n_e$. This is because superelastic collisions are effective with slow electrons which form a large fraction of the electron velocity distribution. Again neglecting δ_j we have then, at any current density,

$$\alpha_j n_0 n_e = n_j(\beta_j n_e + 1/\tau_j). \quad (17)$$

$\bar{Q}_{0j}$ may be obtained from low current density experiments and hence

α_j determined. Observations at high current densities then give β_j and hence the mean cross-section $\bar{Q}_{j0}$ for the superelastic collision.

(c) If j does not refer to the first excited state the term $\sum \alpha_{kj} n_k n_e$ cannot be ignored at high current densities. Instead it may well provide the most important correction to the formula (15). Thus, if one intermediate state k is alone important,

$$\alpha_j n_0 n_e + \alpha_{jk} n_k n_e = n_j / \tau_j. \quad (18)$$

Under these conditions the intensity of radiation emitted per c.c. per sec. from atoms in the j th excited state, which is proportional to n_j / τ_j , will increase with current density in contrast to the preceding case. As before, $\bar{Q}_{0j}$ may be obtained from the low current density measurements and $\bar{Q}_{jk}$ from those at high current densities.

Conventional Langmuir probe techniques may be applied for the determination of n_e and T_e . τ_j may be found by measuring the natural breadth of spectral lines arising from transitions for which j is the final state. If b_j is the breadth, on a frequency scale, of the j th state the mean lifetime $\tau_j = 1/2\pi b_j$. For the determination of n_j the two different optical methods described in § 4.4 have been used while Mohler† has used the power relations in the positive column of a discharge for this purpose.

4.51. Optical methods for determining excited atom concentrations in the gas discharge. The principles of optical methods for determining excited atom concentrations have been described in §§ 4.41, 4.42 in connexion with the measurement of excitation function for metastable levels. The absorption method has been applied to determine excited atom concentrations in discharges in Cs,† Ne,‡ and Hg.§

The anomalous dispersion method has been used to study excited atom concentrations in discharges in Ne, He.||

If, in addition to the anomalous dispersion F_{kj} in the neighbourhood of a critical frequency ν_{kj} , the true intensity I_{kj} of the emission line from the discharge corresponding to the transition $k \rightarrow j$ is also measured, the relative concentration of excited atoms in the j and k states can be determined without using a calculated value of the oscillator strength f_{kj} . For, in this case,

$$F_{kj} = N_j f_{kj}, \quad (11)$$

$$I_{kj} = N_k A_{kj} h \nu_{kj}, \quad (19)$$

so that

$$I_{kj}/F_{kj} = (g_j N_k / g_k N_j) (8\pi^2 e^2 \nu_{kj}^3 / h / mc^3), \quad (20)$$

whence N_k/N_j can be calculated.

4.52. Determination of n_j from power measurements. In this method, due to Mohler,† the power expenditure per unit length of the positive column and the

† Mohler, loc. cit.

‡ Krebs, *Zeits. f. Phys.* **101** (1936), 604.

§ Fabrikant, Butajeva, and Cirg, *C.R. (Doklady), U.R.S.S.* **14** (1937), 423.

|| Ladenburg, *Zeits. f. Phys.* **48** (1928), 15; Kopfermann and Ladenburg, *ibid.* **48** (1928), 26, 51; *ibid.* **65** (1930), 167; Ladenburg and Levy, *ibid.* **65** (1930), 189; Schon, *Ann. der Physik*, **28** (1937), 649; Kruse, *Zeits. f. Phys.* **109** (1938), 312.

power transported by the ions to the walls are measured. The difference between these two quantities is taken to be the energy per unit time converted into radiation per unit length of the column. From a study of the spectrum radiated from the column it is known that almost all the radiated energy is concentrated in a few lines close together in frequency. Dividing the radiation energy by the mean quantum energy for these lines the number of quanta n_j/τ_j emitted per unit volume per second can be obtained.

4.53. Results of measurements - cross-section for superelastic collisions and for further excitation of excited atoms. Fabrikant,[†] using the absorption method to determine n_j , has obtained mean cross-sections $\bar{Q}_j$ for excitation of mercury and the rare gases which are in reasonable agreement with values obtained by more direct methods.

Mohler[†] applied his method for determining n_j , in connexion with the formula (17), to determine, from data obtained by Killian,[‡] the mean cross-sections $\bar{Q}_{0j}$ for excitation, and $\bar{Q}_{j0}$ for deactivation of the $6^3P_{0,1,2}$ states of mercury. The results obtained are tabulated in Table VI. The mean excitation cross-sections

TABLE VI

Pressure in discharge	0.0002 mm. Hg	0.001 mm. Hg	0.0053 mm. Hg
Electron temperature (electron volts)	3.27	2.37	1.71
$\bar{Q}_{0j}$ (inelastic)	6.8×10^{-16} cm. ²	3.55×10^{-16} cm. ²	1.2×10^{-16} cm. ²
$\bar{Q}_{j0}$ (superelastic)	..	5.2×10^{-16} cm. ²	6.6×10^{-16} cm. ²

$\bar{Q}_{0j}$ have to be compared with the maximum value of about 3.2×10^{-16} cm.² obtained by Ornstein, Lindeman, and Oldemann[§] and 1.7×10^{-16} cm.² by Bricout for the 6^3P_1 level of mercury (see Table V).

Fabrikant^{||} has similarly used data obtained by Klarfeld^{††} to deduce mean excitation cross-sections for potassium vapour.

Fabrikant and Cirg^{‡‡} have investigated the excitation of atoms in gas discharges by a multiple process. They studied the variation with current of the intensity of the Hg lines $\lambda 4047$, $\lambda 4358$, and $\lambda 5461$ corresponding to the transitions $6^3P_{0,1,2} - 7^3S_1$. Clearly the 7^3S_1 state could be excited either from the ground state, or by a double process through inelastic collisions with atoms already excited to the $6^3P_{0,1,2}$ state.

We should therefore expect the formula (18) to be applicable. Since n_e is proportional to the discharge current i , the intensity of the emitted lines I would be expected to vary with i according to the relation

$$I = ai + bi^2,$$

a and b being positive. Fabrikant and Cirg verified this relation and from the observed values of a and b estimated the relative mean cross-sections for the two excitation processes. Under the conditions of their discharge (electron temperature 3 eV) they found the mean cross-section for the $6^3P_{0,1,2} - 7^3S_1$ excitation was 13 times that for the direct $6^1S_0 - 7^3S_1$ excitation leading to a mean cross-section of about 4×10^{-16} cm.² for the inelastic collisions with excited 6^3P atoms.

[†] Loc. cit.

[‡] *Phys. Rev.* **35** (1930), 1238.

[§] This value is deduced from their graph which shows the relative excitation cross-section for $\lambda 4358$ and $\lambda 2537$.

^{||} *C.R. (Doklady) U.R.S.S.* **25** (1939), 663.

^{††} *Ibid.* 658.

^{‡‡} *Ibid.* **16** (1937), 263.

An estimate of the cross-section for ionization of mercury atoms excited in a discharge to the $6^3P_{0,1,2}$ states has been made by Klarfeld† using data on ion concentration in a mercury discharge obtained by probe measurements. He concluded that this ionization cross-section exceeded that from the ground state of mercury by an order of magnitude.

4.54. Mean excitation cross-section from the energy balance in a diffusing electron swarm.‡ When a swarm of electrons is diffusing through a gas, at pressure p , under the influence of a steady electric field of strength F , excitation and ionization of the gas atoms will occur to an extent determined by the mean energy and the energy distribution of the electrons. For applications to discharge phenomena it is convenient to define the ionization coefficient η as the mean number of atoms ionized in a gas at 1 mm. pressure by an electron in passing through 1 volt potential difference in the field. If $f(E) dE$ is the energy distribution function of the electrons, η will be given by

$$\eta = N \int_{E_i}^{\infty} f(E) Q_i (2E/m)^{\frac{1}{2}} dE / Fw, \quad (21)$$

where w is the drift velocity, Q_i is the ionization cross-section, and N is the number of gas atoms per c.c. This follows because, in traversing a distance dx in the direction of the field the actual path length of an electron of velocity v will be $v dx/w$. Since w and $f(E)$ are functions of F/p , η will also be such a function. The coefficients ξ_k , κ for excitation of the k th discrete state and for elastic collisions can similarly be defined in terms of the corresponding cross-sections Q_k , Q_0 .

Consider now the steady state of a current i of electrons with mean energy $\bar{E}$ passing through the gas. In passing a potential difference δV the energy $i \delta V$ gained from the field is used up in producing excitation, ionization, and elastic collisions, as well as in accelerating the secondary electrons produced by ionization. This gives for the energy balance

$$i \delta V = i \sum_k \xi_k E_k \delta V + i \eta E_i \delta V + i \kappa \lambda \bar{E} \delta V + i \eta \bar{E} \delta V, \quad (22)$$

λ being the average fraction of energy lost by an electron in an elastic collision. We have then

$$\eta E_i + \eta \bar{E} + \kappa \lambda \bar{E} + \sum_k \xi_k E_k = 1. \quad (23)$$

Of these quantities η and $\bar{E}$ may be measured as functions of F/p (see Chap. I, §§ 5.3, 6). For atomic gases λ is approximately $8m/3M$, where M is the mass of a gas atom. κ may be obtained with sufficient accuracy

† *Techn. Phys. U.S.S.R.* **5** (1938), 913.

‡ Druyvestyn and Penning, *Rev. Mod. Phys.* **12** (1940), 87.

by taking for Q_0 not the true elastic cross-section but the total cross-section given by a Ramsauer or diffusion experiment (see Chap. I, § 3). Since E_i and E_k are known it follows that information may be obtained about ξ_k and hence $\bar{Q}_k$.

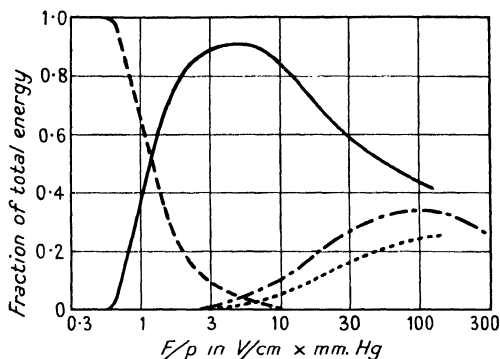


FIG. 32. Energy losses of electrons in neon, showing how the energy received from the electric field is dissipated.

The curves show the fraction of the energy spent in elastic collisions (---), excitation (—), ionization (- · - · -), acceleration of secondary electrons (.....).

An analysis of this sort has been carried through for neon by Penning.† Fig. 32 illustrates for this case the relative magnitudes of the different terms in (23) as functions of the mean electron energy. By methods indicated in Chap. III, § 4.3, it is possible to obtain the form of the energy distribution function $f(E)$ of (21), with allowance for inelastic collisions, with sufficient accuracy to make a determination of the absolute magnitude of $\sum Q_k$ for the strongest excitations at energies close to the threshold. Such an analysis has not yet been carried through.

5. Electrical methods of investigating cross-sections for excitation

5.1. Diffusion through a gas of electrons with energy sufficient to produce inelastic collisions

Most of the electrical methods so far applied for the investigation of excitation cross-sections suffer from the disadvantage that they concern electrons scattered through a limited angular range and it is not possible to obtain from them the total cross-section for the corresponding excitation unless the angular distribution of the inelastically scattered electrons is known. One electrical method has been used, however, which is free

† *Physica*, 5 (1938), 286.

from this objection and is applicable particularly to the study of the form of the excitation function near the excitation potential. It is based on an analysis of the energy distribution of electrons moving through a gas, the electrons possessing sufficient energy to excite the gas.

Consider electrons of mean velocity $\bar{v}$ diffusing through a gas at pressure p in the space between the concentric cylinders A , B of radii ρ_0 and ρ_1 respectively (see Fig. 33). It is supposed that there is no electric field between the cylinders. We first calculate the average number of collisions made by an electron reaching the outer cylinder after diffusing from the inner.

Let J be the number of electrons per unit area per second reaching the outer cylinder of radius ρ_1 . If D is the diffusion coefficient of the electrons in the gas and $n_e(\rho)$ their concentration at a distance ρ from the axis of the cylinder, then

$$2\pi\rho_1 J = -2\pi\rho D \, dn_e/d\rho. \quad (24)$$

This equation has to be solved with the boundary condition $n_e = 0$ for $\rho = \rho_1$, giving

$$n_e = (J\rho_1/D)\log(\rho_1/\rho). \quad (25)$$

Of the electrons at radius ρ a fraction α , which is a function of ρ , will eventually be collected by the outer cylinder, while a fraction $1-\alpha$ will rediffuse to the inner cylinder. On the average each electron will experience $n\bar{Q}\bar{v}$ collisions per unit time, where $\bar{Q}$ is the mean total collision cross-section and n is the number of gas atoms per unit volume. The number of collisions per unit time experienced by electrons in the space between the cylinders which will be eventually collected on unit area of the outer cylinder is therefore

$$n\bar{Q}\bar{v} \int_{\rho_0}^{\rho_1} \alpha n_e(\rho)(\rho/\rho_1) d\rho. \quad (26)$$

As J electrons reach unit area of the outer cylinder per unit time, the average number ν of collisions they must suffer on passing to the outer cylinder is given by

$$\begin{aligned} \nu &= \frac{n\bar{Q}\bar{v}}{J\rho_1} \int_{\rho_0}^{\rho_1} \alpha \rho n_e(\rho) d\rho \\ &= \frac{n\bar{Q}\bar{v}}{D} \int_{\rho_0}^{\rho_1} \alpha \rho \log(\rho_1/\rho) d\rho. \end{aligned} \quad (27)$$

It remains to determine α . This is done as follows. Suppose at the radius ρ between ρ_0 and ρ_1 there exists a source which emits electrons in

all directions and is such that a number j_1 reach unit area of the outer cylinder per unit time, and a number j_0 reach unit area of the inner cylinder per unit time.

The equation for the diffusion will be given by (24), with the boundary conditions $n_e = 0$ at $\rho = \rho_0$ and $\rho = \rho_1$ so we obtain two expressions for the density at ρ in the two cases

$$n_e^1(\rho) = (j_1 \rho_1 / D) \log(\rho_1 / \rho), \quad n_e^0(\rho) = (j_0 \rho_0 / D) \log(\rho / \rho_0). \quad (28)$$

The problem with the hypothetical source at radius ρ will become identical with the actual problem if we put $n_e^1 = n_e^0$, i.e.

$$j_1 \rho_1 \log(\rho_1 / \rho) = j_0 \rho_0 \log(\rho / \rho_0). \quad (29)$$

But $j_1 \rho_1, j_0 \rho_0$ are proportional to the total number of electrons reaching the outer and inner cylinders respectively per unit time, so

$$\alpha = \frac{j_1 \rho_1}{j_1 \rho_1 + j_0 \rho_0} = \frac{\log(\rho / \rho_0)}{\log(\rho_1 / \rho_0)}. \quad (30)$$

Substituting in (27), we obtain for ν , the average number of collisions made by electrons reaching the outer cylinders,

$$\begin{aligned} \nu &= \frac{n \bar{Q} \bar{v}}{D} \frac{1}{\log(\rho_1 / \rho_0)} \int_{\rho_0}^{\rho_1} \rho \log(\rho_1 / \rho) \log(\rho / \rho_0) d\rho \\ &= \frac{n \bar{Q} \bar{v}}{4D} \left\{ \rho_0^2 + \rho_1^2 - \frac{\rho_1^2 - \rho_0^2}{\log(\rho_1 / \rho_0)} \right\}. \end{aligned} \quad (31)$$

This expression was deduced by Harries and Hertz.[†]

The diffusion coefficient D is given to a close approximation by

$$D = \bar{v} / 3nQ_d, \quad (32)$$

where Q_d is the diffusion cross-section defined in Chap. I, § 5.1. This gives

$$\nu = \frac{3}{4} \bar{Q} Q_d n^2 \left\{ \rho_1^2 + \rho_0^2 - \frac{\rho_1^2 - \rho_0^2}{\log(\rho_1 / \rho_0)} \right\}. \quad (33)$$

Let η be the proportion of all impacts that are inelastic. Then, if J_1 is the number of electrons that would reach unit area of A per unit time without appreciable loss of energy in the absence of inelastic collisions and J the actual number, $J = J_1 e^{-\nu\eta}$. Thus if J/J_1 can be estimated, $\nu\eta$ can be determined and the total cross-section for excitation calculated from the expression (33) for ν .

5.2. Measurement of excitation cross-sections by the diffusion method

Fig. 33 shows the form of apparatus used by Maier-Leibnitz[‡] who applied this method to investigate excitation in He, Ne, and A.

The collisions occurred between two coaxial cylinders A, B of 1.5 and

[†] *Zeits. f. Phys.* **46** (1927), 177.

[‡] *Ibid.* **95** (1935), 499.

25 mm. radius respectively, and 150 mm. long. The cylinder *A* was hollow and a slit *S*, 0.2 mm. wide, was cut in it in the plane of its central section. Inside *A* was stretched a tungsten filament *K*, and electrons

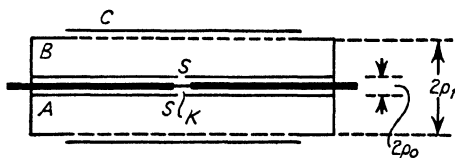


FIG. 33. Apparatus of Maier-Leibnitz for the study of excitation cross-sections by the diffusion method.

accelerated from *K* passed through the slit *S* into the field free space between *A* and *B* containing the gas being investigated at a pressure of the order of 0.1 mm. of Hg. Electrons passing between *A* and *B* would in general make many collisions with the gas atoms. The greater part of the outer cylinder *B* consisted of a wire gauze of 0.25 mm. mesh. Surrounding this gauze and distant about 1.5 mm. from it was a collecting cylinder *C*. A retarding potential between *C* and *B* enabled the energy distribution of the electrons reaching *B* to be studied.

The current collected by *C* was measured as a function of the accelerating potential *V*, between *K* and *A*, with the retarding potential *U* between *C* and *B* so adjusted that *U/V* remained constant ($= \frac{1}{3}$). Apart from the effect of electrons reflected from the cylinder *C*, the current collected by *C* under conditions of constant *U/V* would be expected to remain practically constant, independent of *V*.

When, however, *V* becomes large enough to excite one of the levels of the gas the number of electrons reaching *C* will show a sharp drop. From a study of this decrease in current the absolute yield for the corresponding excitation was estimated.

Fig. 34(a) shows typical results obtained by Maier-Leibnitz in helium at a pressure of 0.326 mm. At about 19 volts the current *i* drops sharply, indicating a critical potential. The dotted line shows the estimated course of the curve if there had been no inelastic scattering.

Let i_0 be the value of the current to *C* if there had been no inelastic collisions, as given by the dotted curve of Fig. 34(a) and *i* the actual observed current. Then $i = i_0 e^{-\eta \bar{Q}}$ from which $\eta \bar{Q}$, the effective cross-section for the inelastic impact, can be calculated as described above.

For values of the incident electron energy above the ionization potential the presence of the ions disturbed the measurements. An alternative procedure was then adopted.

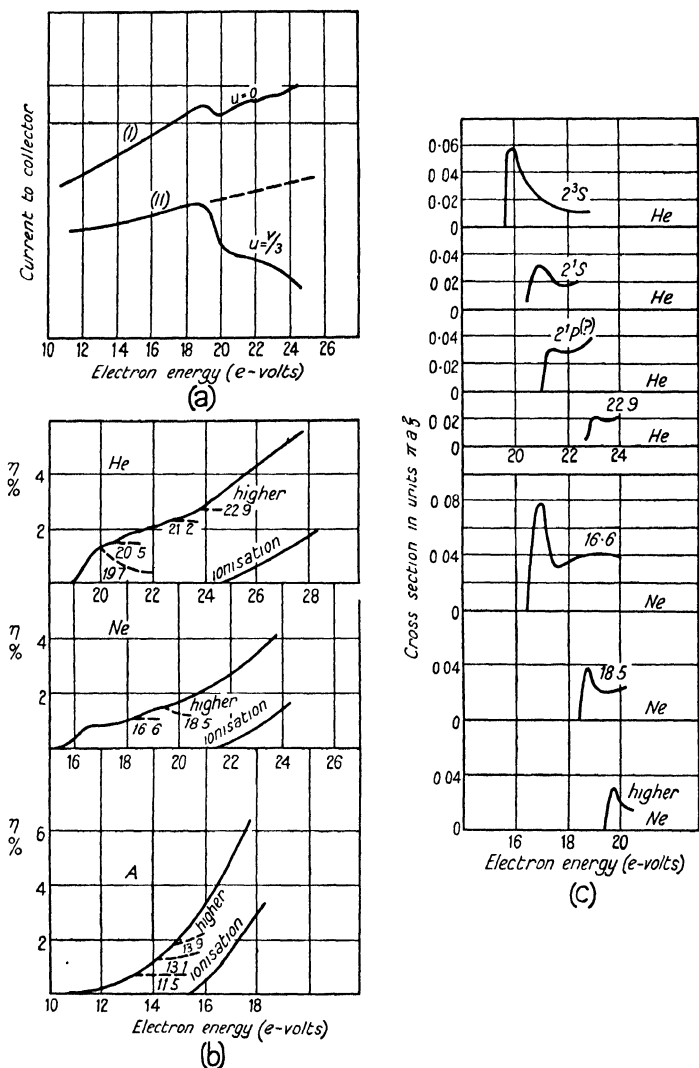


FIG. 34. Illustrating the use of Maier-Leibnitz's method to determine excitation cross-sections for He, Ne, and Ar.

(a) Variation with electron energy of the current to the collector in He for (I) $U = 0$, (II) $U = V/3$. Note the sharp break in the curves at the 19.7-volt excitation.

(b) Percentage of inelastic impacts as a function of electron energy.

(c) Excitation functions for individual levels obtained by analysis of (b). The curves for ionization are derived from Smith's measurements (§ 2.3).

After ν collisions the number of electrons that have undergone inelastic collisions is proportional to $1 - e^{-\nu\eta}$. For a given electron energy a certain fraction of these will be ionizing collisions. Thus the number of ions I collected by C when its potential is made high enough to repel all electrons will be equal to $I_s(1 - e^{-\nu\eta})$, where I_s is the saturation value of the positive ion current for a very high pressure. Thus, if I_s is measured and I obtained for a given pressure corresponding to a given ν , η can be estimated.

To separate out the excitation probabilities corresponding to the individual excitations, a retardation analysis was carried out for each initial electron energy and the relative numbers of electrons present corresponding to the various energy losses measured. Smith's† results on ionization cross-sections were used to separate ionizing collisions from excitation.

Fig. 34(b) and (c) shows the curves obtained by Maier-Leibnitz and his analysis of them. He estimates the error in the determination as 20 per cent. and his results on ionization are consistent with those of Smith within these limits.

A feature of these curves is the very sharp rise of the excitation cross-section to a maximum when the accelerating potential V is less than a volt above the excitation potential. This might be expected in the case of the 19.7-volt excitation in helium corresponding to the transition 1^1S-2^3S involving a change in multiplicity, and possibly for the 20.5-volt excitation in helium corresponding to the optically forbidden transition 1^1S-2^1S , but is surprising for the optically allowed transition 1^1S-2^1P corresponding to the energy loss 21.2 volts, as claimed by Maier-Leibnitz. It is doubtful whether the results are sufficiently accurate to establish definitely such a feature. Nevertheless, using a similar method Seiler‡ obtained evidence of a similar maximum in the case of the $6^1S_0-6^1P_1$ excitation of mercury vapour. Brattain,§ using an apparatus in which he collected electrons after inelastic scattering through a large (but uncertain) range of angles (including zero), found a similar effect for this excitation. The matter will be discussed further in Chap. III, §§ 3.53, 3.54.

5.3. Detection of superelastic collisions between electrons and excited atoms by an electrical method

It was seen in § 4.5 that an interpretation of discharge phenomena made it appear likely that superelastic collision processes, in which an electron gains energy in

† *Phys. Rev.* **36** (1930), 1293; **37** (1931), 808.

‡ *Zeits. f. Phys.* **83** (1933), 789.

§ *Phys. Rev.* **34** (1929), 474.

collision with an excited atom, are important in the positive column of the discharge through gases. It was, in fact, possible to make estimates of the cross-sections for such processes. Great difficulty has been experienced, however, in attempting to detect processes such as these from the direct measurement of the energy gain of a beam of electrons passing through a gas containing a concentration of excited atoms.

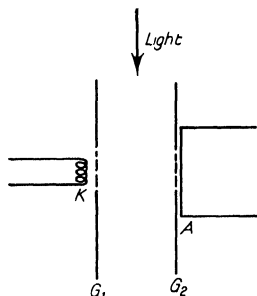


FIG. 35

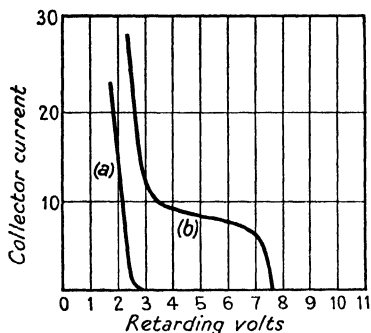


FIG. 36

FIG. 35. Illustrating Latyscheff and Leipunsky's apparatus for studying superelastic collisions of electrons with 6^3P_0 mercury metastable atoms.

FIG. 36. Collector current as a function of retarding potential applied to collector: (a) when the space between G_1 and G_2 is not illuminated; (b) when the space is illuminated. Curve (b) is obtained after making a large correction for photo-electric emission from the collector.

The energy of the incident electrons is 2.5 eV. When the space is illuminated the maximum energy of electrons is 7.2 eV, due to electrons having gained 4.7 eV from the $6^3P_0-6^1S_0$ transition of the excited atoms.

Latyscheff and Leipunsky† have demonstrated the existence of superelastic collisions in mercury in which a metastable mercury atom in the 6^3P_0 state falls to its ground state, and gives up energy of 4.7 eV to the incident electron. Their apparatus is illustrated in principle in Fig. 35. Electrons from the cathode K were accelerated through the grid G_1 and passed between G_1 and a second grid G_2 , at the same potential. A retarding potential between G_2 and A enabled a velocity analysis to be carried out. The space between G_1 and G_2 contained mercury vapour at a pressure of about 0.01 mm. Hg. Light from a Hg arc was now used to illuminate the space between G_1 and G_2 so that the line $\lambda 2537$ of the arc excited the mercury vapour and caused a concentration of 6^3P_0 metastable mercury atoms to be produced.

The velocity analysis of the electron beam was now repeated in the presence of these metastable atoms. Fig. 36 shows, for an accelerating potential of 2.5 volts between K and G_1 , the retardation curves obtained with and without the presence of the metastable Hg atoms. It is seen that when the space between G_1 and G_2 is illuminated the maximum energy of the electrons is 7.2 eV compared with 2.5 eV without illumination. The difference, 4.7 eV, is in very good agreement with the energy of the 6^3P_0 metastable state.

† *Zeits. f. Phys.* **65** (1930), 111.

Latyscheff and Leipunsky also attempted to determine the cross-section for the process by estimating the concentration of the metastable atoms present and obtained a maximum value of 7.1×10^{-18} cm.² for electrons of energy 2.8 eV. However, Mohler† has pointed out that their estimated concentration of metastable atoms was probably much too high and their observed cross-section correspondingly too low.

5.4. The measurement of cross-sections for excitation of metastable states of helium and neon by an electrical method

Excitation cross-sections for metastable states of helium and neon have been determined by Dorrestein‡ using an apparatus shown in Fig. 37. Electrons emitted from the indirectly heated cathode *K* were

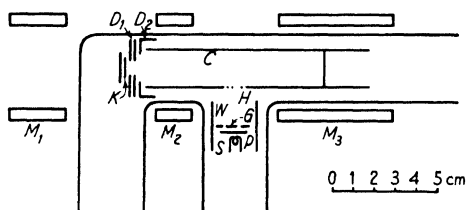


FIG. 37. Dorrestein's apparatus for measuring excitation cross-sections of metastable atoms by electron impact.

accelerated through the slit system D_1, D_2 along the axis of the copper cylinder C . They were collimated by means of an axial magnetic field produced by the coils M_1, M_2, M_3 . The cylinder C contained the gas being studied (He or Ne), at a pressure of about 10^{-3} mm. Hg, and metastable atoms were formed along the path of the electron beam. Some of them left C through the side hole H , which was covered with a wire mesh, and were incident on a platinum collecting plate P which could be thoroughly outgassed by means of the heater S . Secondary electrons were ejected from P by the incident metastable atoms (see Chap. IX, § 6.1) and were collected by the grid G . The cylindrical electrode W surrounding P was positively charged and prevented positive ions reaching the collector.

If i_0 is the electron current passing along C (about 10^{-5} mA in Dorrestein's experiments), n the number of atoms per c.c., $Q(E)$ the cross-section for the excitation of the metastable state being investigated, the current i_m due to electrons ejected from P by the metastable atoms is given by

$$i_m = i_0 n Q(E) \zeta \rho,$$

where ρ is a factor giving the fraction of the metastable atoms produced

† Loc. cit.

‡ *Physica*, 9 (1942), 433, 447.

in unit path which reach P and ζ is the number of electrons ejected from P per incident metastable atom. ρ can be estimated from geometrical considerations but ζ is not known. If $Q(E)$ can be obtained independently this method may be used to estimate ζ (see Chap. IX, § 6.1).

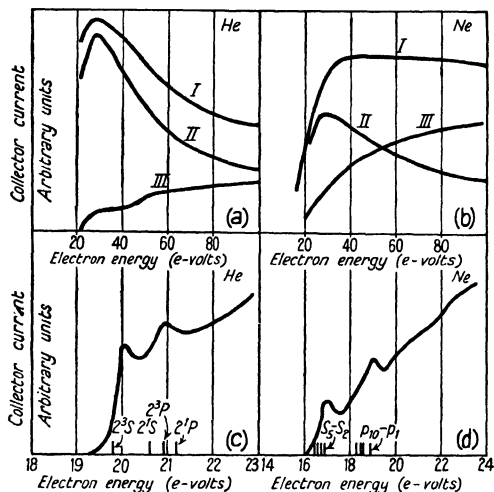


FIG. 38. Excitation curves for metastable atoms of He and Ne obtained by Dorrestein.

In curves (a) and (b) I represents the total electron current ejected from the collector by both metastable atoms and quanta. II is the curve for metastable atoms alone, III for quanta alone.

In curves (c) and (d) the excitation potentials for the various excited states of He and Ne are shown.

Quanta reaching P from C will also eject electrons and may mask the effect of the metastable atoms. To separate the photo-electrons from electrons ejected by metastable atoms Dorrestein pulsed the current through C by applying A.C. of frequency from 900 to 2×10^5 cycles to the slit D_2 . The time taken for a metastable atom of velocity v to reach P is a/v , where a is the distance from H to P . If the frequency is high enough the distribution in energy of the metastable atoms is such that the number incident on P per unit time is practically uniform. The difference between the 'in-phase' and 'out-of-phase' electron current ejected from P therefore measures the effect of radiation.

Fig. 38 (a), (b) shows the excitation curve for the production of metastable atoms of He and Ne by electrons of energy up to 100 eV. Curve I shows the total current from P , curve II the portion of it due to metastable atoms, and curve III that due to radiation.

Dorrestein also made a detailed measurement of the excitation curves for the metastable states for electron energies close to the excitation potential. Since under these conditions the photo-electron emission from *P* was negligible he was able to use steady currents. Typical curves for He and Ne are shown in Fig. 38 (c), (d). Each curve shows two subsidiary maxima within a volt or two of the excitation potential. In helium these were attributed to the excitation of the 2^3S and 2^1S states and in neon to the s_2-s_5 and p_1-p_{10} states, the excitation potentials for which are marked on the figures. The positions of these subsidiary maxima are in agreement with the positions of maxima obtained by Maier-Leibnitz for the excitation of these gases. Thus, referring to Fig. 34 (c), the first two maxima were obtained by Maier-Leibnitz for helium, at energies of 19.9 eV and 20.9 eV compared with 20.0 and 20.9 in the measurements of Dorrestein. For neon Maier-Leibnitz observed maxima at energies of 17.0 and 18.8 eV, exactly the same as found by Dorrestein for this gas.

6. Polarization of radiation excited by electron impact

Radiation emitted as a result of electron impact often exhibits polarization effects, determined by the direction of the exciting electron beam. In spite, however, of the interesting information such measurements can provide about the collision process, very few investigations of the polarization have in fact been made.

6.1. Measurement of the polarization

The most systematic study of the phenomena has been carried out by Skinner and Appleyard† for a number of lines of Hg. The arrangement used by them is illustrated in Fig. 39.

The radiation emitted from a tube *E* by the passage of electrons of a definite energy through mercury vapour was focused on the slit *S* by means of the quartz lens *L*. It then entered the quartz prism *D*, where it was split into two components by double reflection at the oblique face, the angular separation between the two components being about $\frac{1}{2}^\circ$. The light then entered the refracting quartz prism *R* of the spectrograph and two images of the slit corresponding to the two components were produced on the photographic plate *P*.

From the relative intensity of these two images the polarization of the radiation can be calculated. Let $I_{\parallel}$, $I_{\perp}$ be respectively the intensity of the two images produced by light parallel and perpendicular to the direction of the electrons in the tube *E*. Then the percentage polarization, Π , is defined as

$$\Pi = 100 \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}.$$

Care had to be taken to prevent spurious effects arising from differential reflection of the two components of the radiation at the prism *R* which could cause

† Skinner and Appleyard, *Proc. Roy. Soc. A*, **117** (1928), 224; also Skinner, *ibid.* **112** (1926), 642.

an error up to 25 per cent. in II. To avoid this the quartz prism D was cut so that its optic axis was parallel to the direction AB . After the beams had been separated by double reflection the light then emerged from D along the optic axis. Large rotation effects were produced which varied from different parts of the beam and thus the beam was effectively depolarized. Experiments with an unpolarized source at E showed that the error due to apparent polarization produced by the apparatus was always less than 5 per cent.

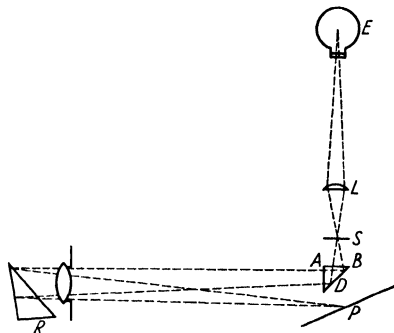


FIG. 39. Skinner and Appleyard's apparatus for studying the polarization of impact radiation.

Apart from several other studies on mercury† lines, the only other measurements on polarization of electron excited radiation concern Ne and He.‡

The measurements of II described above refer to radiation emitted at right angles to the incident electron beam. Smit§ studied the polarization of the radiation emitted at angles ranging from 30° to 150° with this direction, but found no significant departure from the relation to be expected on classical grounds for the variation of II with angle, viz.

$$\Pi_\theta = \frac{\Pi \sin^2 \theta}{1 - \Pi \cos^2 \theta / 100},$$

where Π is the percentage polarization at 90° .

6.2. Results of the measurement of polarization

Some of the results obtained by Skinner and Appleyard for the polarization of mercury lines are shown in Fig. 40 as functions of the energy of the exciting electrons. Some of the lines are seen to be polarized positively, some negatively. For high velocities there is usually a reversal of sign of the polarization, but there are some exceptions. In some cases (e.g. $\lambda 4078$, ($6^3P_1 - 7^1S_0$), $\lambda 4108$ ($6^1P_1 - 9^1S_0$)) there is no appreciable polarization.

The polarization seems to be zero at the excitation potential but increases sharply at low velocities and passes through a maximum a few volts above the excitation potential.

† Ellett, Foote, and Mohler, *Phys. Rev.* **27** (1926), 31; Eldridge and Olson, *ibid.* **28** (1926), 1151; Quarder, *Zeits. f. Phys.* **41** (1927), 674.

‡ Steiner, *ibid.* **52** (1928), 516; Haule and Quarder, *ibid.* **54** (1929), 819; Smit, *Physica*, **2** (1935), 104.

§ Loc. cit.

Lines of a given spectral series are polarized to the same extent within the limits of experimental error and the polarization curves are similar. The polarization depends on the subsequent transition as well as on the initial excitation. This is illustrated by the difference between curves (5) and (6) for the lines $\lambda 4358$ ($6^3P_1-7^3S_1$) and $\lambda 4047$ ($6^3P_0-7^3S_1$) respectively.

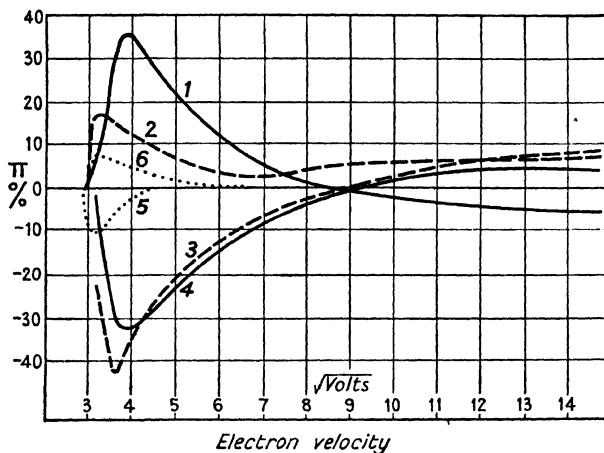


FIG. 40. Skinner and Appleyard's measurements of the polarization percentage Π of mercury lines as a function of electron energy.

- (1) $\lambda 4347$ ($6^1P_1-7^1D_2$); (2) $\lambda 3650$ ($6^3P_2-6^3D_3$); (3) $\lambda 3663$ ($6^3P_2-6^3D_3$);
 (4) $\lambda 3655$ ($6^3P_2-6^3D_3$); (5) $\lambda 4358$ ($6^3P_1-7^3S_1$); (6) $\lambda 4047$ ($6^3P_0-7^3S_1$).

The results for He and Ne are qualitatively similar to those for Hg.

7. Measurement of the angular distribution of scattered electrons

Very extensive measurements have been made of the angular distribution function $I(\theta)$ both for elastically scattered electrons and electrons scattered in specific inelastic impacts. The general principle of most of the methods used is illustrated in Fig. 41 (a). A beam of electrons of definite energy emerges from a source S into the gas contained in a region free from electrostatic fields. Those electrons scattered from the area $ABCD$ of the beam through angles in the small range between θ_1 and θ_2 ($\simeq \theta_1$) pass through the entrance slit L of a collector. This collector includes some analysing device to ensure that only scattered electrons with energies in the required range are measured. Either the source S or the collector C may be rotated about an axis perpendicular to the plane of the paper at E , so that the variation of the collected current with the angle θ may be measured. The volume of the region from which the scattered current is observed increases as $\text{cosec } \theta$ so that the observed

current at an angle θ must be multiplied by $\sin \theta$ in order to obtain the true relative scattered intensity per unit solid angle.

To ensure that the observations refer only to single scattering it is necessary to work with a sufficiently low gas pressure (checked from the linearity of the relation between pressure and scattered current) and beam current (checked from the linearity of the relation between scattered and beam currents). When working at energies above the ionization energy of the gas the restriction to small beam currents must also be adhered to in order to prevent the setting up of a positive ion space charge large enough to disturb the path of the scattered electrons. It is also of the greatest importance that no stray fields should be present due to charging up of the bounding walls of the scattering chamber. To avoid this the wall is bounded by a metal enclosure, usually cylindrical in form. Finally, to avoid effects due to the presence of impurities which may not only contribute markedly to the scattering but also affect the collecting power of slits, it is necessary to design apparatus so that it can be thoroughly outgassed by baking.

7.1. *Types of apparatus*

The forms of apparatus used by different observers differ mainly in the design of the collector. The following have been employed:

(a) *Shielded Faraday cylinder.* The simplest collector was that used by Bullard and Massey† who were concerned with the angular distributions of elastically scattered electrons with energies ranging from 4 eV to 40 eV. The design of their collector is illustrated in Fig. 41(b). The slits *F* and *G* were of width 2 mm. and thickness 0.6 mm., were 6 mm. apart, and the front was 7 mm. from the axis of rotation.

The source used by Bullard and Massey, which is typical of most employed, consisted of a tungsten filament *K* (Fig. 41(c)) from which the electrons were accelerated through a pair of slits *B* (4×1.5 mm.) and *C* (2×0.6 mm.), 7 mm. apart.

To ensure that elastically scattered electrons alone were collected the outer case *E* of the collector was kept at such a positive potential with respect to the inner cylinder that only electrons retaining their initial energy would be able to penetrate through the slit *G*. When working at electron energies above the ionization energy the collection of positive ions was prevented by application of a small positive potential between the outer case *E* and a surrounding metal enclosure.

With this apparatus the angular range of collection was about 10° .

† *Proc. Roy. Soc. A*, **130** (1931), 579.

A more elaborate collector of the Faraday cylinder type was used by Arnot† in studying the elastic scattering of electrons with energies up to 800 eV. At these higher energies secondary emission from the inner collector and high positive ion currents becomes serious. Arnot therefore used two further insulated enclosing cylinders in his collector, which is illustrated in Fig. 41 (*d*). It consisted of three concentric cylinders containing slits S_1 (8×0.2 mm.), S_2 (5×0.2 mm.), S_3 (2×2 mm.), equally spaced 5 mm. apart, and a concentric innermost Faraday cylinder F .

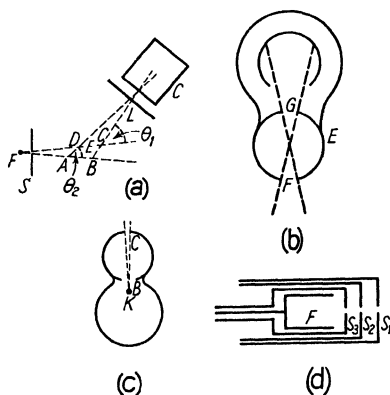


FIG. 41. (*a*) Illustrating principle of the method of measuring angular distribution of electrons scattered in gases and vapours. (*b*) Illustrating electron source used by Bullard and Massey. (*c*) and (*d*) Illustrating design of collectors used in the experiments of Bullard and Massey and Arnot respectively.

The outermost cylinder was kept at the same potential as the nickel cylinder enclosing the scattering space. Taking this as zero, the potentials on the slits S_2, S_3 , and the Faraday cylinder were maintained respectively at 9, $-V_0 + 3$, $-V_0 + 23$ volts, V_0 being equal to the energy of the incident electron in electron volts. The potential between S_1 and S_2 prevented positive ions from entering S_2 , that between S_2 and S_1 permitted only elastically scattered electrons to enter S_1 , and that between F and S_1 prevented secondary emission from the Faraday cylinder.

With the small dimensions involved some penetration of fields occurred so that considerable care had to be taken to check that the applied potentials really did achieve what they were designed for. Owing to the complexity of the collector it was kept fixed and the source rotated, in contrast to the experiments of Bullard and Massey.

In both sets of experiments the electron beam current employed was of

† *Proc. Roy. Soc. A*, **130** (1931), 655.

the order of a microampere. The collected currents were of the order 10^{-12} amp., or less, and were measured by a quadrant or Compton electrometer. The gas pressure used depended on the electron energy, but was usually between 10^{-3} and 10^{-2} mm. Hg.

(b) *Electrostatic analyser.* This method of analysis has been used by Hughes and McMillen,[†] who were mainly concerned with elastic scattering, and by Mohr and Nicoll,[‡] who have made the most extensive series of measurements of angular distributions for inelastic as well as elastic scattering.

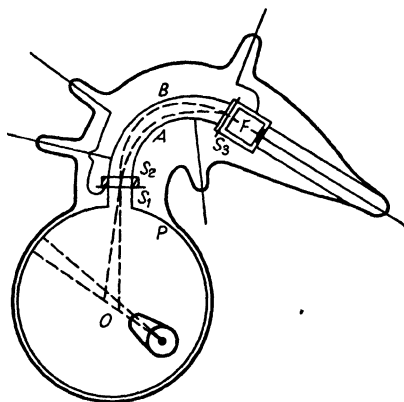


FIG. 42. Apparatus of Mohr and Nicoll for studying the angular distribution of inelastically scattered electrons.

The principle of the electrostatic analyser has been discussed by Hughes and Rojansky.[§] If a narrow beam of electrons of various energies enters a uniform radial electrostatic field, then those electrons whose energies bear a certain relation to the strength of the field are focused at the point whose angular displacement from the entrance slit is $\pi/\sqrt{2}$ radians.

Fig. 42 illustrates the application of this principle in the collector used by Mohr and Nicoll. The electrons from the region O entered the space between two duralumin plates A and B of width 3 cm., curved in concentric circular arcs of radii 2.5 and 3.8 cm., through two slits S_1 (0.27×8 mm.) and S_2 (0.4×5 mm.), 7 mm. apart. The metal shield P of the scattering chamber was shaped so as to prevent electrons from the scattering chamber from entering the analyser in any other way. An

[†] *Phys. Rev.* **39** (1932), 585.

[‡] *Proc. Roy. Soc. A*, **138** (1932), 229, 469; *ibid.* **142** (1933), 320, 647.

[§] *Phys. Rev.* **34** (1929), 284.

adjustable potential difference could be applied to the plates so as to focus electrons of the required energy on the slit S_3 (0.6×5 mm.), whence they could pass into the Faraday cylinder F . The slits S_2 and S_3 were kept at a potential midway between those of the two plates A and B . A retarding potential was maintained between the Faraday cylinder and the slit to reject all electrons with velocities lower than those it was desired to collect. This was a precaution to remove any background of slow electrons. A potential difference could also be maintained between S_1 and S_2 to accelerate electrons before entering the analyser, if necessary to eliminate disturbance by the earth's magnetic field.

The whole apparatus was enclosed in a pyrex tube, and, except for the ground joint which rotated the electron gun, could be thoroughly baked out at 450° C. By suitably enclosing the collision chamber within the metal shield it was possible to maintain a large pressure between this chamber and the analyser. With a pressure as high as 10^{-2} mm. Hg in the former the pressure in the latter could be kept down to 10^{-5} mm. Hg. Scattering in the angular range 10 – 155° could be observed with this apparatus.

7.2. Apparatus for special conditions

7.21. *Scattering of very slow electrons.* In order to study the scattering of very slow electrons for which only weak sources are available

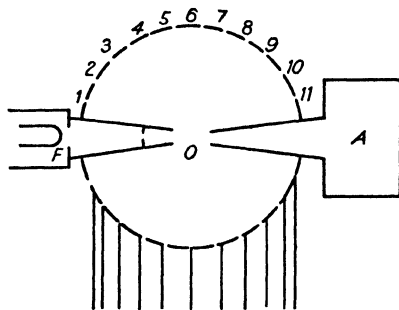


FIG. 43. 'Zone' apparatus of Ramsauer and Kollath for studying the angular distribution in the elastic scattering of very slow electrons.

Ramsauer and Kollath† introduced the 'zone' apparatus illustrated in Fig. 43. The collectors 1 to 11 were metal plates shaped to the form of the zones of a sphere with centre O . As secondary emission was negligible and no slow electrons arose from inelastic collisions this simple arrangement sufficed and had the advantage of giving comparatively large

† *Ann. der Physik*, **12** (1932), 529, 837.

scattered currents. The geometry of the scattering chamber had to be carefully considered in reducing the observations. With this apparatus Ramsauer and Kollath were able to observe the scattering of electrons with energies as low as 0.6 eV.

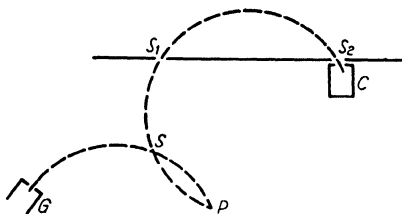


FIG. 44. Principle of Gagge's apparatus for the study of electrons scattered at large angles.

7.22. Scattering at 180° . In the conventional type of apparatus described above, scattering cannot be observed out to angles of 180° because of the interference of the source. An apparatus which does enable observations to be made of the scattering at these angles was developed by Gagge.[†] The principle of his method is illustrated in Fig. 44. The whole experiment was carried out in a uniform magnetic field perpendicular to the plane of the paper. Electrons fired from the gun moved in a circular path in the field. After scattering, the electrons moved on another circular path such as PS_1S_2 . Corresponding to each such path there is a definite angle of scattering. To select different angles the collector with its slit S_2 could be moved parallel to S_1S_2 , the slit S_1 remaining fixed. Allowance had to be made, in calculating the variation of scattering volume with angle of scattering, for the fact that electrons pursuing the path PS_1S_2 arose from scattering, through the same angle, at both P and S . Since electrons scattered at 180° did not strike the source in this arrangement, there was no difficulty in carrying out measurements at large angles up to and including 180° .

7.23. Scattering by metal vapours. Two methods have been used for investigating the scattering from the vapours of metals which do not have sufficient vapour pressure at room temperature. McMillen[‡] studied the scattering in potassium vapour by maintaining the whole collision chamber at 150°C ., at which the vapour pressure was sufficient (0.001 mm. Hg). Childs and Massey[§] adopted, in their experiments on the scattering of cadmium and zinc, an alternative arrangement illustrated

[†] *Phys. Rev.* **44** (1933), 808.

[‡] *Ibid.* **46** (1934), 983.

[§] *Proc. Roy. Soc. A*, **141** (1933), 473; *ibid.* **142** (1933), 509.

in Fig. 45. The scattering vapour was provided as a cloud emerging from an oven source D . The vapour was condensed on the liquid air trap T . Electrons from the gun G were fired across the vapour cloud as it emerged from the oven slit and the scattered current measured at various angles by the collector C .

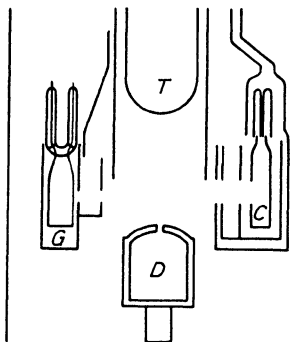


FIG. 45. Apparatus of Childs and Massey for study of angular distribution of electrons scattered by vapours.

7.3. Observed angular distributions

7.31. Elastic scattering. A thorough survey has been made of the angular distributions of electrons scattered from helium, neon, argon, krypton, xenon, and mercury, and less detailed observations for cadmium, zinc, and potassium. Measurements made for scattering from molecular gases and vapours are described in Chap. IV, §§ 2 and 3.

The results obtained by different observers usually agree very well so that in giving the observed data the measurements with a particular apparatus are often given instead of a mean of all the available observations.

The most conspicuous feature of the angular distributions, at least for scattering by the heavier atoms, is the appearance of maxima and minima reminiscent of diffraction patterns. This phenomenon was first observed by Bullard and Massey† in 1931 for argon and it arises from diffraction of the electron waves by the spherically symmetrical scattering atoms in much the same way as in the scattering of light by spheres of dimensions comparable with the wave-length. This aspect will be discussed in detail in the next chapter. In this section we shall merely call attention to certain salient features.

Referring to Figs. 46 and 47, in which observed angular distributions for the rare gases and mercury are illustrated, the following features will be noted:

- (a) For a given atom the diffraction pattern smooths out at a sufficiently high electron energy leaving a monotonic decrease of scattered intensity with angle.
- (b) As the electron energy decreases, the pattern becomes at first more complicated and then begins to smooth out once more at the lowest

† *Proc. Roy. Soc. A*, **130** (1931), 579.

energies. Thus with mercury the pattern is at its most complex at about 450 eV electron energy.

- (c) At low energies, for helium and neon, the variation of scattering with angle becomes very much less marked so that at the lowest energies it is very nearly uniform.

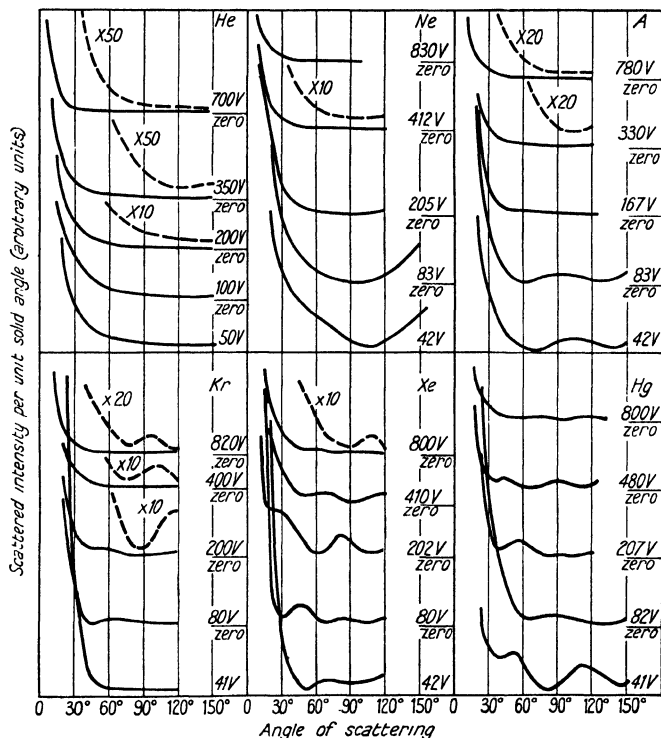


FIG. 46. Observed angular distributions of electrons with energies between 30 and 800 eV scattered elastically by the rare gases and by mercury.

- (d) For the other rare gases the angular distribution remains far from uniform even at the lowest observed energies (0.5 eV). It is to be noted that at these energies the total collision cross-section is very small (Ramsauer-Townsend effect, Chap. I, § 3).
- (e) The complexity of the diffraction pattern is more marked the greater the atomic number of the scattering atom. Thus helium exhibits very little departure from the monotonic distribution at any energy, neon gives a distribution with a single minimum

near 90° , at most, whereas two minima appear in the argon distributions between 4 and 150 eV energy and three or more for the heavier atoms.

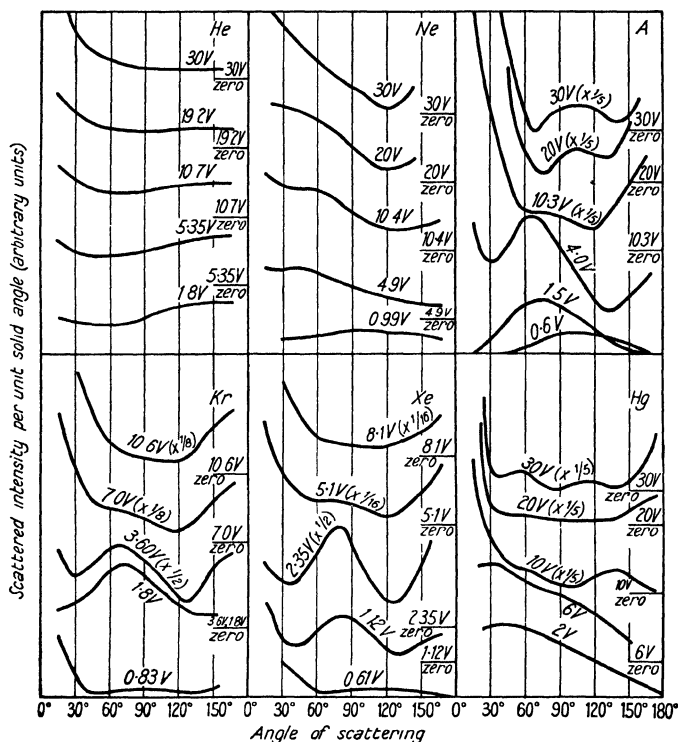


FIG. 47. Observed angular distributions of electrons with energies between 0.5 and 30 eV scattered elastically by the rare gases and by mercury.

Fig. 48 compares the angular distributions observed for cadmium† and zinc‡ with those for mercury. It will be seen that electrons with energies less than 50 eV or so are scattered in very much the same way by all three atoms. This indicates a great similarity in the scattering field of these atoms at distances from the nucleus at which the energy of the field is of the order 50 eV or less.

It is possible from the observations of angular distributions to check the validity of the quantal prediction that the scattering per unit angle, $I(\theta)\sin\theta$, tends to zero as $\theta \rightarrow 0$ for a field which falls off as rapidly as

† Childs and Massey, *Proc. Roy. Soc. A*, **141** (1933), 473.

‡ Ibid. **142** (1933), 509.

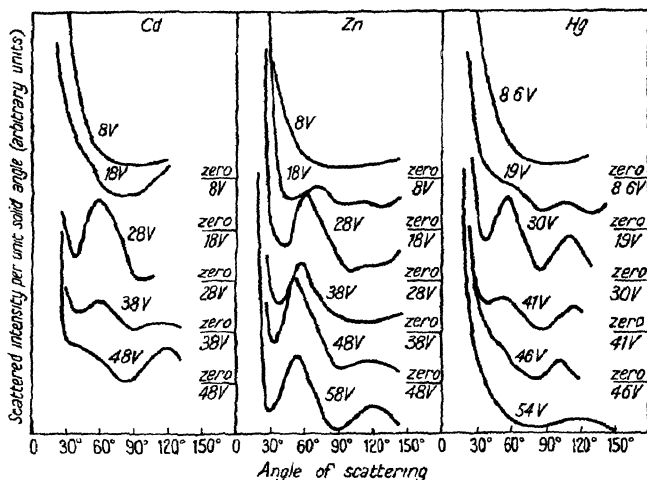


FIG. 48. Angular distribution of electrons scattered elastically in Cd, Zn, and Hg.

that of an atom. Fig. 49 illustrates some observed scattering distributions per unit angle. Although obvious experimental limitations prevent the measurement of the scattering in the zero angle limit, it is nevertheless clear that extrapolation to zero as $\theta \rightarrow 0$ is strongly indicated in all cases.

By integrating the observed angular distributions the variation of the elastic cross-section with electron energy may be obtained approximately, the limitation being that the angular range covered in the experiments is rarely quite large enough. Good agreement is found with the variation with energy of the collision cross-section given from measurements of the type described in Chap. I, § 3, when it would be expected, i.e. at energies below that of the resonance levels of the atoms concerned.

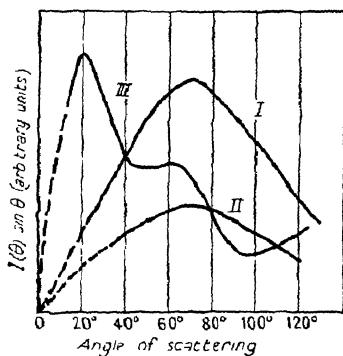


FIG. 49. Observed values of $I(\theta)\sin\theta$ plotted as a function of θ , indicating it tends to zero with θ .

I. 6 eV electrons in neon; II. 2 eV electrons in mercury; III. 10 eV electrons in mercury.

7.32. Inelastic scattering. The first measurements of the angular distribution of inelastically scattered electrons were carried out by Dymond† in He for electrons of 50–500 eV energy scattered after

† *Phys. Rev.* **29** (1927), 433.

excitation of helium atoms to the 2^1P state. The angular range covered was $0-90^\circ$. Mohr and Nicoll,[†] using the apparatus shown in Fig. 42, have investigated inelastic scattering between 10 and 155° in helium, neon, argon, and mercury as well as a number of molecular gases including hydrogen and methane. They observed separately not only electrons which had excited the resonance level but also electrons which had produced ionization and suffered various amounts of energy loss in doing so. Measurements have also been carried out in mercury vapour by Tate and Palmer.[‡]

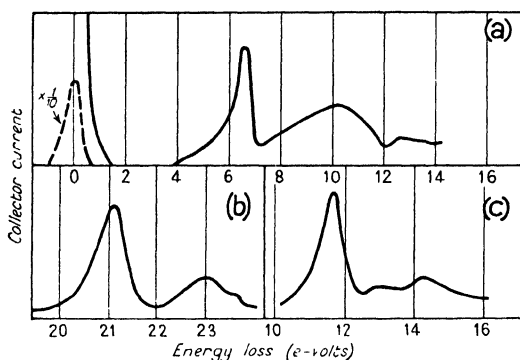


FIG. 50. Velocity analysis of electrons after inelastic scattering through a fixed scattering angle.

(a) 90° in Hg vapour. (b) 30° in He. (c) 20° in A.

The procedure used by Mohr and Nicoll in their comprehensive investigations was as follows. With the electron gun set at a convenient angle the energy distribution of the electrons scattered at that angle was investigated by measuring the variation of the current to the Faraday cylinder with change of plate voltage. Fig. 50 illustrates typical energy distribution curves for incident electrons of 42 eV energy. Fig. 50(a) was obtained for incident electrons at 90° in mercury vapour. The peak due to the 6.7 eV energy loss arising from the excitation of the 6^3P_1 level is clearly visible. Above 8 eV are unresolved energy losses leading up to the ionization energy at 10.4 eV. At greater energy losses there is a continuous spectrum of electrons scattered by or ejected from atoms in an ionizing collision. Fig. 50(b) for 30° in helium exhibits peaks corresponding to the excitations 1^1S-2^1P (21.11 eV) and 1^1S-3^1P (22.96 eV), while Fig. 50(c), for 20° in argon, exhibits a strong peak

[†] *Proc. Roy. Soc. A*, **138** (1932), 229, 469; *ibid.* **142** (1933), 320, 647.

[‡] *Phys. Rev.* **40** (1932), 731.

corresponding to an energy loss of 11.6 eV resulting from the excitation of the 3P_1 level.

To investigate the angular distribution of electrons scattered after suffering a particular energy loss the plate voltage was adjusted to focus electrons with the appropriate energy and measurements taken at different scattering angles by rotating the electron gun. It was verified that

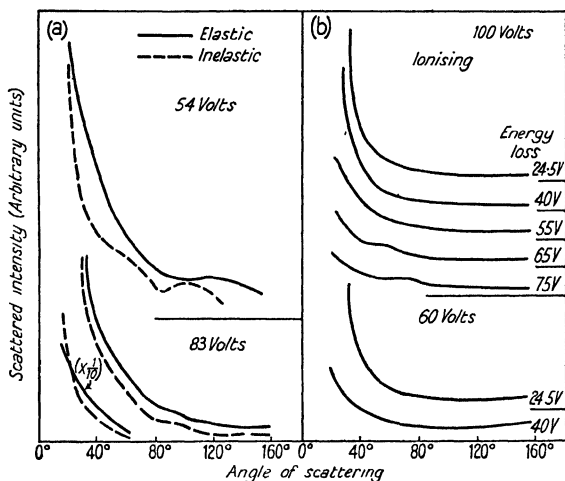


FIG. 51. Observed angular distributions of electrons scattered in helium.
 (a) Elastic (—) and inelastic (---) collisions involving excitation of the 2^1P level.
 (b) Ionizing collisions with different energy losses.

the shape of the peaks did not change appreciably throughout the angular range so that the peak height was a true measure of the relative intensity of the scattered electrons. Special care was taken to check the linearity of the relations between the scattered current and the gas pressure and main beam currents respectively.

The principal features of the observed angular distributions are as follows:

(a) At small angles the scattered intensity falls off very rapidly with angle for inelastic collisions in which the fractional energy loss is not too great. This may be seen by reference to Fig. 51, in which the angular distributions of electrons scattered in collisions in which the 2^1P level of helium is excited and in which ionization occurs with different energy losses are respectively illustrated. Fig. 53 gives corresponding curves for argon, and Fig. 54 for mercury.

(b) The distributions at small angles of the electrons scattered after exciting the 2^1P and 3^1P levels of helium respectively are nearly the same, the intensity ratio being 2.7 to 1 (see Fig. 52).

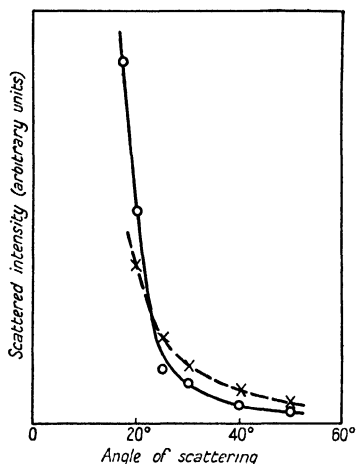


FIG. 52. Comparison of angular distributions of electrons of 83 eV incident energy, scattered after exciting the 2^1P and 3^1P levels of helium respectively. —○—○— 2^1P ; --×--×-- 3^1P .

(c) The angular distribution of electrons which have suffered small energy losses in inelastic collisions with heavy atoms exhibit, at large angles, diffraction maxima and minima which closely resemble those appearing in the corresponding distributions of elastically scattered electrons. This may be seen by reference to the observed distributions for argon illustrated in Fig. 53 and for mercury in Fig. 54. The resemblance between the shape of the distributions at large angles of the elastic and inelastic scattering is found also for the lighter atoms which do not exhibit very complicated diffraction effects.

This remarkable feature of the observations was conclusively shown by Mohr and Nicoll to be associated with single scattering and not to arise from successive collisions, one, elastic, giving rise to the diffraction and another, inelastic, giving the energy loss. As the intensity of the inelastic scattering at large angles is very much smaller than that of the elastic, special care had to be taken to exclude the double scattering explanation. Apart from careful verification that the inelastically scattered current at large angles was proportional to the gas pressure in the experimental range, a study of the relative intensities of the elastic

and inelastic scattering showed that at the low gas pressures employed (less than 10^{-3} mm. Hg) double scattering would be far too small. Furthermore, Mohr and Nicoll's results for mercury were reproduced by Gagge† with a rather different apparatus.

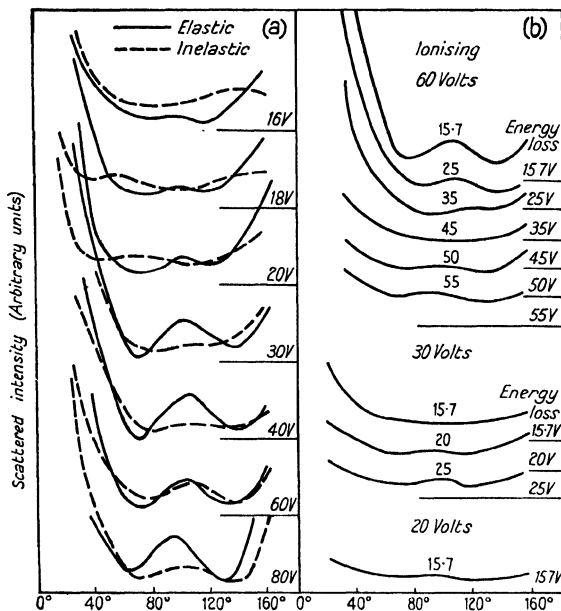


FIG. 53. Observed angular distribution of electrons scattered in argon.

- (a) Elastic (—) and inelastic (---) collisions involving excitation of the 3P_1 level in which the energy loss is 11.6 eV.
 (b) Ionizing collisions with different energy losses.

(d) The resemblance noted in (c) becomes progressively less marked when the inelastic collision concerned involves a considerable fractional energy loss. Thus in Fig. 53 the resemblance between the distribution for electrons scattered elastically in argon and those scattered in a collision involving the 11.6 eV energy loss ceases to be marked when the incident electron energy falls below 40 eV. Further, in Fig. 53 a set of distribution curves for electrons which have suffered different losses of energy in producing ionization of argon atoms is shown. At the lowest energy loss the resemblance to the elastic distribution is close but becomes progressively less apparent as the energy loss increases. Fig. 54 illustrates the corresponding features for mercury.

† Loc. cit.

(e) For the lightest atoms the angular distributions of electrons which have undergone ionizing collisions with large fractional energy loss

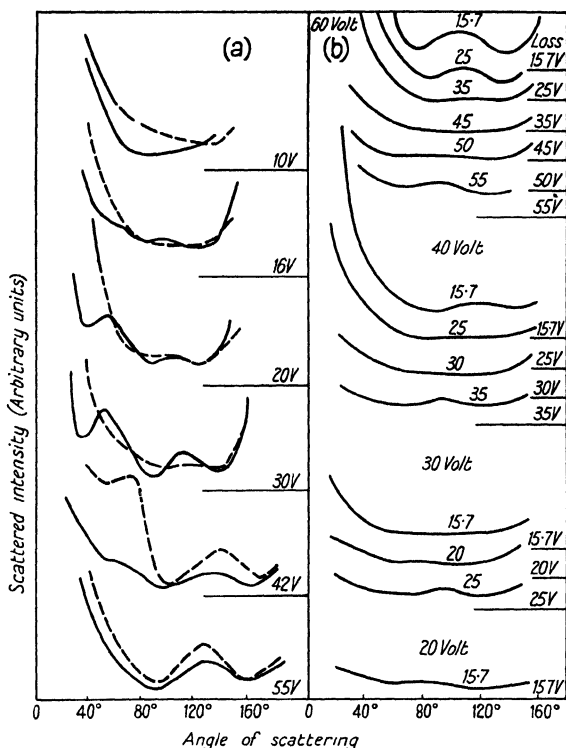


FIG. 54. Observed angular distribution of electrons scattered in mercury.

(a) Elastic (—) and inelastic (---) collisions involving excitation of the 6^3P_1 level.

(b) Ionizing collisions with different energy losses.

exhibit at the higher incident energies a maximum which is of a character quite distinct from the diffraction patterns observed with heavy atoms and small fractional energy loss. This is illustrated most clearly in the observed curves for hydrogen in Fig. 55. The maximum is most marked at the highest electron energy and moves out to larger angles the greater the fractional energy loss. The same effect appears to a less pronounced extent with helium.

The effect is still perceptible for electrons with 200 eV incident energy in methane, nitrogen, and neon, but was not observed for the heavier

atoms for electrons with incident energies up to 200 eV. As far as can be judged the position of the maximum for given incident energy and energy loss occurs at nearly the same angle for all the gases in which it was observed.

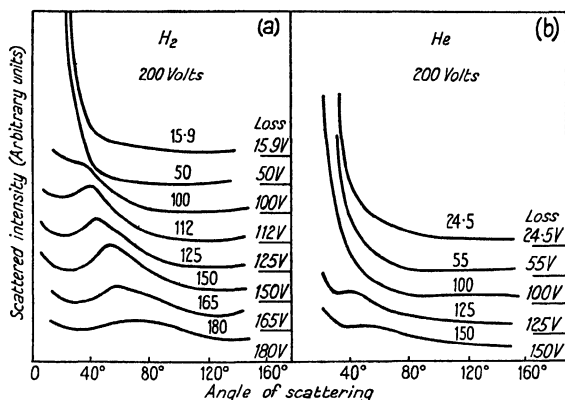


FIG. 55. Angular distribution in scattering of fast electrons in ionizing collisions in (a) H_2 , (b) He, illustrating a maximum in the distribution for large energy losses.

8. Measurement of cross-section for inelastic scattering through a fixed range of angles

Most of the earlier investigators who studied inelastic collisions of electrons in gases were interested primarily in the measurement of critical potentials of the gas following the classical investigations of Lenard† and of Franck and Hertz.‡ These measurements were of the utmost importance in establishing our present model of the atom and providing an essential link between spectroscopic data and inelastic collisions. Since the measurement of such critical potentials is described adequately in many text-books we shall not discuss them here.

Experimental arrangements of the type suitable for the study of critical potentials have also been used to measure, for various electron energies, the quantity

$$\int_{\theta_1}^{\theta_2} I_s(\theta) \sin \theta \, d\theta,$$

where θ_1 and θ_2 are limits fixed by the instrumental arrangements.

† *Ann. der Physik*, **8** (1902), 149.

‡ *Verh. der Phys. Ges.* **16** (1914), 457.

Since, as we shall see in Chap. III, § 3, this quantity can be calculated theoretically in certain cases, such experiments are interesting in themselves. It is not possible to obtain the total cross-section for a given inelastic collision from such measurements unless the angular distribution of the scattering for the collision is known from other measurements. However, it is known that at high energies most of the inelastically scattered electrons are confined to small angles, so that useful information about the probability of inelastic collisions at such energies may be obtained by performing a velocity analysis of undeviated electrons in a beam after passage through a gas. Such velocity analyses have been made using retardation methods, magnetic analysis, or electrostatic analysis.

The retardation method was originally applied to experiments of this type by Franck and Hertz.† More recent applications of the method to the study of inelastic collisions in mercury have been made by Vetterlein,‡ who analysed electrons scattered inelastically through small angles, and by Arnot and Baines§ for electrons scattered inelastically over a large range of angles between 9° and 171° .

Electrostatic analysis has been used by van Atta|| to study energy losses of electrons scattered inelastically through small angles in He, Ne, and A. Womer†† has used a similar method for He. The electrons, after collision, were analysed in energy by an analyser of the Hughes–Rojansky type described in § 7.1.

8.1. *The magnetic deflexion method*

The most extensive set of measurements employing the magnetic deflexion method to determine the energy loss of electrons which have suffered inelastic collisions has been made by Whiddington and his associates.‡‡ Fig. 56 illustrates Whiddington's apparatus which analysed electrons that have been scattered through small angles only.

Electrons from the filament F were accelerated through the hole H_1 into the chamber C containing the gas being investigated. After emerging through the hole H_2 , 0.145 mm. in diameter, the electrons passed through the defining slit S , situated 8.5 mm. from H_2 , into the (evacuated) camera K . The camera was placed in a magnetic field with lines of force

† *Zeits. f. Phys.* **17** (1916), 409.

‡ *Ann. der Physik*, **35** (1939), 251.

§ *Proc. Roy. Soc. A*, **151** (1935), 256.

|| *Phys. Rev.* **38** (1931), 876.

†† *Ibid.* **45** (1934), 689.

‡‡ Jones and Whiddington, *Phil. Mag.* **6** (1928), 889; Roberts and Whiddington, *ibid.* **12** (1931), 962; Whiddington and Taylor, *Proc. Roy. Soc. A*, **136** (1932), 651; *ibid.* **145** (1934), 465; Whiddington and Priestley, *ibid.* **462**; Whiddington and Woodroffe, *Phil. Mag.* **20** (1935), 1109; Lee, *Proc. Roy. Soc. A*, **173** (1939), 569.

in a direction perpendicular to the plane of the paper, produced by the magnet with pole face *B*. The electrons were analysed by the magnetic field into a number of beams of different energy corresponding to inelastic scattering after excitation of different states of the molecules of the

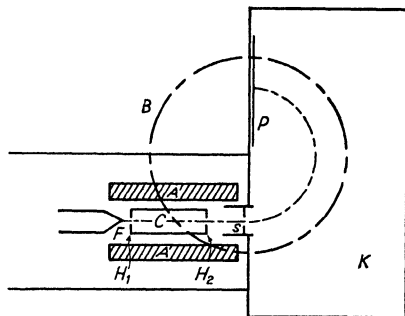


FIG. 56. Whiddington's apparatus for study of magnetic spectrum of electrons scattered inelastically through small angles.

scattering gas. They were detected by the photographic plate *P* after deflexion through 180° . The iron cylinder *A* served to shield the filament *F* and the collision chamber *C* from the magnetic field of the velocity analyser. Measurements were carried out on H_2 , He, Ne, and A.

8.2. Results of observation of inelastic scattering through a fixed angle.

Fig. 57 shows the variation with incident electron energy of the quantity $q(0 \rightarrow \theta_0) = \int_0^{\theta_0} I_s(\theta) \sin \theta d\theta$ for the 1^1S-2^1P excitation in helium, as obtained from the measurements of Womer,[†] van Atta,[‡] and Whiddington and Taylor.[§] In these cases θ_0 was less than 10° . Compared with the total cross-section for excitation of this level, the quantity *q* continues to rise over a larger range of electron energies. This is because a greater fraction of the inelastic scattering is confined to small angles as the incident energy increases (see Chap. III, § 3.7).

Whiddington and Priestley also observed a beam corresponding to an energy loss of 59.25 eV in He. This beam was too intense to be attributed to electrons that had suffered three inelastic collisions, each involving a loss of 21.2 eV, corresponding to excitation of the 2^1P state. Whiddington and Priestley interpreted this energy loss as due to a double excitation

[†] *Phys. Rev.* **45** (1934), 689.

[‡] *Ibid.* **38** (1931), 876.

[§] *Proc. Roy. Soc. A*, **145** (1934), 465.

of a helium atom in which both electrons were raised to $2p$ states. This interpretation appears now to be well established (see Chap. III, § 3.72).

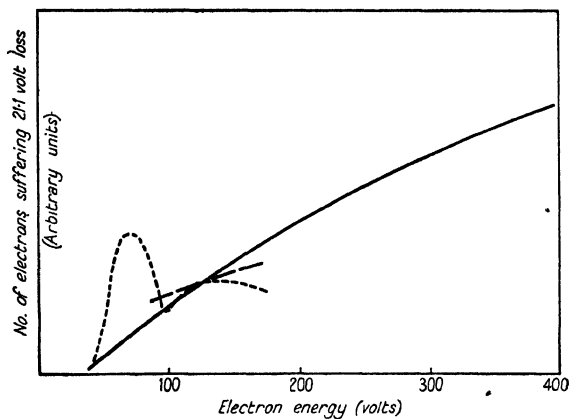


FIG. 57. Probability of electron scattering through a small angle in He after excitation of 2^1P level.

—— Whiddington and Taylor; - - - - van Atta; Womer.

III

ELECTRON COLLISIONS WITH ATOMS— THEORETICAL DESCRIPTION

IN the previous chapters we have described the information, about the various effective cross-sections for collisions of electrons with atoms, which has been obtained by a variety of experimental methods. This information is necessarily incomplete and has to be supplemented by theoretical methods. To do this we must first establish a theory which gives a satisfactory description of the observations. If, however, we do not succeed in developing theoretical methods of calculation which provide values of the cross-sections in agreement with all the observed data, it is important to establish under what conditions such a partial theory is valid. Having done this it will be known when the theory can be used to predict the values of cross-sections which, while difficult to observe, are important in many applications of collision data. For example, the cross-section for excitation of an atom, such as oxygen, by electron impact may be required. This is very difficult to measure experimentally owing to the molecular character of gaseous oxygen.

In general we shall find that the theory of elastic collisions is quite well established. This is also the case for inelastic collisions when the fractional energy loss is small. No really accurate theory exists for impacts in which the fractional energy loss is large.

1. Subdivision of the theoretical problem

Even if we regard the nucleus as a fixed centre of force, the collision of an electron with the simplest atom is essentially a three-body problem. However, it is possible to proceed by a series of successive approximations in which the first already provides a good description of a wide range of observations and each succeeding one enables the description to be extended over a wider range.

The first approximation consists in ignoring the inner structure of the atom and treating it as a centre of force which is unperturbed by the colliding electron. Such a model necessarily excludes the possibility of inelastic collisions, but it does lead to a description of elastic scattering which is remarkably accurate over a wide range of electron energy and angle of scattering.

Higher approximations take account of the electronic structure of the atom. Allowance is made for the interference effects which arise in

elastic scattering due to the possibility of the impinging electron and an atomic electron changing places, an exchange which is not observable owing to the identity of the electrons. A technique can be developed for calculating probabilities of various inelastic collisions on the assumption that they are relatively infrequent. Finally, when this assumption is not made it becomes necessary to allow for the interaction between inelastic and elastic scattering. Thus, if during a collision there is a high probability of energy exchange between an electron and an atom, it may happen that an excitation process is reversed by a return of the energy to the electron before the collision has terminated. Such a 'double collision' with the same energy exchange would be observed as an elastic collision.

In this chapter we shall give an account of the quantum theory of electron collisions in physical rather than mathematical terms. As far as possible the formulae used will be shown to appear physically plausible and detailed mathematical proofs will usually be avoided.

2. Elastic scattering

2.1. *Scattering of electrons by the static field of an atom*

The first approximation regards the atom as a source of a central scattering potential $V(r)$ which is the average potential at a distance r from the nucleus of the unperturbed atom. If $\rho(r)$ is the density of the atomic electrons at a distance r from the nucleus which possesses a charge $Z\epsilon$, then

$$V(r) = -\frac{Z\epsilon^2}{r} + 4\pi \left[\frac{1}{r} \int_0^r \rho(r') r'^2 dr' + \int_r^\infty \rho(r') r' dr' \right]. \quad (1)$$

The function $\rho(r)$ may be calculated accurately for hydrogen to give

$$V(r) = -\epsilon^2 e^{-2r/a_0} \left(\frac{1}{r} + \frac{1}{a_0} \right), \quad (2)$$

where $a_0 = \hbar^2/m\epsilon^2$ is the radius of the first Bohr orbit. For other atoms $\rho(r)$ may only be determined approximately by use of the Hartree self-consistent field method† or by the somewhat more refined Fock method† in which electron exchange effects within the atom are included. It is conventional to express the potential $V(r)$ in the form

$$V(r) = -Z_p \epsilon^2 / r, \quad (3)$$

where Z_p , the effective nuclear charge for potential, is a function of r .

† See Mott and Sneddon, *Wave Mechanics and its Applications*, Clarendon Press 1948, Chap. VI.

In general Z_p falls off exponentially for large r so that, according to quantum theory, the scattering cross-section due to the mean atomic field will be finite (see Chap. I, § 2).

Tables of the function Z_p , or of the electron charge density from which Z_p may be calculated, are available† for the following atoms and ions: H^- , H , He , Li , Li^+ , Be , Be^+ , Be^{++} , B , B^+ , B^{++} , B^{+++} , C , C^+ , C^{++} , C^{+++} , C^{4+} , N , N^{++} , N^{+++} , N^{4+} , O^- , O , O^+ , O^{++} , O^{+++} , O^{4+} , F^- , F , F^{4+} , Ne , Na^- , Na , Na^+ , Mg^{++} , Al^+ , Al^{+++} , Si^{++} , Si^{+++} , Si^{4+} , Cl^- , Cl , A , K^- , K , K^+ , Ca , Ca^+ , Ca^{++} , Sc^{++} , Sc^{+++} , Ti^{4+} , Ti^{5+} , Cr , Cr^{++} , Fe , Ni , Cu^+ , Zn , Ga , Ga^+ , Ga^{+++} , Ge , Ge^{++} , As , As^+ , As^{++} , As^{+++} , Br^- , Br , Kr , Rb^+ , Ag^+ , Cs^+ , W , Hg , Hg^+ .

Alternatively, for heavy atoms, the Thomas-Fermi‡ statistical atom model may be used. This gives

$$V(r) = -\frac{Ze^2}{r}\phi(r/\mu),$$

where $\mu = 0.885Z^{-1/3}a_0$. Tables of the function ϕ are available.§

2.2. Quantum theory of scattering by a centre of force

2.21. Total cross-section. Let us consider a particle of mass m and velocity v which is projected towards a centre of force in such a direction that, if undeviated, it would pass the centre at a distance p . This quantity is called the impact parameter. According to classical theory the particle will certainly be deviated unless the force due to the centre vanishes everywhere along its path. In the quantum theoretical treatment of the problem it is natural to attach a probability $\alpha(p)$ that a particle with impact parameter between p and $p+dp$ will suffer an *observable* deviation. The effective collision area would then be

$$Q_0 = 2\pi \int_0^\infty \alpha(p)p \, dp. \quad (4)$$

To consider other quantum modifications it is convenient to rewrite this in terms of angular momenta. The angular momentum J of a particle about the centre of force is equal to mvp , so that

$$Q_0 = (2\pi/m^2v^2) \int_0^\infty J\beta(J) \, dJ, \quad (5)$$

where β is now the chance that a particle with angular momentum

† A complete list of references to all the work on the calculation of atomic fields is given in an article by Hartree, *Reports on Progress in Physics*, **11** (1946-7), 113.

‡ See Mott and Sneddon, *Wave Mechanics and its Applications*, Clarendon Press 1948, Chap. VI.

§ Bush and Caldwell, *Phys. Rev.* **38** (1931), 1898.

between J and $J+dJ$ should suffer an observable deviation. Now we must take account of the fact that, according to quantum theory, the angular momentum about the centre of force is quantized so that

$$J = \{l(l+1)\}^{\frac{1}{2}}\hbar. \quad (6)$$

This converts the integral in (5) to the sum

$$\begin{aligned} Q_0 &= (\pi\hbar^2/m^2v^2) \sum_{n=0}^{\infty} (2l+1)\gamma(l) \\ &= (\pi/k^2) \sum_{n=0}^{\infty} (2l+1)\gamma(l), \end{aligned} \quad (7)$$

where $k = 2\pi/\lambda$, λ being the wave-length of the incident particle and

$$\gamma(l) = \beta[\{l(l+1)\}^{\frac{1}{2}}\hbar].$$

We must now consider the probability $\gamma(l)$. It is easy to see how, in a wave theory, $\gamma(l)$ may actually be zero in circumstances in which, on classical theory, it would be unity. For simplicity, consider the scattering by a potential which has the form

$$\begin{aligned} V(r) &= D, & r < a \\ &= 0, & r > a, \end{aligned} \quad (8)$$

where D is a constant. We shall first discuss head-on collisions for which $l = 0$, and for which there is no doubt that $\gamma(0) = 1$ on the classical theory.

According to the quantum theory the motion of the particles, making head-on collisions, will be represented by a train of waves with wave-length $\lambda = h/mv$ outside the obstacle ($r > a$) and $\lambda = h/(m^2v^2 - 2Dm)^{\frac{1}{2}}$ inside. The two trains of different wave-length must join smoothly at the boundary $r = a$. In order to achieve this, and at the same time keep the amplitude finite at the centre $r = 0$, a phase change must be introduced in the train, for $r > a$, relative to that which would exist in the absence of the obstacle. This phase change, due to the obstacle, will be observable at infinity and it alone indicates the presence of the obstacle. However, we must remember now that it is impossible, in principle, to count the waves between the obstacle and the observer so that a phase change which is an integral multiple of 2π will not be observable. In these circumstances the obstacle produces no observable effect on the particles with zero angular momentum so $\gamma(0) = 0$. This will be so when the obstacle either introduces or eliminates a whole number of complete waves.

On these grounds it is to be anticipated that $\beta(0)$ will be a periodic function of the phase shift η_0 produced by the scattering potential in

the de Broglie waves which represent the stream of particles of zero angular momentum. It must vanish with the phase change, have a maximum value of unity, and never be negative. The simplest function satisfying all of these conditions is $\sin^2\eta_0$ and an exact calculation shows that this is correct. In a similar way $\gamma(l) = \sin^2\eta_l$, where η_l is the phase shift produced in the waves of angular momentum $\{l(l+1)\}^{1/2}\hbar$.

We have now reached the expression

$$Q_0 = \frac{\pi}{k^2} \sum (2l+1) \sin^2\eta_l, \quad (9)$$

but there still remains a further factor 4 to be introduced. One factor 2 arises in the following way. It is to be expected that, when the phases η_l are large for l between 0 and a large number l_0 , the classical and quantum formulae, obtained by the argument we have introduced, should correspond. This requires that the average value of $\gamma(l)$ between 0 and l should be 1 and not $\frac{1}{2}$.

The second factor 2 is purely a wave effect. Owing to diffraction round the edge the effective area exposed by a rigid spherical obstacle of radius a to the scattering of waves is not πa^2 but $2\pi a^2$. This effect, discussed further in Chap. VII, § 3.2, introduces a second factor 2, so that we have finally†

$$Q_0 = \frac{4\pi}{k^2} \sum (2l+1) \sin^2\eta_l. \quad (10)$$

Although the concept of the phase shift, as determining the probability of a deviation, has been introduced in connexion with a potential function with a sharp boundary there is no difficulty in applying it to a field, such as the static field of an atom, which falls off gradually to zero at infinity.

2.22. *The variation of the phase shifts with energy and angular momentum.*‡ In classical theory, the deviation produced by the scattering potential on a particle of impact parameter p will be small if

$$V(p) \ll \frac{1}{2}mv^2,$$

the kinetic energy of the particle. This may be expressed in a form appropriate for the quantum treatment as follows.

Corresponding to the angular momentum J , the impact parameter $p = J/mv$. We expect then that $\sin^2\eta_l$ will be small for such values of l that

$$V(J/mv) \ll \frac{1}{2}mv^2,$$

† For a proof of this result see *The Theory of Atomic Collisions*, Oxford, 2nd edition, 1949, Chap. II.

‡ See also *ibid.* §§ 2, 3, 4.

where $J = \{l(l+1)\}^{\frac{1}{2}}\hbar$ is the quantized angular momentum corresponding to this value of l , i.e.

$$V(r_0) \ll \frac{1}{2}mv^2, \quad (11)$$

where

$$kr_0 \simeq \{l(l+1)\}^{\frac{1}{2}}. \quad (12)$$

This condition is the correct one to apply in the quantum theory, it being understood that, because of the uncertainty of position characteristic of the wave treatment, r_0 is to be interpreted as meaning all values of r in the neighbourhood of $\{l(l+1)\}^{\frac{1}{2}}/k$.

Before examining the consequences of this condition for the calculation of Q it is of interest to see how it arises in terms of the form of the de Broglie waves. In the classical theory, if the angular momentum about the centre of force is J , then the impact parameter is *certainly* J/mv . On the quantum theory the impact parameter is most likely to be J/mv , but there is a finite chance that it has some other value. This is exhibited by the form of the probability amplitude functions when the scattering potential is negligible. These are given by f_l/r , where

$$\frac{d^2 f_l}{dr^2} + \left\{ k^2 - \frac{l(l+1)}{r^2} \right\} f_l = 0, \quad (13)$$

and $f_l = 0$ at the centre $r = 0$. The term $l(l+1)/r^2$ arises in the following way. In a Schrödinger equation there appears in its place $2mV/\hbar^2$, where V is the potential energy. If we substitute for V the energy of the centrifugal force $J^2/2mr^2$ with $J = \{l(l+1)\}^{\frac{1}{2}}\hbar$, then this term becomes $l(l+1)/r^2$ as in (13).

The forms of the functions f_l/r are illustrated in Fig. 58 for $l = 0, 1, 2, 3$. These exhibit the main feature that the first maximum appears close to $\{l(l+1)\}^{\frac{1}{2}}/k$ as l increases.

We can now see how the condition (11) for a small phase shift arises. Considering a particular value of l , it is clear that to introduce an extra half-wave, i.e. produce a phase shift of $\frac{1}{2}\pi$, the scattering potential must be large enough to affect the wave-length very markedly at least as far as r_0 the first maximum, where $r_0 \simeq \{l(l+1)\}^{\frac{1}{2}}/k$. To produce such an effect at any point it must be comparable there with the kinetic energy $\frac{1}{2}mv^2$, i.e. $V(r_0)$ must be comparable with, or greater than, $\frac{1}{2}mv^2$. With the condition (11) satisfied this is not so and no large phase shift is introduced.

We may now obtain a qualitative picture of the behaviour of η_l as the energy and angular momentum vary. Consider first a scattering potential of the form

$$V(r) = C/r^s.$$

Then the condition (11) for a small phase η_l is that

$$C/r_0^s \ll E,$$

where E is the kinetic energy. This requires that

$$r_0 \gg (C/E)^{1/s},$$

i.e.

$$l \gg E^{1-1/s} C^{1/s} (2m/\hbar^2)^{1/2} = l_0, \text{ say.} \quad (14)$$

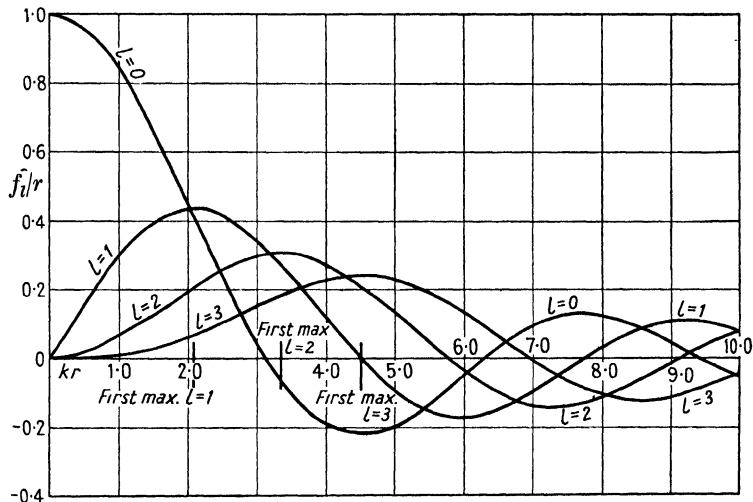


FIG. 58. Probability amplitude functions, $f_l(r)/r = (\pi/2kr)^{1/2} J_{l+1/2}(kr)$ when the scattering potential is negligible ($l = 0, 1, 2, 3$). The position of the first maximum is indicated in each case.

From this result it follows that, if $s > 2$, all phases, except perhaps the zero-order one, must tend to zero as the kinetic energy tends to zero. It also follows that, at a given kinetic energy, all phases for l much greater than l_0 will be small and that the greater the value of E the larger the number of important phases in the series (10). For very low kinetic energies, only the zero-order phase will be important and the scattering cross-section will reduce simply to

$$Q_0 = \frac{4\pi}{k^2} \sin^2 \eta_0.$$

These conclusions remain valid for a scattering potential which falls off exponentially, as for an atomic field.

There is one further point which we must discuss, which is important in dealing with scattering by attractive potentials such as those of atoms. A particular angular momentum makes only a small contribution to the

scattering if $\sin \eta_l$ is small. This is so, not only if η_l is nearly zero, but also if it is nearly equal to an integral multiple of π , say $s\pi$. It is largely conventional what we choose as the low-velocity limit of a phase, zero or $s\pi$, but there is one special choice which has real theoretical advantages. Although when the condition (11) is satisfied the amplitude of the

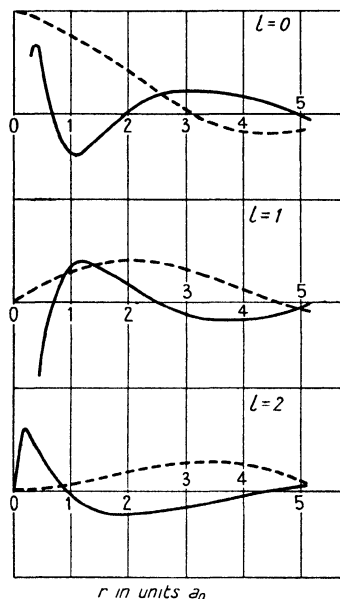


FIG. 59. Radial wave functions ($l = 0, 1, 2$) for krypton for $ka_0 = 1$ (13.54 eV) showing how the scattering field introduces additional zeros.

— wave modified by field;
 --- plane wave.

tion, η_l is a steadily decreasing function of l for a fixed electron velocity and a given atomic field. This is to be expected because, with increase of l , the effective penetration into the field is reduced and hence also its effect in distorting the wave. Use will be made of this in § 2.4.

Fig. 60(a) illustrates typical forms of variation of the phase η_0 with electron energy, following the above convention. Similar behaviour is characteristic of phases for other values of l .

Reference may be made also to Figs. 62, 64 which illustrate the behaviour of the phases for certain atomic fields.

It is of interest to note the connexion here between the scattering

wave function for the particles of l th order angular momentum will be small within the scattering field, except in very special circumstances which will be discussed shortly, the strength of the field may be so large that additional zeros of the wave function are introduced within it. This is illustrated in Fig. 59, which compares the plane wave functions for $l = 0, 1$, and 2 with the corresponding ones for motion in the field of a krypton atom. It may occur even in the low-velocity limit. In view of this it is natural to define the phase η_l so that it tends to an integral multiple s of π , where s is the number of zeros introduced by the field in the wave function for zero velocity particles. This has the great advantage that, in the limit of very fast collisions, the phase so defined will tend to zero. This will be so because, as the energy increases, the number of additional zeros will gradually decrease. A further advantage is that, with this conven-

power of the field and the bound energy levels which can exist within it.† If, with the convention described above, the phase $\eta_l \rightarrow s\pi$ as the velocity tends to 0, then s bound energy levels exist with angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$. The special circumstances mentioned above arise when the uppermost energy level falls at the energy zero. In that case the wave function is not small within the range of the scattering potential but very large and the corresponding value of $\sin^2\eta_l$ falls off more slowly with velocity. Indeed, for $l = 0$ it tends in the low-velocity limit to unity, giving an infinite cross-section. This resonance effect is quite a sharp one and can be ignored in most of the applications to atoms.

A repulsive scattering potential, as it increases the local wave-length, cannot introduce any new waves but only cancel some which would otherwise be present within its range of action. In the low-velocity limit, as the unperturbed wave-length is infinitely great there is no wave to eliminate and all the phases tend to zero according to our convention. This corresponds to the fact that in a repulsive field no bound energy levels can exist.

2.23. 'Classical' approximation for the phase η_l . In order to test whether the theory we have discussed is capable of describing any of the main features of the observed cross-sections, it is necessary to have some convenient method for estimating the phase shifts which are produced by a particular atomic field. This may be done by taking account of the fact that the variation of the potential $V(r)$ within a wave-length is small, except for very low electron energies.

The general form of the amplitude function for a given angular momentum, in the absence of a scattering potential, is illustrated in Fig. 58. The number of wave-lengths between the scatterer and any great distance R from it would be given by R/λ if λ were a constant. When λ varies we may define a local wave-length λ_a , valid between r and $r+dr$, such that

$$\lambda_a = h / \left[2m \left\{ E - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right\} \right]^{\frac{1}{2}}.$$

Under the conditions stated above the number of wave-lengths will become

$$\int_{r_1}^R dr / \lambda_a.$$

The lower limit r_1 may be taken as the greatest distance at which $1/\lambda_a$ vanishes. This amounts to ignoring the small contribution from that

† See Mott and Massey, *Theory of Atomic Collisions*, 2nd edition, Chap. II, § 3.2.

part of the wave which exists within the classical closest distance of approach.

When the scattering potential is present, the number of wave-lengths, to the same approximation, will be changed to

$$\int_{r_2}^R dr/\lambda'_a,$$

where
$$\lambda'_a = h / \left[2m \left\{ E - V - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right\} \right]^{\frac{1}{2}},$$

and r_2 is the greatest distance at which $1/\lambda'_a$ vanishes.

The phase shift is equal to 2π times the difference in the number of waves between the scatterer and infinity so that, approximately,

$$\eta_l = \int_{r_2}^{\infty} \left\{ k^2 - \frac{2mV}{\hbar^2} - \frac{l(l+1)}{r^2} \right\}^{\frac{1}{2}} dr - \int_{r_1}^{\infty} \left\{ k^2 - \frac{l(l+1)}{r^2} \right\}^{\frac{1}{2}} dr. \quad (15)$$

With this approximation the phase will be given with the appropriate multiple of π , according to our convention. This is because the formula is derived by counting the actual number of waves present with and without the field.

This approximation may be derived more rigorously from Jeffreys's approximate solution† of a second-order differential equation such as (13). It is very useful for the study of the scattering of electrons by atoms, as in most circumstances it gives at least a fair estimate of the phase considered. For $l = 0$ the formula (15) clearly breaks down as no zero r_1 or r_2 exists. A more accurate approximation, given by Langer,‡ in which $l(l+1)$ in (15) is replaced by $(l+\frac{1}{2})^2$ may be used, however, even for $l = 0$.

When the phase is small a more accurate approximation, due to Mott,§ may be used. It gives

$$\eta_l = -\frac{4\pi^2 m}{\hbar^2} \int_0^{\infty} V(r) \{J_{l+\frac{1}{2}}(kr)\}^2 r \, dr, \quad (16)$$

where $J_{l+\frac{1}{2}}(kr)$ is the usual Bessel function.

When greater accuracy is required, the phases may be calculated by numerical solution of the appropriate differential equation. A discussion of these and other methods is given in *The Theory of Atomic Collisions*, Chap. VII.

† *Proc. Lond. Math. Soc.* (2), **23** (1923), 428; Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. I, § 6.

‡ *Phys. Rev.* **51** (1937), 669.

§ *Proc. Camb. Phil. Soc.* **25** (1929), 304.

2.3. Application to calculation of elastic cross-sections of atoms

In Chap. I, § 4, the measured total cross-sections of different atoms towards electrons are described. We can now see how the salient features of these observations may be understood. This discussion will be based on the formula for the elastic scattering cross-section

$$Q_0 = \sum q_l$$

where

$$q_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \eta_l,$$

and is known as the l th-order partial cross-section.

2.31. The Ramsauer-Townsend effect.

Let us consider first the behaviour of very slow electrons. If the energy is low enough the only important phase will be η_0 and

$$Q_0 = \frac{4\pi}{k^2} \sin^2 \eta_0.$$

As $k \rightarrow 0$, $\eta_0 \rightarrow s\pi$ where s is, in general, a whole number determined by the strength of the atomic field. For a weak field $s = 0$ and the variation of η_0 with k is of the form of curve I in Fig. 60(a). As the energy of the electron increases the phase η_0 rises to a maximum which will be less than π —the field is not strong enough to introduce an additional wave even at zero energy. The corresponding forms for q_0 which can occur in this case are illustrated in Fig. 60(b). In the low-velocity limit q_0 will be finite as $\sin \eta_0$, in general, tends to zero as k . As $\sin \eta_0$ is never zero at any higher energy the cross-section is also never zero. Clearly the Ramsauer-Townsend effect does not arise in these cases.

For a stronger field, for which $s = 1$, the variation of η_0 with k can have the form either of curve II or curve III of Fig. 60(a). With curve II q_0 is never zero except in the special case in which it vanishes as $k \rightarrow 0$. On the other hand, with curve III q_0 returns to the value π at a finite electron energy and the variation of q_0 with k is of the form

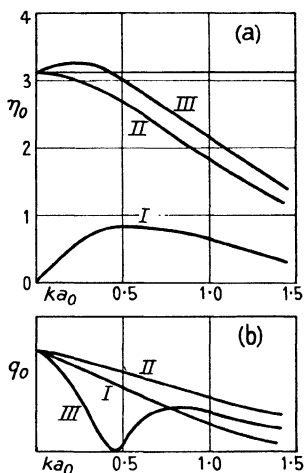


FIG. 60. (a) Typical forms of variation of the phase η_0 with electron energy. Curve I refers to a field which is not strong enough to introduce an additional zero, so that there is no stationary s -state in this field. The phase η_0 therefore tends to zero in the low-velocity limit. Curves II and III refer to a field strong enough to introduce one additional zero so that one stationary s -state exists in the field and the phase η_0 tends to π in each case, from below in curve II and from above in curve III.

(b) Variation of the corresponding cross-sections q_0 with electron energy. Curves I, II, and III refer to the same conditions as the corresponding curves of (a).

typical of the Ramsauer-Townsend effect. Similar possibilities arise when $s = 2$, or more. The vanishing cross-section occurs because, at a particular energy, the scattering potential is just strong enough to introduce a *whole* number of additional waves within its range at this energy.

One further condition for the appearance of the Ramsauer-Townsend effect, which must not be overlooked, is that at the zero of q_0 the contributions to Q from the partial cross-sections q_1, q_2 , etc., must be negligible.

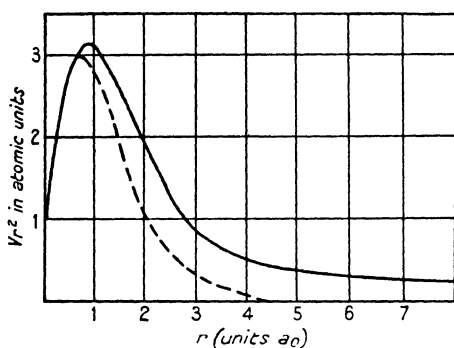


FIG. 61. Field used by Holtsmark in the calculation of electron scattering in argon. Quantities are expressed in atomic units.

----- Hartree field; ——— Hartree field with polarization.

A detailed confirmation of the explanation has been given by Holtsmark,[†] who calculated the phases, by accurate numerical solution of the differential equations, for scattering of electrons by argon atoms. He found that, whereas the scattering potential given by the Hartree field did not lead to the Ramsauer-Townsend effect, a modification to this field, which was arrived at by introducing a polarization correction, did give very good agreement with observation. Fig. 61 illustrates the modification which was introduced. This modification essentially represents a correction to the approximation which regards the atomic field as unperturbed by the incident electron. It was obtained by assuming that the polarization effectively introduced an additional attraction which fell off, at large distances r from the atom, as $\alpha e^2/2r^4$ where α is the polarizability of the argon atom ($= 10.819$ atomic units). This asymptotic form was smoothly joined to the unmodified field so that the polarization was negligible at distances of the order $0.6a_0$ from the nucleus.

[†] *Zeits. f. Phys.* **55** (1929), 437.

The phases calculated by Holtsmark for this field are illustrated in Fig. 62, and Fig. 63 shows how the Ramsauer-Townsend effect is reproduced by substitution in the formula (10). Reference to the phases shows that, for argon, $s = 3$.

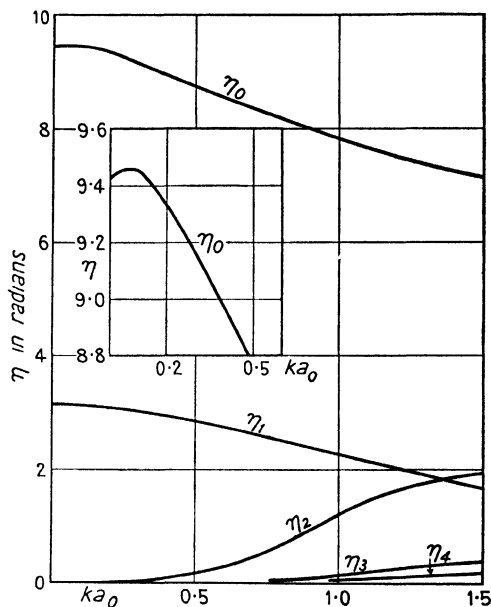


FIG. 62. Phases for argon using the field of Fig. 61 'with polarization'. The variation of η_0 with electron energy is clearly similar to case III of Fig. 60 (a). η_0 tends to 3π at zero energy.

It is now of interest to consider the contribution from higher-order cross-sections. These are very small at the Ramsauer-Townsend minimum, but reference to Fig. 62 shows that at higher energies first q_1 and then q_2 becomes important. The maximum observed in the cross-section for electrons of about 13 eV energy is largely due to q_2 . Higher-order phases never produce a marked individual effect, for the atomic field of argon is not strong enough to produce, at any energy, a large phase shift in the waves associated with more than two units of angular momentum. It will be noted that the second-order cross-section is dominant when the corresponding phase η_2 is nearly equal to $\frac{1}{2}\pi$, as would be expected.

2.32. Similar behaviour of the heavier rare gases. The reason why the heavier rare gases also produce a Ramsauer-Townsend effect can be

traced to the quasi-periodic behaviour of the cross-section q_0 as the atomic number of the scattering atom changes. In going from argon to krypton

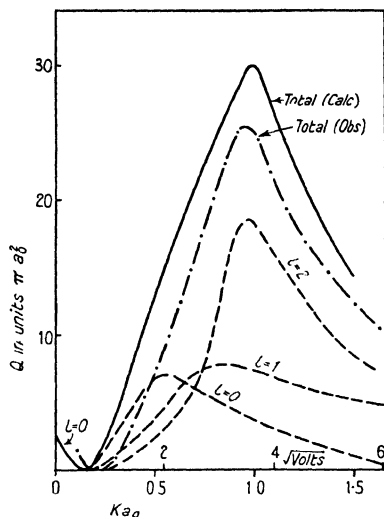


FIG. 63. Partial and total cross-sections for elastic scattering in argon calculated from the phases of Fig. 62. The Ramsauer effect follows from the variation of η_0 and hence of q_0 with electron energy. The strong maximum in the total elastic cross-section for electrons of about 13 eV energy is due to η_2 passing through $\frac{1}{2}\pi$ at this energy.

--- partial cross-section for $l = 0, 1, 2$; - - - total calculated cross-section; - . . . measured results.

the atomic field becomes just so much stronger that, for low-energy collisions, one whole additional wave-length is added within the range of the field. This increases the zero-order phase by π but does not change q_0 . Similarly, in going from krypton to xenon, the zero-order phase increases again by nearly π . Confirmation of this is provided by the detailed calculations of Holtsmark† for krypton, using again a Hartree field modified by a polarization correction. The phases which he obtained are illustrated in Fig. 64 and the corresponding cross-sections in Fig. 65.

Argon, krypton, and xenon give similar cross-sections, not only for low-velocity electrons, but also over a wide energy range. Thus for all three a maximum appears at an electron energy near 13 eV. This is due to periodic behaviour of $\sin \eta_2$ in proceeding from one rare gas to the other. Thus, referring to Fig. 63 it will be seen that, for argon, the

† *Zeits. f. Phys.* **66** (1930), 49.

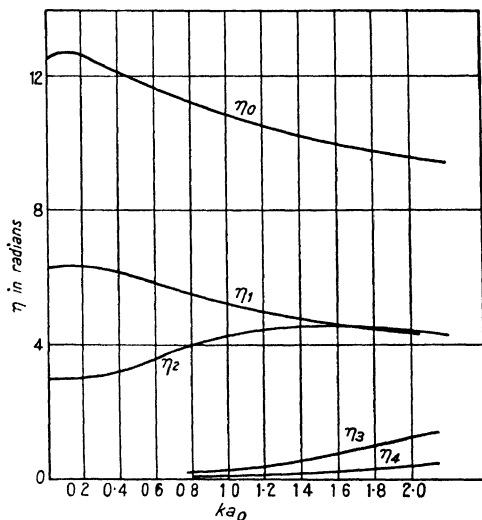


FIG. 64. Phases calculated for krypton using a Hartree field with polarization. η_0 tends to 4π at zero energy. Note that the η_0 , η_1 , η_2 phases are approximately equal to those for argon (Fig. 62) with the addition of π .
(To convert from ka_0 to $\sqrt{\text{volt}}$ multiply by 3.68.)

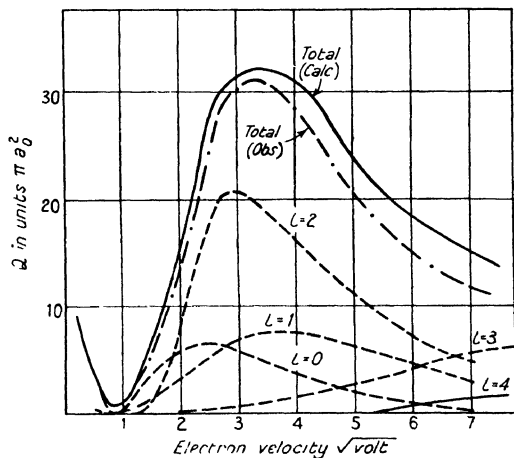


FIG. 65. Partial and total cross-sections for elastic scattering in krypton calculated from the phases of Fig. 64.
- - - partial cross-sections for $l = 0, 1, 2, 3, 4$; ——— total calculated cross-section; — · — total measured cross-section.

maximum arises from the maximum of the second-order partial cross-section when $\eta_2 = \frac{1}{2}\pi$. For krypton, and electrons of the same energy, the same phase is nearly equal to $\frac{3}{2}\pi$ (see Fig. 64) and presumably for xenon it is nearly $\frac{5}{2}\pi$.

One further point to be noticed concerns the highest-order phase, which reaches a maximum in excess of $\frac{1}{2}\pi$. For argon it is η_2 (see Fig. 62), but for krypton it is η_3 (see Fig. 64) and for xenon, presumably η_4 . This has important consequences when the angular distribution of scattered electrons is considered (§ 2.42).

2.33. Behaviour of neon and helium. The marked similarity in the behaviour of xenon, krypton, and argon does not extend to the lighter rare gases, neon and helium. This is because, in passing say from argon to neon, the phase η_0 , for low electron energies, does not pass through a complete period. It appears, in fact, that the molecule methane gives a mean scattering field which provides a phase η_0 differing from that for argon by nearly π and thus becomes the fourth member of the series, preceding argon (see Chap. IV, § 3.2 and Fig. 103).

The neon field is never strong enough to produce a phase shift of $\frac{1}{2}\pi$ in any order except η_0 and η_1 , while the weaker helium field cannot even produce such a phase shift in the first-order wave.

Summarizing the effectiveness of the fields of the rare-gas atoms in producing phase shifts we have the following:

TABLE I

In the limit of very low velocities	$\left\{ \begin{array}{l} \eta_0 \rightarrow 3\pi, 4\pi, 5\pi \text{ from above for A, Kr, Xe respectively, the slope } d\eta_0/dk \text{ increasing in that order. Ramsauer-Townsend effect.} \\ \eta_0 \rightarrow \pi, 2\pi \text{ from below for He, Ne respectively. No Ramsauer-Townsend effect.} \end{array} \right.$
At cross-section maximum	$\left\{ \begin{array}{l} \eta_2 \rightarrow \frac{1}{2}\pi, \frac{3}{2}\pi, \frac{5}{2}\pi \text{ for A, Kr, Xe respectively. No such effect in He or Ne.} \end{array} \right.$
Highest-order phase reaching $\frac{1}{2}\pi$	$\left\{ \begin{array}{l} \eta_2, \eta_3, \eta_4 \text{ for A, Kr, Xe respectively.} \\ \eta_0, \eta_1 \text{ for He, Ne respectively.} \end{array} \right.$

2.34. Large cross-sections for alkali metals. A conspicuous feature of the observed cross-sections is the very large magnitude attained for the heavier alkali metal atoms at low electron energies. Thus, referring to Chap. I, Fig. 5, the cross-section for sodium will be seen to reach a value of $400\pi a_0^2$ for an electron energy of 3 eV. At this energy the wave-length λ is $44a_0$. The maximum value of the partial cross-section q_l , $(2l+1)\lambda^2/\pi$, is therefore $(2l+1)(44/\pi)^2\pi a_0^2$. To explain the observed cross-section for sodium it is only necessary to suppose that the cross-section q_1 has practically its maximum value for the energy concerned, i.e. that η_1 is

nearly equal to an odd multiple of $\frac{1}{2}\pi$ at that energy. Reference to Fig. 62 shows that, for argon, η_1 is equal to $\pi - 0.25$ and is making very little contribution to the cross-section. For the alkali metals, however, the atomic field extends over much greater distances than for argon so that, for low-energy electrons, the first-order phase shifts are much bigger.

2.35. Similarity of behaviour of chemically similar atoms. We have already discussed the similarity of the cross-section velocity curves for the heavier rare-gas atoms. This similarity between elements with similar chemical properties, i.e. between elements occupying similar positions in the periodic table, extends also to the alkali metals and the zinc, cadmium, mercury triad. In terms of the quantum collision theory this similarity, for low-velocity electrons, can be explained if the phase shifts important at these low velocities (η_0 and η_1) change by nearly a whole multiple of π in passing through a complete period of the periodic table. This we found to be the case for the heavier rare gases. It is also true for the alkali metals and the zinc, cadmium, mercury triad.

In order to show the generality of this behaviour, Allis and Morset† calculated the cross-sections to be expected for a schematic atomic field given by

$$V = Z\epsilon^2 \left(\frac{1}{r} - \frac{1}{r_0} \right), \quad r \leq r_0, \\ = 0, \quad r \geq r_0, \quad (17)$$

for which the accurate calculation of the phases could be carried out without too much labour for a variety of values of the constants Z and r_0 . Defining a quantity $\beta = (Zr_0/2a_0)^{\frac{1}{2}}$, Allis and Morse showed that, for a fixed value of $kr_0 (= x)$, the partial cross-sections are quasi-periodic in β with a period unity. Examples of this are given in Fig. 66. Allis and Morse were able to show that a change of β by unity did correspond to passage through one complete period of the periodic table. To do this the best choice of β for different atoms was made in the following way.

By using the rules given by Slater‡ for determining atomic radii the constant r_0 was obtained directly, since Slater considers the electrons in any shell as equivalent to a spherical shell of negative charge of radius equal to the mean radius for the shell. These shells screen the positive charge of the nucleus according to definite rules depending on the quantum numbers of the shell electrons. From the potential energy V due to this distribution Z was also determined as follows.

Fig. 67 shows the radial variation of rV as given by Slater's rules for an

† *Zeits. f. Phys.* **70** (1931), 567.

‡ *Phys. Rev.* **36** (1930), 57.

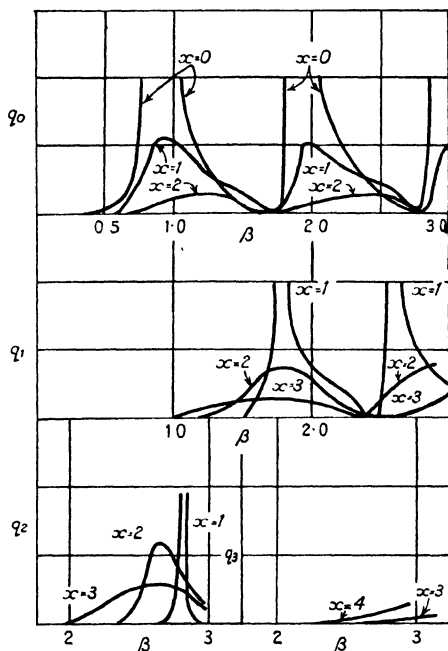


FIG. 66. Partial cross-sections for scattering of electrons of a fixed energy by different atomic fields. x ($= kr_0$) is proportional to the electron velocity. The cross-sections are quasi-periodic in the quantity β ($= (Zr_0/2a_0)^{1/2}$) with period unity.

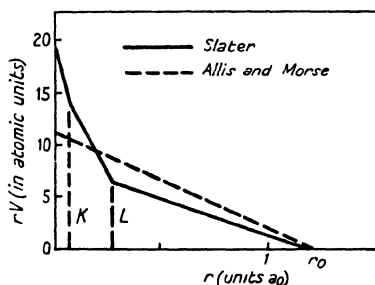


FIG. 67. Radial variation of rV assumed by Allis and Morse, compared with that given by Slater's rules.

atom. Allis and Morse approximated to this form by means of the broken line of Fig. 67 drawn so as to enclose with the axes the same area as the Slater curve. The intercept of this curve at the $r = 0$ axis is equal to

$Z\epsilon^2$ in the expression (17). The values of β found in this way for the different elements are given in Table II.

TABLE II

Lithium 1.36	Zinc 3.77	Helium 0.77
Sodium 2.54	Cadmium 4.87†	Neon 1.73
Potassium 3.51		Argon 2.68
		Krypton 3.66

† The value of β for Cd was not given by Allis and Morse but has been estimated by the method described in their papers.

This shows that, between the heavier atoms in a column of the periodic table, β does change by very nearly unity. With the lighter atoms the change is not so nearly unity, as would be expected since the cross-sections for helium and neon do not resemble those for the heavier rare gases. Lithium should also fall out of place in the alkali metal series, but no measurements have been made for it.

Morse† carried out a similar investigation with a schematic potential

$$V = (Z\epsilon^2/r)\exp(-2r/r_0), \quad (18)$$

defined in terms of a similar pair of parameters Z and r_0 but which has no definite boundary. The results obtained with this potential agreed closely with those from (17).

2.4. Angular distribution of elastically scattered electrons

2.41. The quantal formula. So far we have considered only the description of the total elastic cross-section in terms of quantum theory and have paid no attention to the angular distribution of the scattered electrons. This provides a further severe test of the theory.

In the classical picture of a collision, a particle with a definite angular momentum about the scattering centre will undergo a definite deviation, but on the quantum theory, as would be expected, this is no longer the case. Associated with each quantized angular momentum there is an amplitude function which gives the distribution in angle of the associated scattered amplitude (not the scattered *intensity*). The total scattered amplitude is obtained by adding the contributions from the separate angular momenta, each of which contributes at *all* angles. A suitable weighting factor, related to the probability of any deviation occurring, must be included in each contribution.

Thus the contribution to the amplitude scattered between angles θ and $\theta + d\theta$ from the angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$ is of the form

$$g(\eta_l)F_l(\theta),$$

† *Rev. Mod. Phys.* **4** (1932), 577.

where $F_l(\theta)$ is the angular function associated with the particular angular momentum and the weight factor $g(\eta_l)$ is a measure of the chance that any deviation will occur. It will vanish when $\eta_l \rightarrow 0$ or an integral multiple of π , and can be expected to have a maximum influence when η_l tends to an odd integral multiple of $\frac{1}{2}\pi$.

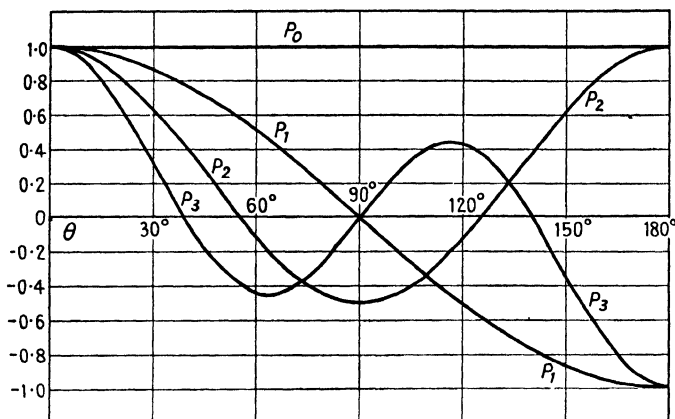


FIG. 68. Zonal harmonics, $P_l(\cos \theta)$, for $l = 0, 1, 2, 3$.

The total scattered amplitude will then be

$$\sum_l g(\eta_l) F_l(\theta) \quad (19)$$

and the scattered intensity will be

$$\left| \sum_l g(\eta_l) F_l(\theta) \right|^2,$$

allowing for the possibility that $g(\eta_l)$ may be complex, as it is in fact.

Since the scattered amplitude is obtained by summing the contributions from different angular momenta, it is to be expected that interference effects, leading to maxima and minima in the angular distribution, will arise in some circumstances.

The functions $F_l(\theta)$ are the zonal harmonics $P_l(\cos \theta)$, the forms of which are illustrated in Fig. 68 for $l = 0, 1, 2, 3$. It will be noticed that, at $\theta = 0$, all are equal to 1 while, at $\theta = \pi$, they are equal to $(-1)^l$. The number of zeros the functions possess in the range 0 to π is equal to the order l .

The weight factor $g(\eta_l)$ may be calculated by the methods of diffraction theory and is found to be given by

$$g(\eta_l) = (2l+1)\{\exp(2i\eta_l) - 1\}.$$

This gives for the differential cross-section

$$I_0(\theta) = \frac{1}{4k^2} \left| \sum (2l+1) \{ \exp(2i\eta_l) - 1 \} P_l(\cos \theta) \right|^2. \quad (20)$$

As

$$\begin{aligned} \int_0^\pi P_l(\cos \theta) P_m(\cos \theta) \sin \theta \, d\theta &= 4\pi/(2l+1), & l = m, \\ &= 0, & l \neq m, \end{aligned}$$

it can easily be verified that

$$2\pi \int_0^\pi I_0(\theta) \sin \theta \, d\theta = Q_0.$$

We may now obtain some idea of the forms to be expected for the angular distributions of slow elastically scattered electrons. At very low energies only η_0 is important and

$$I_0(\theta) = \frac{1}{4k^2} |\{ \exp(2i\eta_0) - 1 \} P_0|^2.$$

Reference to Fig. 68 shows that $P_0(\cos \theta)$ is equal to 1 for all θ , so that the angular distribution should be uniform under these conditions.

With increasing energy the phase η_1 will become appreciable and the distribution will be modified by the introduction of the harmonic $P_1(\cos \theta) = \cos \theta$. When $\eta_1 = \frac{1}{2}\pi$ we can expect the angular distribution to be largely determined by this function, possessing a low minimum at 90° . If the atomic field is strong enough the phase η_2 will approach $\frac{1}{2}\pi$ as the energy increases still farther so, in this energy range, we expect the distribution to be strongly influenced by the harmonic $P_2(\cos \theta)$ giving minima near 60° and 120° and a maximum at 90° (see Fig. 68), and so on. It is not to be expected, of course, that there will be many circumstances in which the contributions from the other angular momenta will be negligible so that the distribution, while similar in these general features to that given by a single harmonic, will usually be more complicated in detail.

This is exactly the kind of behaviour which is observed.

2.42. Angular distribution for scattering of low-energy electrons by rare-gas atoms. Referring to Table I, which summarizes the general scattering properties of the rare-gas atoms, it will be seen that the following general forms of the angular distributions are to be expected for the scattering of slow electrons:

Helium. Very flat, because η_0 is the only phase which passes through a value of $\frac{1}{2}\pi$ whereas η_1 , and all higher phases, are always small.

Neon. The influence of η_1 should be apparent at not too low velocities in producing a minimum at 90° . No important influence of higher order phases is to be expected.

Argon. In the neighbourhood of the cross-section maximum the influence of η_2 should be strong (see Table I which shows that $\eta_2 \simeq \frac{1}{2}\pi$ there). The angular distribution should therefore show minima near 60° and 120° and a maximum at 90° .

Krypton. The influence of the harmonic $P_3(\cos\theta)$ is likely to be important at energies near 50 eV, and beyond, for which the phase η_3 is near $\frac{1}{2}\pi$ (see Fig. 64). As the contribution from η_2 is also large, at least at the lower energies in this range, the interference between the two contributions may rather modify the distribution. Near the cross-section maximum (10 eV) the distribution should be dominated by $P_2(\cos\theta)$.

Xenon. The harmonic $P_4(\cos\theta)$ will play an important part here, though important contributions from second- and third-order phases will complicate the picture.

In Fig. 69 a number of observed angular distributions† are illustrated which show that these predictions are substantially correct. The sequence of curves representing the angular distributions for 80-eV electrons scattered by He, Ne, A, Xe, and Hg atoms are particularly interesting in this respect. It is quite clear by comparing these curves with those given respectively by the single harmonics $(P_0)^2$, $(P_1)^2$, $(P_2)^2$, $(P_3)^2$, $(P_4)^2$, that the predominant phase angle changes successively from η_0 to η_4 in going from helium to xenon, as predicted.

It is possible to trace the gradual change in the atomic field in proceeding from phosphorus to potassium with reference to the scattering of 80-eV electrons. Mohr and Nicoll‡ measured the angular distribution for scattering of such electrons by phosphine PH_3 and hydrogen sulphide H_2S . Owing to the comparatively small effect of the hydrogen atom these distributions are essentially those characteristic of phosphorus and sulphur atoms (see Chap. IV, § 2.1). McMillen§ has measured the distribution for scattering by potassium. The three distributions as well as one for argon are illustrated in Fig. 70. Although it is clear that η_2 is the dominant phase for all four, it is clearly less important for sulphur and phosphorus, as would be expected from their somewhat weaker fields. Similar relations are found between nitrogen and neon

† For references see Chap. II, § 7.31.

‡ *Proc. Roy. Soc. A*, **138** (1932), 469.

§ *Phys. Rev.* **46** (1934), 983.

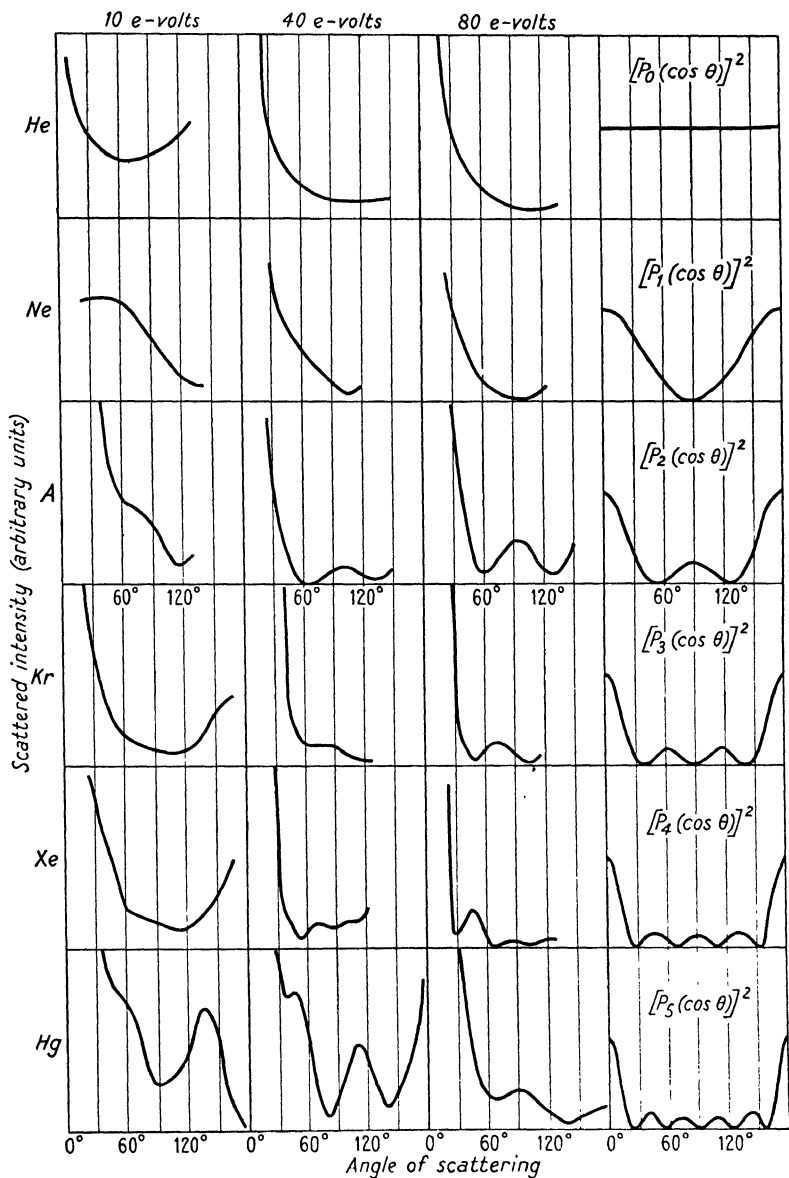


FIG. 69. Observed angular distributions for elastic scattering of 10-, 40-, and 80-eV electrons in neon, argon, krypton, xenon, and mercury together with distributions $\{P_l(\cos \theta)\}^2$ corresponding to the dominant phase η_l for the 80-volt case in each gas.

(η_1 dominant), between zinc, krypton, and bromine (η_3 dominant), and between iodine and xenon (η_4 dominant).

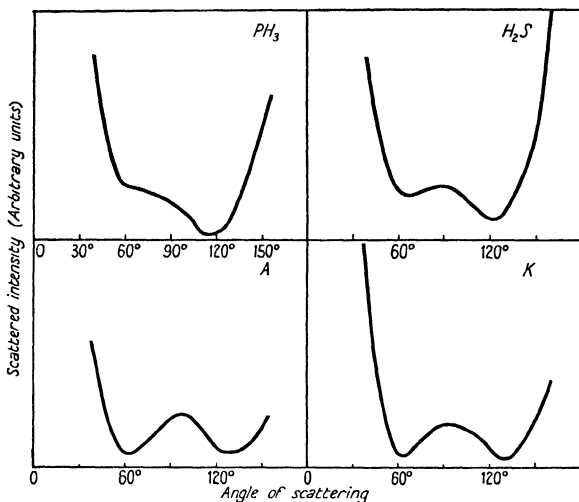


FIG. 70. Comparison of observed angular distribution for elastic scattering of 80-eV electrons by phosphine, hydrogen sulphide, argon, and potassium, showing that η_2 is the most important phase for all four at these energies.

For 40-eV electrons the distributions for xenon and krypton have already become less variable, showing that the phases η_3 and η_4 respectively are becoming less important. For 10-eV electrons it is clear that these phases have become unimportant, but the form of the distribution shows that η_2 is still effective. At this energy the distribution for helium has already come close towards uniformity, indicating that η_1 and higher-order phases are becoming unimportant.

It was noted in Chap. II, § 7.31, that even for very-low-energy electrons (0.5 eV) in argon, krypton, and xenon the angular distribution is far from uniform (see Fig. 47 of Chap. II). This is rather surprising at first sight because for these electrons η_1 , η_2 , and all higher phases are very small (Figs. 62 and 64). It must be remembered, however, that in this energy range the Ramsauer-Townsend effect occurs. As explained in § 2.31, this effect arises because η_0 varies with energy according to curve I of Fig. 60 and is equal to π at the cross-section minimum. Hence, although η_1 and η_2 are very small for 0.5 eV, their contributions to the scattering are by no means necessarily small compared with that from η_0 . The resultant angular distribution may therefore be characteristic of first- or

second-order scattering, and reference to Fig. 47 of Chap. II shows that η_2 must indeed be relatively important. The variability of the angular distributions for electrons of very low energy in argon, krypton, and xenon may thus be regarded as additional confirmation of the general correctness of the explanation of the Ramsauer-Townsend effect given in § 2.31.

To understand the behaviour of the angular distributions at higher electron energies it is best to start from the limiting case of very high electron energies for which a simplified approximation may be used.

2.43. Angular distribution for high-energy electrons—Born's approximation. It is possible to obtain a simple formula for the angular distribution when the electron energy is so high that all the phases are small. This formula, known as Born's approximation, is of great value for many applications (see, for example, § 1 of Chap. IV). Although it is only valid over the entire angular range when *all* the phases are small, it remains a good approximation at small angles even when some of the phases are large. In this case it provides a background against which the observed forms of the distributions may be built up.

The principle of the approximation is that, for high-energy electrons, the distortion of the incident waves by the atomic field is very small, and may be treated as a small perturbation. It is found then that

$$I_0(\theta) = |f(\theta)|^2,$$

$$\text{where} \quad f(\theta) = \frac{2m}{\hbar^2} \int_0^\infty V(r') \frac{\sin(2kr' \sin \frac{1}{2}\theta)}{2k \sin \frac{1}{2}\theta} r' dr', \quad (21)$$

and k is as before equal to $mv/\hbar$, v being the electron velocity. This formula may be derived as follows.

The Schrödinger wave equation for the motion in the field of potential V is

$$\nabla^2 \psi + [k^2 - U(r)]\psi = 0, \quad (22)$$

where $U = 2mV/\hbar^2$. In the absence of the potential V the incident electron beam is represented by the plane wave

$$\psi = Ae^{ikz}, \quad (23)$$

where $v|A|^2$ gives the flux of electrons/sq. cm./sec. in the beam, which is directed along the z -axis. The effect of the potential is to scatter electrons. At a great distance r from the centre these scattered electrons will appear as an outgoing spherical wave

$$Ar^{-1}e^{ikr}f(\theta).$$

The differential cross-section is then given by $|f(\theta)|^2 d\omega$, for the total scattered flux is

$$|A|^2 v \iint |f(\theta)|^2 \sin \theta d\theta d\phi. \quad (24)$$

To calculate $f(\theta)$ approximately we take $U(r)$ to be small so that the scattered amplitude is small. We may then write

$$U(r)\psi \simeq U(r)e^{ikz}, \quad (25)$$

neglecting the small product of U and the amplitude of the scattered waves.

The solution is now required of the equation

$$\nabla^2\psi + k^2\psi = U(r)e^{ikz} \quad (26)$$

which has the form, for large r ,

$$\psi \sim e^{ikz} + r^{-1}e^{ikr}f(\theta).$$

This may readily be obtained by the method of Green's function† and gives

$$f(\theta) = -\frac{2\pi m}{\hbar^2} \int V(r') \exp(2ikr' \sin \frac{1}{2}\theta \cos \theta') d\tau'. \quad (27)$$

Integration over the angles θ, ϕ gives (21).

The function $f(\theta)$ may be expanded in a series of zonal harmonics for comparison with the exact expression (19) and it is found that,‡ in the approximate formula, the expression η_l of the exact formula is replaced by

$$\zeta_l = -\frac{4\pi^3 m^2}{k\hbar^2} \int_0^\infty V(r) \{J_{l+\frac{1}{2}}(kr)\}^2 dr. \quad (28)$$

It may be shown‡ that when η_l is small it is given, to a good approximation, by ζ_l (see § 2.23, equation (16)).

2.44. Nature of the angular distribution for high energy impacts. The function $f(\theta)$ falls off steadily as θ increases, exhibiting no maxima and minima. The higher the energy of impact, the steeper the angular distribution becomes. To see the reason for this more clearly it is convenient to transform the expression for $f(\theta)$ by writing the potential $V(r)$ in the form

$$V(r) = -\frac{Z\epsilon^2}{r} + \epsilon^2 \int \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|} d\tau', \quad (29)$$

where the first term represents the potential due to the nucleus, of charge $Z\epsilon$, the second that due to the atomic electrons whose density at distance r from the nucleus is $\rho(r)$. It may then be shown§ that

$$f(\theta) = \frac{\epsilon^2}{2mv^2} [Z - F(\theta)] \operatorname{cosec}^2 \frac{1}{2}\theta, \quad (30)$$

where
$$F(\theta) = 4\pi \int_0^\infty \rho(r') \frac{\sin(2kr' \sin \frac{1}{2}\theta)}{2k \sin \frac{1}{2}\theta} r' dr', \quad (31)$$

and is known as the atom form factor.

† See Mott and Massey, *The Theory of Atomic Collisions*, Oxford, 2nd edition, 1949, Chap. VI, § 2, and Chap. VII, § 1.

‡ Ibid., Chap. II, § 2.

§ Ibid., Chap. VII, § 1.

The function $r^2\rho(r)$ vanishes at the origin and possesses a maximum at $r = r_0$, say. For such electron energies that $kr_0 \sin \frac{1}{2}\theta$ is large $F(\theta)$ will be small owing to the rapid oscillations of $\sin(2kr' \sin \frac{1}{2}\theta)$ for $r' \simeq r_0$. In particular $F(\theta) \rightarrow 0$ as $k \rightarrow \infty$. In that case

$$f(\theta) = (Z\epsilon^2/2mv^2)\operatorname{cosec}^2 \frac{1}{2}\theta$$

and the differential cross-section $I_0(\theta) d\Omega$ has the familiar form of the Rutherford formula for scattering by a bare nucleus:

$$I_0(\theta) d\Omega = (Z^2\epsilon^4/4m^2v^4)\operatorname{cosec}^4 \frac{1}{2}\theta d\Omega. \quad (32)$$

However, as long as λ is finite, $I(\theta)$ will tend to a finite value for $\theta = 0$, given by

$$I_0(0) = (4m^2/\hbar^4) \left[\int_0^\infty V(r')r' dr' \right]^2. \quad (33)$$

This limit is independent of the electron energy.

We therefore have, at high energies, a distribution falling from the constant value at $\theta = 0$ to a value, at a moderate to large angle θ , which decreases as $(v \sin \frac{1}{2}\theta)^{-4}$. The distribution thus gets rapidly steeper as the electron energy increases.

If the Fermi-Thomas statistical model for the atomic field is used (§ 2.1), $I_0(\theta)Z^{-3}$ may be calculated as a function of $Z^{-1}v \sin \frac{1}{2}\theta$, giving in one table the distribution function for all atoms for which the model is valid. Such a table is given in *The Theory of Atomic Collisions*, by Mott and Massey, Chap. IX.

For the lighter atoms the statistical model is not very accurate and it is then necessary to use the Hartree self-consistent field or, if available, the Fock field. Tables of $I_0(\theta)$ calculated in this way are also given in *The Theory of Atomic Collisions*, Chap. IX.

For many applications in which the scattering of fast electrons through small angles is important it is convenient to have available a simple approximate form for $I_0(\theta)$. One useful representation is to take†

$$I_0(\theta)\sin \theta d\theta = \frac{4Z^2\epsilon^4}{m^2v^4\gamma^2} d\theta \begin{cases} \theta^{-3}, & \theta > \theta_1 \\ \theta_1^{-3}, & \theta < \theta_1 \end{cases} \quad (34)$$

$\gamma = (1 - v^2/c^2)^{-1/2}$, is a relativistic correction factor. The cut-off angle θ_1 is determined by the screening of the nuclear charge by the atomic electrons. With the Fermi-Thomas statistical model, valid for all but the lightest atoms,

$$\theta_1 \simeq cZ^{1/3}/180r\gamma. \quad (35)$$

When $Z < 6$, θ_1 may still be written in the form $cA/180r\gamma$ but A

† E. J. Williams, *Proc. Roy. Soc. A*, **139** (1933), 163; Marton and Schiff, *J. App. Phys.* **12** (1941), 759.

is no longer given accurately by Z^4 . More accurate values may be obtained from the Hartree fields of the atoms and these are listed in Table III.

TABLE III

Values of A occurring in the Approximate Formula for the Elastic Scattering Cross-section

H . . .	1.73	Li ⁺ . . .	1.81	N . . .	2.15	F . . .	2.68	Na ⁺ . . .	2.88
He . . .	2.87	C . . .	1.78	O . . .	2.57	Ne . . .	3.18	Al ⁺⁺⁺ . . .	2.61

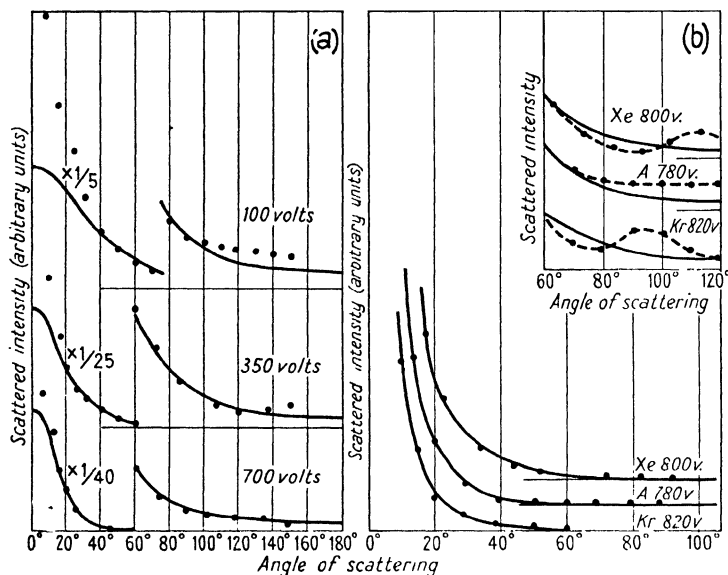


FIG. 71. Observed angular distribution of scattered electrons compared with theoretical calculations based on Born's approximation for (a) He for 100, 350, and 700 eV electrons, (b) Ar, Kr, and Xe for electrons of about 800 eV energy.

The validity of Born's approximation may be thoroughly checked for helium from the observations of Hughes, McMillen, and Webb† (Chap. II, § 7). The comparison is given in Fig. 71 (a). It will be seen that the agreement is very good for the highest electron energies, but becomes progressively worse at the lower energies, at which two distinct types of disagreement may be distinguished. At large angles the distribution is flatter, and at small, steeper, than the calculated.

Fig. 71(b) exhibits a similar comparison for argon, krypton, and xenon

† *Phys. Rev.* **41** (1932), 154.

for 800-volt electrons. The most interesting feature here is that, while good agreement is obtained over a considerable part of the angular range, at angles greater than 60° there is a considerable divergence. For argon it takes the same form as for helium, the observed distribution being very flat but, for krypton and xenon, the observed curve exhibits maxima and minima.

It is not difficult to trace the way in which deviations from Born's approximation will begin to set in at large angles, as the electron energy decreases. We may write for the scattered amplitude $f(\theta)$

$$f(\theta) = f_b(\theta) + \{f(\theta) - f_b(\theta)\}, \quad (36)$$

$$\text{where } f(\theta) - f_b(\theta) = \sum (2l+1) \{ \exp(2i\eta_l) - 1 - 2i\zeta_l \} P_l(\cos \theta) \quad (37)$$

η_l is here the exact value for the l th-order phase, ζ_l that, (28), given by Born's approximation. At high energies η_l is small and nearly equal to ζ_l for all l . As the energy decreases, the first phase which becomes too large for it to be given closely by the expression (28) is η_0 , as this is the largest phase. Under these conditions the amplitude will take the form

$$f(\theta) = f_b(\theta) + \exp(2i\eta_0) - 1 - 2i\zeta_0. \quad (38)$$

$f_b(\theta)$ is very small at large angles, so the effect of the additional constant term will be to make the scattering very flat at these angles. This is just what is observed in helium (see Fig. 71 (a)) and in argon (Fig. 71 (b)) for 780-volt electrons.

As the energy decreases, η_1 will become large if the scattering field is strong enough, giving rise to an additional correcting term in the amplitude of the form $\{ \exp(2i\eta_1) - 1 - 2i\zeta_1 \} \cos \theta$. This will predominate over the zero-order correction when η_1 approaches $\frac{1}{2}\pi$ and the deviation from Born's approximation at large angles will have a form characteristic of $P_1(\cos \theta)$ with a minimum near 90° . This is observed with argon for 500-volt, and neon for 200-volt, electrons.

If the atomic field is large enough η_2 will next approach $\frac{1}{2}\pi$ and dominate the distribution. This is noticeable with 84-volt electrons in argon (see Fig. 72) for which the distribution exhibits the minimum at 60° and maximum at 90° characteristic of $P_2(\cos \theta)$. No important influence of this term appears for neon at any energy (see Fig. 69 or Figs. 46 and 47 of Chap. II) because the phase shift η_2 is never large for that atom. Again no effect due to phases of higher order than η_2 is apparent in argon, whereas, in krypton, η_3 is clearly important for 200-volt electrons, for example, and in xenon for 400-volt electrons. This is illustrated in Fig. 72. At lower energies (120 volts) in xenon, η_4 is clearly effective, but no sign of its influence is detectable in the results for krypton.

We see then that the different harmonics become successively effective in the same order both as the energy increases from the lowest value and as it decreases from very high values. In the second case, of course,

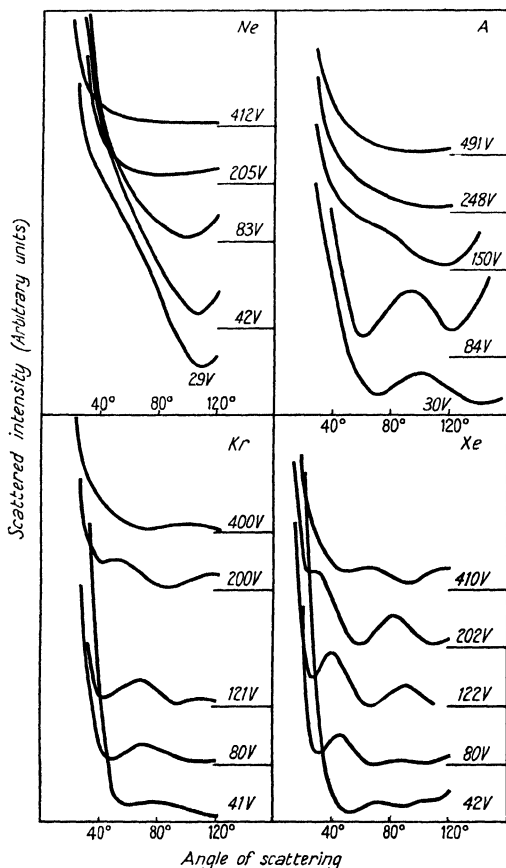


FIG. 72. Observed angular distribution of electrons of energy 30–400 eV scattered in Ne, A, Kr, Xe, showing how the shape of the distribution changes as the energy decreases and higher-order harmonics become important.

the effect is the correction to be superposed on the smoothly falling distribution given by Born's approximation. This is the explanation of the phenomenon noted in Chap. II, § 7.3, that the diffraction pattern becomes at first more complicated as the energy increases and then smooths out again with further increase of energy, after going through the same sequence in the reverse order. The maximum complexity is

determined by the highest-order harmonic for which the phase attains a value $\frac{1}{2}\pi$. The heavier the atom, the greater this order will be, and hence the more complex the pattern.

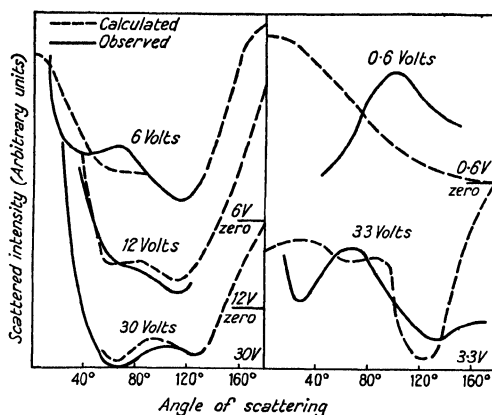


FIG. 73. Comparison of observed and calculated angular distribution of slow electrons scattered in argon.

--- calculated; — observed.

2.45. Summary of detailed calculations of angular distributions and their comparison with observation. Calculations of angular distribution using the exact formula (19) and the phases calculated by Holtsmark† in his theory of the Ramsauer–Townsend effect in argon and krypton are compared with observed distributions‡ in Figs. 73 and 74. It will be seen that there is good general agreement except at the lowest energies.

It is not surprising that the theory fails to give good results at these energies because, as explained in § 2.42 above, the distribution, in the energy region in which the Ramsauer–Townsend effect occurs, depends on the relative values of three very small terms arising from the phases η_0 , η_1 , and η_2 . A very accurate theory would be required to predict these terms correctly.

Calculations have also been carried out for mercury,§ zinc,|| and potassium†† using the approximate formula (15) for the phases. For mercury and potassium the unmodified Fermi–Thomas field was used, while for zinc a Fermi–Thomas field modified at large distances to agree more closely with ionization potential data was employed. The energy

† Loc. cit.

§ Henneberg, *Naturwiss.* **20** (1932), 561.

|| Childs and Massey, *Proc. Roy. Soc. A*, **142** (1933), 509.

†† McMullen, *Phys. Rev.* **46** (1934), 983.

‡ See Chap. II, § 7.31.

range covered was from 135–812 eV for mercury, 20–122 eV for zinc, and 5–150 eV for potassium. Good general agreement was obtained throughout.

The most interesting comparison between the theory of scattering by a static field and the observed data is that for helium. The phases for

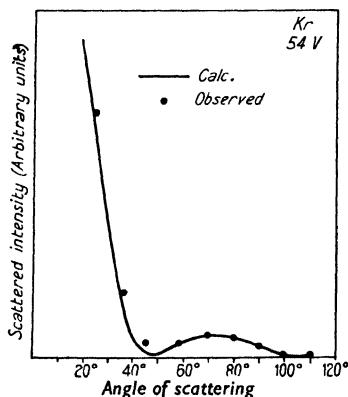


FIG. 74.

FIG. 74. Comparison of observed and calculated angular distribution of 54 eV electrons elastically scattered in krypton.

— calculated; ● observed.

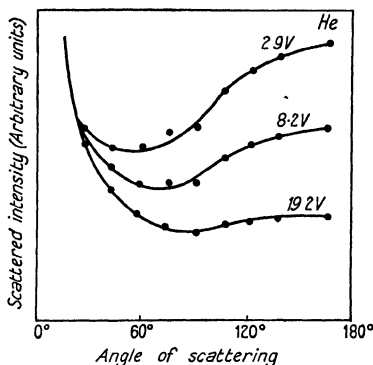


FIG. 75.

FIG. 75. Observed angular distribution of slow electrons scattered in helium.

scattering by the Hartree field of helium, with no allowance for polarization, were calculated by Macdougall† by exact numerical integration of the differential equations. For energies below 10 eV all the phases other than η_0 are less than 0.02 radian, so that the angular distribution should be quite uniform for these energies. The observed data show (Fig. 75) that this is by no means the case. Even for 3-eV electrons the distribution shows a weak minimum at 60° , indicating appreciable influence from the first-order phase. At small angles also the intensity decreases very steeply, even for energies as low as 3 eV. To understand these discrepancies we must look beyond the static-field approximation.

2.5. Electron exchange and elastic collisions

One of the first possibilities to be taken into account, in allowing for the electronic structure of the struck atom, is that of electron exchange. An event indistinguishable from elastic scattering is one in which the incident electron changes place with an atomic electron which leaves the

† *Proc. Roy. Soc. A*, **136** (1932), 549.

atom with the same energy as that of incidence. According to the quantum theory, the net effect of direct and exchange scattering must be obtained by suitably combining the appropriate amplitudes, not intensities. Interference may therefore take place, leading to the possibility of a reduction as well as of an increase in the observed scattering.

Exchange effects in scattering were first pointed out by Oppenheimer† in 1928, who suggested at that time that they might provide the explanation of the Ramsauer–Townsend effect. Although we now know that this is not so, it is of interest to see whether any failure of the static-field theory can be ascribed to neglect of electron exchange. This question was first examined by Massey and Mohr,‡ who found that, for helium, electron exchange was likely to become significant for electron energies below 15 eV. These are just the energies for which the static-field theory is manifestly not accurate (see Fig. 75). It was further shown that the effect of the exchange was probably to make the first-order scattering more important, as required to remove the discrepancy at all but small angles. This was finally confirmed by an accurate numerical analysis carried out by Morse and Allis,§ who verified that inclusion of exchange removed all important discrepancies except those at small angles.

As long as the possibility of inelastic collisions is ignored, the scattering can still be represented by the formulae (10) and (19) even when exchange is included, the phases η_l still remaining real. They are no longer obtained, however, by the solution of a differential equation, but of a more complicated integro-differential equation. This is because the effect of exchange cannot be represented by a suitable modification of the scattering potential which is independent of electron velocity. Morse and Allis solved the integro-differential equations for helium by a numerical procedure and obtained revised values of the phases η_0 and η_1 . These are compared in Fig. 76 with those obtained when exchange is neglected. The zero-order phase is already greater than $\frac{1}{2}\pi$ for electrons of energy 10 eV, so that its effect on the scattering is reduced and that of the first-order phase increased. Using these phases much better agreement is obtained with the observed angular distributions (see Fig. 77). The corresponding total cross-sections also agree very well in absolute magnitude with those observed (Fig. 78).

It will be seen, however, that the discrepancy at small angles still persists and cannot be explained without allowing for the possibility of

† *Phys. Rev.* **32** (1928), 361.

‡ *Proc. Roy. Soc. A*, **132** (1931), 605; **136** (1932), 289.

§ *Phys. Rev.* **44** (1933), 269.

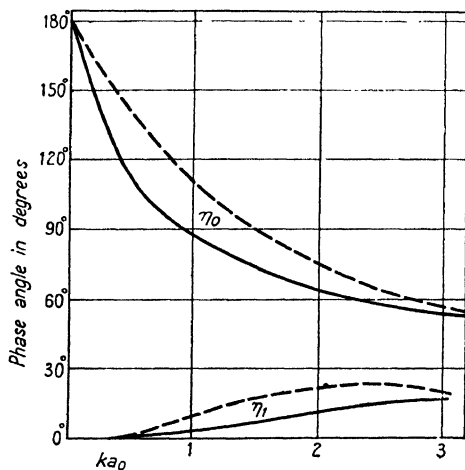


FIG. 76. Effect of exchange on the phases η_0 , η_1 for helium.
 ——— without exchange; --- with exchange.

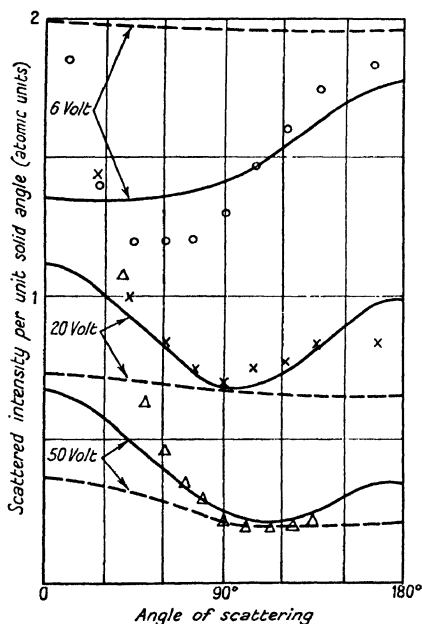


FIG. 77. Comparison of observed angular distributions in helium with distributions calculated with and without exchange. Experimental points: $\circ$. . . 6 eV; $\times$. . . 20 eV; Δ . . . 50 eV. Calculated curves with exchange ———, without exchange ———.

inelastic scattering (see § 3.6), which manifests itself in a further velocity-dependent distortion of the atomic field.

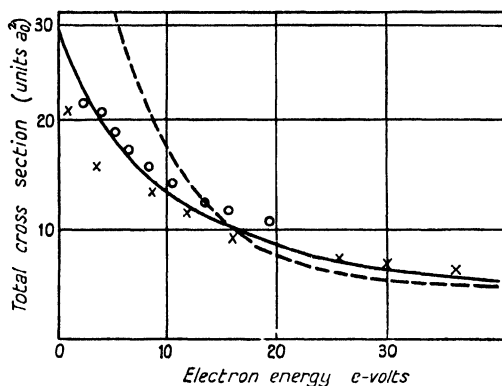


FIG. 78. Comparison of observed total collision cross-sections in helium (see Chap. I, § 4) with those calculated with exchange —, without exchange ---.

No detailed calculations of exchange effects which can be compared with observations have been carried out for heavier atoms, although Bates and Massey† included both exchange and a polarization correction in a calculation of scattering by atomic oxygen. However, Morse and Allis gave reasons why the effect of exchange, which increases as the number of atomic electrons, tends to become unimportant for heavy atoms compared with direct scattering, which increases as the square of the atomic number. Nevertheless, it is possible that the failure of the static-field theory to give detailed agreement for low electron energies in argon and krypton may also be partly due to neglect of exchange. The theoretical discussion has now been carried as far as it is possible to go without consideration of inelastic collisions which we next proceed to discuss.

3. Inelastic collisions

3.1. Born's approximation

We must now consider what may be done to calculate the cross-sections for inelastic scattering. Although it is not possible in this case to carry the theory quite as far as for elastic collisions, much may be done. It is best to start first from the standpoint of Born's approximation, which actually seems to possess a somewhat wider range of validity than might have been anticipated.

† *Proc. Roy. Soc. A*, **192** (1947), 1.

The differential cross-section for excitation of the n th state of an atom from the ground state by an electron is given, according to Born's approximation, by

$$I_{0n} = \frac{4\pi^2 m^2}{\hbar^4} \frac{k_n}{k} \left| \int V_{0n}(\mathbf{r}') \exp\{i(\mathbf{k}\mathbf{n}_0 - \mathbf{k}_n \mathbf{n}) \cdot \mathbf{r}'\} d\mathbf{r}' \right|^2, \quad (39)$$

where $2\pi/k$, $2\pi/k_n$ are the wave-lengths of the colliding electron before and after impact respectively and $\mathbf{n}_0$ and $\mathbf{n}_1$ are unit vectors in the direction of incidence and of scattering. V_{0n} is given by

$$V_{0n}(r) = \epsilon^2 \int \sum_1^N \frac{1}{r_{0s}} \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \psi_n^*(\mathbf{r}_1, \dots, \mathbf{r}_N) d\tau_1 \dots d\tau_N, \quad (40)$$

where r_{0s} is the distance of the incident electron from the s th atomic electron and ψ_0 , ψ_n are the respective wave functions of the ground and n th state of the atom. V_{0n} is thus a cross mean of the interaction energy between the electron and the atom, taken over the initial and final amplitude functions of the atomic electrons.

To see how this formula is obtained† we may consider the simple case of a collision with a hydrogen atom. The wave equation for the system is

$$\left[\nabla_1^2 + \nabla_2^2 + \frac{8\pi^2 m}{\hbar^2} \left(E + \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}} \right) \right] \Psi = 0, \quad (41)$$

in which the total energy $E = E_0 + T$, where E_0 is the energy of the ground state of the atom and T is the kinetic energy of the incident electron. We write now

$$\Psi = e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1} \psi_0(\mathbf{r}_2) + F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) + F_n(\mathbf{r}_1) \psi_n(\mathbf{r}_2), \quad (42)$$

in which $e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1}$ represents the incident wave, so that $k^2 = 2mT/\hbar^2$, and F_0 the elastically scattered wave, both of which are associated with the atom in its ground state with wave function ψ_0 . F_n represents the inelastically scattered wave associated with the atom in its n th state with wave function ψ_n . The interaction $\epsilon^2\left(\frac{1}{r_{12}} - \frac{1}{r_1}\right)$ is responsible for the scattering, which is assumed to be small so that F_0 and F_n are small and the product of either with the interaction potential is negligible.

Since

$$\begin{aligned} \nabla_1^2 e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1} &= -k^2 e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1}, \\ \nabla_2^2 \psi_0 + \frac{8\pi^2 m}{\hbar^2} \left(E_0 + \frac{\epsilon^2}{r_2} \right) \psi_0 &= 0, \end{aligned}$$

and

$$\nabla_2^2 \psi_n + \frac{8\pi^2 m}{\hbar^2} \left(E_n + \frac{\epsilon^2}{r_2} \right) \psi_n = 0,$$

we have, substituting in (41) and ignoring the small terms,

$$\psi_0(r_2) \{ \nabla_1^2 F_0 + k^2 F_0 \} + \psi_n(r_2) \{ \nabla_1^2 F_n + k_n^2 F_n \} = \frac{2m}{\hbar^2} \left(\frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1} \psi_0(r_2), \quad (43)$$

† For a more detailed discussion see Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition 1949, Chap. VIII, §§ 2, 3.

where $k_n^2 = 2m(E - E_n)/\hbar^2$. Since $\int \psi_0(r_2) \psi_n^*(\mathbf{r}_2) d\tau_2 = 0$ we have, on multiplication of both sides by $\psi_n^*(\mathbf{r}_2)$ and integration over $d\tau_2$, the equation

$$\nabla_1^2 F_n + k_n^2 F_n = \frac{8\pi^2 m}{\hbar^2} V_{0n} e^{i\mathbf{k}_0 \cdot \mathbf{r}_1}. \quad (44)$$

This equation may be solved in the same way as the equation (26) which appears in Born's approximation for elastic collisions, and we find

$$F_n \sim r_1^{-1} e^{i\mathbf{k}_n \cdot \mathbf{r}_1} f_n(\theta_1, \phi_1), \quad (45)$$

where

$$f_n(\theta_1, \phi_1) = \frac{2\pi m}{\hbar^2} \int V_{0n}(\mathbf{r}') e^{i(\mathbf{k}_0 - \mathbf{k}_n) \cdot \mathbf{r}} d\tau. \quad (46)$$

The differential cross-section, measured in terms of the ratio of the scattered to incident currents, is given by $|f_n(\theta)|^2 k_n/k$, not $|f_n(\theta)|^2$, because the elastically scattered electrons have a velocity k_n/k times that of the incident.

In this derivation we have neglected, in the expression (42) for Ψ , all excited states of the atom but the n th. However, it is clear that, to the approximation we are working, this neglect will have no effect on the excitation of the n th state.

The expression (39) for I_{0n} may be simplified by carrying out the integration over the coordinates of the incident electron.† This gives

$$I_{0n} = \frac{4\pi^2 m^2 \epsilon^4}{\hbar^4} \frac{k_n}{K^2} \left| \frac{4\pi}{K^2} \int \psi_0 \left(\sum_1^N e^{i(\mathbf{k}_0 - \mathbf{k}_n) \cdot \mathbf{r}_i} \right) \psi_n^* d\tau_1 \dots d\tau_N \right|^2, \quad (47)$$

where $K^2 = k^2 + k_n^2 - 2kk_n \cos \theta$. In many cases the transition concerned can be regarded as one involving a single electron only so that, henceforward, we shall drop the summation over the atomic electrons.

3.2. The cross-sections for excitation and ionization

We have for the cross-section Q_{0n} for excitation of the n th state

$$Q_{0n} = 2\pi \int I_{0n}(\theta) \sin \theta d\theta.$$

It is convenient to change the variable of integration from θ to K so that

$$Q_{0n} = \frac{2\pi}{kk_n} \int_{K_{\min}}^{K_{\max}} I_{0n}(K) K dK, \quad (48)$$

where $K_{\min} = k - k_n$, $K_{\max} = k + k_n$.

Since $k^2 = k_n^2 + (2m/\hbar^2)(E_n - E_0)$, we have, for collisions in which the energy transfer is small,

$$\begin{aligned} K_{\min} &= k - k_n \simeq (k^2 - k_n^2)/2k \\ &= (E_n - E_0)m/k\hbar^2, \end{aligned} \quad (49)$$

since

$$k + k_n \simeq 2k.$$

† Betho, *Ann. der Physik*, **5** (1930), 325.

An approximate expression may be found for Q_{0n} for these collisions.† The function I_{0n} falls off very steeply as K increases. This may be seen as follows.

We have
$$I_{0n}(K) = \frac{4m^2}{h^4} \frac{k_n}{k} \frac{\epsilon^4}{K^4} |\epsilon_n(K)|^2, \quad (50)$$

where
$$\epsilon_n(K) = \int \psi_0 e^{iKz} \psi_n^* d\tau. \quad (51)$$

The integral will obviously be very small when many oscillations of e^{iKz} occur within the range of the functions ψ_0, ψ_n , i.e. when

$$K \gg Z/a_0 = K_0, \quad (52)$$

Z being the effective nuclear charge in the ground state so that the radius of the ground-state orbit is a_0/Z . Alternatively since $Z^2\epsilon^2/2a_0$ is the ionization energy V_i of the normal atom, I_{0n} will be negligible when

$$K^2 \gg 2mV_i/\hbar^2 = K_0^2. \quad (53)$$

To evaluate $\epsilon_n(K)$ approximately we expand

$$e^{iKz} = 1 + iKz + \dots \quad (54)$$

Since $\int \psi_0 \psi_n^* d\tau = 0$, we have

$$\begin{aligned} \epsilon_n(K) &\simeq iK \int \psi_0 z \psi_n^* d\tau \\ &= iK z_{0n}, \text{ say.} \end{aligned} \quad (55)$$

This gives

$$I_{0n}(K) = \frac{4m^2}{h^4} \frac{k_n}{k} \frac{\epsilon^4}{K^2} |z_{0n}|^2, \quad (56)$$

an approximation certainly valid when $K < K_0$. For greater values of K , $I_{0n}(K)$ may be neglected so that we have, on substitution in (48),

$$\begin{aligned} Q_{0n} &\simeq \frac{8\pi m^2 \epsilon^4}{k^2 h^4} |z_{0n}|^2 \int_{K_{\min}}^{K_0} \frac{dK}{K} \\ &\simeq \frac{4\pi m^2 \epsilon^4}{k^2 h^4} |z_{0n}|^2 \log \frac{2mv^2}{E_n - E_0}, \end{aligned} \quad (57)$$

on insertion of the expressions (49) and (53) for $K_{\min}$ and K_0 respectively.

This shows that the cross-section falls off as $v^{-2} \log v$ at high velocities v of impact provided z_{0n} does not vanish. If the transition from the ground to the n th state is optically allowed this will be so but, if it is not, z_{0n} will vanish and it is necessary to proceed to the next term in (54), to give

$$\epsilon_n(K) \simeq K^2 (z^2)_{0n}$$

and

$$Q_{0n} \simeq \frac{2\pi m^3 \epsilon^4}{k^2 h^6} |(z^2)_{0n}|^2 |E_0|. \quad (58)$$

This differs from the result for the optically allowed transition in that the rate of decrease at high velocities is slightly faster, as v^{-2} instead of $v^{-2} \log v$.

† See Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. XI, § 3.

A corresponding expression may be found for the cross-section for ionization. We first consider ionization in which the wave number κ of the ejected electron lies between κ and $\kappa + d\kappa$, i.e. so that its energy lies between $\kappa^2\hbar^2/2m$ and

$$(\kappa^2 + 2\kappa d\kappa)\hbar^2/2m.$$

The corresponding cross-section $Q_{0\kappa} d\kappa$ is then found, by the same method as used above, to be given approximately by

$$Q_{0\kappa} d\kappa = \frac{4\pi m^2 \epsilon^4}{k^2 \hbar^4} |z_{0\kappa}|^2 \left(\log \frac{2mv^2}{E_0 - E_0'} \right) d\kappa. \quad (59)$$

The total cross-section for ionization, Q_i , is given by

$$Q_i = \int_0^{\kappa_{\max}} Q_{0\kappa} d\kappa.$$

This may be evaluated approximately, using (59), to give

$$Q_i = \frac{2\pi \epsilon^4}{mv^2} \frac{c}{|E_0'|} \log \frac{2mv^2}{C}, \quad (60)$$

where

$$c = \int |z_{0\kappa}|^2 d\kappa,$$

and C is a certain mean of $E_0 - E_0'$ which is of the order E_0 .

The ionization cross-section thus decreases with the velocity of the incident electron at the same rate as that for an optically allowed excitation.

These approximations are very convenient for impacts with small fractional energy loss but they are not correct when a considerable fraction of the incident energy is lost. Exact evaluation of the expressions for I_{0n} and Q_n must then be carried out.

3.3. *Electron exchange in inelastic collisions†*

According to the formula (47) the chance of exciting a level with a multiplicity different from that of the ground state would be zero for an atom in which spin-orbit coupling is negligible. Physically, this is due to the impossibility of changing the total electron spin in the impact; mathematically, to the different symmetry properties possessed by the functions if they correspond to states of different multiplicity so that the integral in (47) always vanishes. Thus, for the helium singlet states, ψ is symmetrical in the coordinates of the two electrons whereas for the triplet states it is antisymmetrical.

It must be remembered, however, that it is the total spin of the atom plus the incident electron which must be conserved, not necessarily that of the atom alone. The formula (47) requires conservation of the spin of the atomic levels because it ignores the possibility of electron exchange occurring in the collision.

† Oppenheimer, *Phys. Rev.* **32** (1928), 361; Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. VIII, § 4, Chap. XI, § 5.

Suppose that the total electron spin in the initial state of the atom is $s\hbar$, so that the multiplicity is $2s+1$. The spin of the incident electron is $\frac{1}{2}\hbar$, so that the total spin of the atom+incident electron is either $(s\pm\frac{1}{2})\hbar$. If a state of the atom with total spin $s'\hbar$ is excited the total spin will be $(s'\pm\frac{1}{2})\hbar$, so that, in order for this excitation to be possible without change of the total spin, $s'\pm\frac{1}{2}$ must fall within $s\pm\frac{1}{2}$, i.e. $s' = s-1, s$, or $s+1$. The multiplicity of the state can therefore change by ± 2 , but this may occur only if the spin direction of the outgoing electron is opposite to that of the incident—electron exchange must have taken place in the collision, for we are assuming that spin-orbit interaction is negligible so the spin of the incident electron cannot be reversed by the impact. Exchange can also occur between electrons with the same spin but in this case it will not be associated with a change of multiplicity.

These considerations need modification if spin-orbit coupling is not negligible. This will be so for heavy atoms such as mercury. Under these conditions the multiplet classification in terms of the total spin (L - S coupling) is no longer a good approximation. For a two-electron system such as the outer shell of mercury this means that certain triplet states include a singlet admixture and vice versa. The formula (47) will not give a vanishing cross-section for a singlet-triplet transition when this is so (see § 3.53)—either or both of the functions ψ_0, ψ_n will not be completely symmetric and antisymmetric respectively in the space coordinates of the two electrons.

It is possible to allow for electron exchange to a degree of accuracy comparable with Born's approximation. In the formula (46), $f_n(\theta)$ can be regarded as the amplitude contributed by direct scattering. It represents a cross mean of the interaction energy between the electron and the atom, averaged over the initial and final wave functions of the combined system. The wave functions are $\psi_0(r_2)e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1}$, $\psi_n(\mathbf{r}_2)e^{ik\mathbf{n} \cdot \mathbf{r}_1}$ respectively. We would expect that the corresponding amplitude $g_n(\theta)$ due to exchange should be given by a similar expression in which the initial wave function is as above but, in the final one, the electrons 1 and 2 are interchanged so that it becomes $\psi_n(\mathbf{r}_1)e^{ik\mathbf{n} \cdot \mathbf{r}_2}$.

This is indeed the case. For collisions of electrons with hydrogen atoms the exchange amplitude is given by†

$$g_n(\theta) = \frac{2\pi m \epsilon^2}{h^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \psi_0(r_2) \psi_n^*(r_1) e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1 - k\mathbf{n} \cdot \mathbf{r}_2} d\tau_1 d\tau_2. \quad (61)$$

In this case, however, it is to be noted that the contribution from the nuclear interaction ϵ^2/r_1 does not vanish. This must be regarded as a defect in the approximation.‡ Nevertheless, neglect of this term is not justifiable, as modifications in

† Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. VIII, § 4.1.

‡ Ibid., Chap. XI, § 5.1.

the formula which would eliminate it would also modify the contribution from the interelectronic interaction. Until a more satisfactory formula is available it is best to retain the nuclear interaction term. One further question occurs here. It is not clear whether this term should be taken as ϵ^2/r_1 or ϵ^2/r_2 . This difficulty does not arise if the wave functions ψ_0, ψ_n are exact solutions of the wave equation for the atom as both terms then give the same result.† If approximate solutions only are available for ψ_0 and ψ_n , this is no longer true. In this case there exists no means of deciding whether the prior, ϵ^2/r_1 , or post, ϵ^2/r_2 , interaction, or some mean between them, is the best to choose.

The total scattered amplitude is obtained by a linear combination of f and g determined by the number of electrons and multiplicities of the states involved. Thus for atomic hydrogen, in which there can be no change of multiplicity, $|f_n|^2$ in the expression for I_{0n} is replaced by

$$\frac{1}{2}|f_n + g_n|^2 + \frac{3}{2}|f_n - g_n|^2. \quad (62)$$

For helium, on the other hand, for which the ground state is a singlet, excitation can occur either to a singlet or triplet state. In the former case, in which no multiplicity change occurs $|f_n|^2$ is replaced by $|f_n - g_n|^2$ and in the latter, which can only arise from electron exchange, by $3|g_n|^2$. g_n is now given by

$$g_n(\theta) = \frac{2\pi m\epsilon^2}{h^2} \iiint \left(\frac{2}{r_1} - \frac{1}{r_{12}} - \frac{1}{r_{13}} \right) \psi_0(r_2, r_3) \psi_n^*(\mathbf{r}_1, \mathbf{r}_3) e^{i(\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}_1 - \mathbf{k}_n \cdot \mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (63)$$

Again, if ψ_0 and ψ_n are exact solutions of the helium wave equation, it is immaterial whether the interaction is taken as in (63) or replaced by one in which 1 and 2 are interchanged. This holds also if the Hartree self-consistent approximations (see § 2.3) to ψ_0 and ψ_n are used, provided the energy difference between the states is taken to be that given by the same approximation. For other approximations, such as those obtained by use of the variation method, or by the Hartree-Fock method, it is no longer true. This presents a serious difficulty in applying these formulae to atoms with many electrons and already leads to uncertainty for helium. This and other aspects of the approximate theory of electron exchange are further discussed in § 3.53.

For convenience of reference we shall refer to the approximation in which $g_n(\theta)$ is included in forms such as (63) as the Born-Oppenheimer approximation to distinguish it from the Born approximation in which $g_n(\theta)$ is ignored.

3.4. Theoretical limit to the magnitude of collision cross-sections

In view of the difficulty of obtaining accurate methods of calculating the cross-sections for inelastic collisions, it is important to have available any general formulae which enable an upper limit to be placed on the size of the cross-section. Although it is not possible to do this when the angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$ about the centre of force is not known to lie within fairly narrow limits, a definite limit may be obtained for the partial cross-section due to electrons with a definite angular momentum.

† Bates, Fundaminsky, and Massey, *Phil. Trans. Roy. Soc. A.* **243** (1950), 93.

Correspondence with classical theory indicates that such a limit is likely to exist.

The contribution dQ to the cross-section due to particles with angular momentum about the centre of force between J and $J+dJ$ is, as in (5),

$$dQ = 2\pi J dJ/m^2v^2,$$

where m is the mass and v the velocity of the electron. Allowing for quantization of angular momentum so that $J dJ \simeq (2l+1)\hbar$, we would expect this to be replaced in quantum theory by

$$q_l = \pi(2l+1)p(l)/k^2,$$

where $k = mv/\hbar$ and $p(l)$ is a probability factor ≥ 1 . This suggests that the maximum cross-section for electrons of angular momentum $\{l(l+1)\}^{1/2}\hbar$ should be $\pi(2l+1)/k^2$, but care must be taken to allow for the effect of edge diffraction.

A detailed formulation† of the problem in terms of the conservation of particles shows that the limits are as follows:

- (a) The maximum possible partial cross-section for all inelastic collisions is $\pi(2l+1)/k^2$.
- (b) When this maximum is obtained the partial cross-section for elastic collisions must also be $\pi(2l+1)/k^2$.
- (c) The maximum possible partial cross-section for all collisions is $4\pi(2l+1)/k^2$, in which case there are no inelastic collisions.

These limits are not useful when many partial cross-sections contribute. This is the case for direct excitation of atoms by electron impact. On the other hand, as will appear below, the exchange contribution, when it is at all large, only arises from incident electrons with one, or at most two, particular angular momenta. The limit $\pi(2l+1)/k^2$ provides an effective check in these cases and will be made use of in § 3.53.

3.5. Comparison of observed and theoretical cross-sections--the validity of Born's approximation‡

Information about the magnitudes of the cross-sections for the various inelastic collision processes involving electrons and atoms is required for the understanding of a number of physical phenomena. The theory of electric discharges in gases and its application to such practical problems as the design of light sources of specified quality, and of ion sources, depend on such knowledge. A full understanding of the spectrum of the polar aurora is likely to lead to much important information concerning

† See Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. VIII, § 1.

‡ Bates, Fundaminsky, Leech, and Massey, *Phil. Trans. Roy. Soc. A.* **243** (1950), 117.

the earth's upper atmosphere. Reliable information of the cross-sections for excitation of oxygen and nitrogen is required before such an understanding is possible.† In the solar corona excitation of highly ionized atoms such as Fe^{14} by electrons is a major source of the coronal emission.‡ A complete theory of the corona must await reliable information about the cross-sections for such collisions. Electronic excitation is also of primary importance in other astrophysical phenomena, as, for example, in the atmospheres of gaseous nebulae.§

Direct measurements of the cross-sections required in the elucidation of such phenomena as the above can rarely be made. It will already be apparent from Chap. II, §§ 4, 5, that in any case the measurement of absolute values of excitation cross-sections is very difficult. This difficulty is greatly enhanced when cross-sections for excitation of such systems as atomic oxygen or any ionized atoms are required. It is important therefore to have available theoretical methods for estimating the cross-sections for the various inelastic collision processes which can occur between electrons and atoms, neutral or ionized. As such methods must always be approximate it is further necessary to be able to assess the reliability of any theoretical predictions. We shall therefore discuss the comparison between the predictions based on the Born and Born-Oppenheimer approximations and the various observed results obtained in the manner described in Chap. II.

A useful indication of the range of validity of the approximation is obtained in this way, but there are still uncertainties which remain to be cleared up by further investigation.

3.51. Some general properties of inelastic cross-sections. Before proceeding to a detailed discussion we shall give first a number of general properties of inelastic cross-sections most of which are well established on both experimental and theoretical grounds and will be exemplified in §§ 3.52–3.55 below. They may be summarized as follows:

- (a) At electron energies very much greater than the threshold for the excitation, all inelastic cross-sections fall off with electron energy E . For optically allowed transitions this rate of fall is as $E^{-1} \log E$ (see § 3.2). For transitions which, while optically forbidden, do not involve any change of multiplicity the decrease is as E^{-1} (see § 3.2). It is very much more rapid for transitions involving change of multiplicity. (See Figs. 80, 82, 83, 84, 85.)

† Bates, Massey, and Pearse, *Report on the Emission Spectra of the Night Sky and Aurora*, Physical Society (1948), 97.

‡ Bondy, Hoyle, and Lyttleton, *M.N.R.A.S.* **107** (1947), 184.

§ See, for example, Rosseland, *Theoretical Astrophysics*, Clarendon Press (1936).

- (b) Cross-sections for transitions involving change of multiplicity are only large, if at all, at electron energies in a narrow range close to the threshold. In other words, the exchange amplitude g_n is only appreciable in this energy range. (See Figs. 82, 83, 84.)
- (c) At electron energies for which electron exchange is negligible, the cross-sections for optically allowed transitions are considerably larger than for any others. (See Table IV.)
- (d) Less definite information is available concerning the relative cross-section in the energy range in which electron exchange is important, but there is some indication that excitations in which there is no change of azimuthal quantum number of the atomic electron are the strongest in this case. (See Table IV.)
- (e) In the energy range in which exchange is unimportant the angular distribution of scattered electrons falls very steeply with increasing angle. (See Fig. 79.)
- (f) When exchange is predominant the angular distribution is much more uniform.

It will be seen that the differential and total cross-sections depend very much on whether the transition concerned is optically allowed, optically forbidden but involving no change of multiplicity, or optically forbidden involving a change of multiplicity. Because of this it is convenient to discuss the comparison between the predictions of the two approximations and the observed data under three heads, according as the transition concerned falls in one or other of the three categories.

In detailed application of the approximations to different atoms it is necessary to employ approximate wave functions for the atomic electrons. This will introduce errors quite apart from those due to failure of the approximations themselves. In order to avoid confusion arising in this way we shall devote most attention to comparison of observed and theoretical data for helium, an atom for which good approximate wave functions are available. Supplementary evidence from more complex atoms will also be considered but with less weight attached.

Consideration will also be given to the rather meagre data obtained for atomic hydrogen, but in this case the practical difficulties of measurement are so great that the theoretical simplicity is outweighed by the experimental complication.

3.52. *Optically allowed transitions.* The optically allowed transitions about which evidence is available may be classified under four heads:

- (a) Excitation of p -states from s -states. This occurs in the excitation of the 1P terms of helium from the ground 1S state as well as in

other atoms with outer shells of two electrons. Of these mercury has been the most thoroughly investigated experimentally.

- (b) Ionization of atoms with outer s electrons. This is similar to (a).
- (c) Excitation of s - and d -states from p -states. This arises in the excitation of rare gas atoms other than helium.
- (d) Ionization of atoms with outer p -electrons. As (c).
- (e) Inner shell ionization of atoms. This may include transitions similar to (b) (ionization of K and L_I shells) or (d) (ionization of L_{II} and L_{III} shells).

3.521. *Excitation of p -states from s -states.* The most definite evidence concerning inelastic collisions of this type comes from the study of the optical excitation of helium.

In Chap. II, § 4, the principles and technique of such measurements have been described and, in Tables III and IV of that chapter, the cross-sections derived from Lees's and from Thieme's observations for helium are given. It will be seen that the agreement between the two sets of data as far as the absolute magnitudes of the cross-sections are concerned is not good enough to provide any useful check on the theoretical calculations. In Table IV, therefore, the absolute values of the cross-sections for excitation of the 3^1P level by electrons of 200 eV energy has been normalized to unity and all other cross-sections are given relative to this. It will be seen that the two sets of observations agree rather better as regards relative magnitudes of the cross-section, whether compared at different energies for the same excitation or for different excitations.

We first consider the comparison of these observed results with theoretical calculations using Born's approximation in which electron exchange is neglected. Such calculations have been carried out for helium by Massey and Mohr† and more recently by Bates, Fundaminsky, Leech, and Massey.‡ To compare with the observed data the theoretical values are given in Table IV in terms of that for the excitation of the 3^1P level by 200 eV electrons. It will be seen that for the excitation of the 3^1P level there is good agreement between the calculated and observed results except at the lowest electron energy (60 eV) at which the calculated value is over 80 per cent. greater than the observed. For both the 4^1P level and the 5^1P level, for which only one set of observations is available, the agreement is poor as far as the absolute value relative to that for 3^1P is concerned, but the energy variation shows the same features. It is probable also that the observed data relative to 3^1P are

† *Proc. Roy. Soc. A*, **140** (1933), 613.

‡ *Loc. cit.*

TABLE IV
Comparison of Calculated and Observed† Relative Cross-sections for Excitation of Helium by Electron Impact

Electron energy	Level excited	60 eV			100 eV			200 eV			400 eV		
		Observed†		Calculated	Observed		Calculated	Observed		Calculated	Observed		Calculated
		Thieme†	Lees†		Thieme	Lees		Thieme	Lees		Thieme	Lees	
2P	2P	..	1.01†	..	1.22†	1.21†	5.01	1.00†	..	3.29	..	0.68†	2.24
3P	3P	0.228	0.212	0.74	0.269	0.225	1.48	0.213	0.191	1.00	0.114	0.136	0.62
4P	4P	..	0.035	0.39	..	0.045	0.57	..	0.033	0.22	..	0.025	0.29
5P	5P	..	..	0.67	..	..	0.30	..	..	0.22	..	..	0.16
2S	2S	..	..	0.15	..	..	0.41	..	..	0.23	..	..	0.12
3S	3S	..	..	..	..	..	0.09	..	..	0.06	..	..	0.03
4S	4S	0.0069†	..	..	0.0048†	..	..	0.0031†	..	..	0.0020†	..	..
5S	5S	0.0045	0.0014	..	0.0033	0.00105	..	0.0020	0.0.78	..	0.0012	..	..
6S	6S	0.0023	0.0.84	..	0.00145	0.0.67	..	0.0.74	0.0.35	..	0.0.51	..	..
3D	3D	..	..	..	..	..	0.024	..	..	0.013	..	..	..
4D	4D	0.0087†	0.0038†	0.020	0.0062†	0.0034†	0.013	0.0036†	0.0024†	0.0072	0.0035†	0.0016†	0.027
5D	5D	0.0032	0.0023	0.011	0.0040	0.0024	0.0073	0.0021	0.0017	0.0040	0.00122	0.0011	0.0037
6D	6D	0.0028	..	..	0.0020	..	..	0.00115	..	..	0.0.70	..	0.0021
4F	4F	..	..	..	..	..	0.0.19	..	..	0.0.95	..	..	..
2F	2F	..	..	..	..	..	0.035	..	..	0.0033	..	..	0.0.48
3F	3F	0.170†	0.0046†	0.03	0.057†	0.0011†	0.0037	0.0156†	0.0010	0.0.8	0.0069†	0.0.8	0.0.33
4F	4F	..	..	..	..	..	0.0020	..	..	0.0.8	..	..	0.0.21
2S	2S	..	..	0.03	..	..	0.013	..	..	0.003	..	..	0.0.29
4S	4S	0.0011†	0.0013	..	0.0005†	0.0.49	..	0.0.7†	..	..	0.0.1†	..	..
5S	5S	0.0028	0.0.55	..	0.0010	0.0.17	..	0.0.34	..	..	0.0.14	..	..
6S	6S	0.0.98	..	..	0.0.34	..	..	0.0.3	..	..	..	..	..
3D	3D	0.0047†	..	0.0.7	0.0029†	..	0.0.15	0.0016†	..	0.0.21	0.0012†	..	0.0.28
4D	4D	0.0032	0.0028	..	0.0018	0.0026	..	0.0.9	0.0020	..	0.0.5	0.0013	..

† The figures given as 'observed values' are those estimated from the measurements of Lees and Thieme on absolute intensity of a line for which the upper energy state is the level specified. These intensities are then multiplied by a calculated factor to allow for the effect of all other transitions from that level (see Chap. II, § 4.31).

† Values marked with the asterisk have been corrected for population of the state from higher energy levels (cascade correction). The values not so marked have not been so corrected. In most cases, however, the cascade correction is small (see Chap. II, Table IV).

unreliable, for the theory also predicts correctly the ratio of the cross-sections for the 2^1P and 3^1P excitations for 83 eV electrons observed by Mohr and Nicoll (see Chap. II, § 7.32).

Reference to Fig. 80 (a) shows more clearly how the theoretical values begin to deviate from the observed values as the electron energy falls.

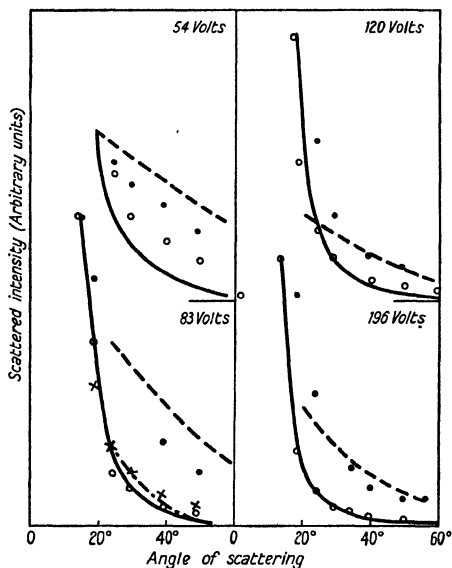


FIG. 79. Comparison of observed and calculated angular distributions of electrons scattered in helium after exciting the 2^1P and 3^1P levels respectively, and after elastic scattering.

Elastic: --- (theor.), . . (exp.). Inelastic: 2^1P ——— (theor.), ○ ○ (exp.); 3^1P - - - (theor.), × × (exp.).

Further evidence concerning the detailed validity of the theory may be obtained from a comparison of calculated angular distributions for electrons scattered by helium atoms after excitation of the 2^1P and 3^1P levels with the distributions observed by Mohr and Nicoll (see Chap. II, § 7.32). Such a comparison is illustrated in Fig. 79. It will be seen that good agreement prevails until the electron energy falls below 80 eV. Below these energies a tendency for the observed intensity to exceed the calculated at the larger angles becomes gradually more marked. Since the theory predicts too large a cross-section at low electron energies, the discrepancy at large angles must be more than compensated by one in the opposite sense (the theoretical value too large) at small angles. No evidence is at present available to confirm and amplify

this conclusion, though it would be of considerable value in determining which is the most important defect of the theory.

Some evidence concerning relative magnitudes of differential cross-sections is also available from experiments designed to measure the relative intensity of inelastic collisions involving small deviations (see Chap. II, § 8). As the angular range covered in such observations is not very definite it is not possible to make a truly quantitative test of the theory. However, the measurements of Whiddington and Woodrooff[†] of the relative cross-sections for small angle inelastic collisions involving respectively the excitation of 2^1P , 3^1P , and 4^1P levels by 100 eV electrons agree quite well with those calculated for zero angle scattering (observed ratios 10:2.4:0.9, calculated 10:2.35:0.87). Similarly, for the 2^1P excitation,[‡] the variation with electron energy of the cross-section for small angle deviations is at least not in contradiction with the theory, although in this case the ratio is very sensitive to the angular range concerned (see Table VII and Chap. II, Fig. 57).

The general nature of the divergence between theory and observation illustrated in Fig. 80 (a) is exhibited also by the excitation of the $3P$ state of sodium from the ground state. The onset energy for this process is 2.1 eV. For electrons of energy 11 eV the cross-section calculated by Fundaminsky[§] is about three times larger than that observed by Christhof,^{||} but at higher energies the theoretical and observed cross-sections are in closer agreement (see Fig. 80 (b)).

On the other hand, the excitation function for the three quantum levels of atomic hydrogen measured by Ornstein and Lindeman (see Chap. II, § 4.33 and Fig. 27) agrees quite well over the observed electron energy range (from 16 eV to 70 eV) with that calculated using Born's approximation. In view of this rather unexpected result it would be very desirable for further experiments to be carried out for atomic hydrogen.

The only other atoms for which measurements of total cross-sections for optically allowed excitations from s -states have been made are mercury, cadmium, and zinc. In all these the situation is complicated by the existence of j - j rather than L - S coupling, so the resonance transition is actually from a 1S to a 3P_1 state. For this reason it is best to consider the comparison between theory and experiment in § 3.53. At electron energies considerably greater than the excitation threshold the behaviour

[†] *Phil. Mag.* **20** (1935), 1109.

[‡] Womer, *Phys. Rev.* **45** (1934), 689; van Atta, *ibid.* **38** (1936), 876; Whiddington and Taylor, *Proc. Roy. Soc. A*, **145** (1934), 465.

[§] Bates, Fundaminsky, Leech, and Massey, *loc. cit.*

^{||} *Ann. der Physik*, **23** (1935), 51.

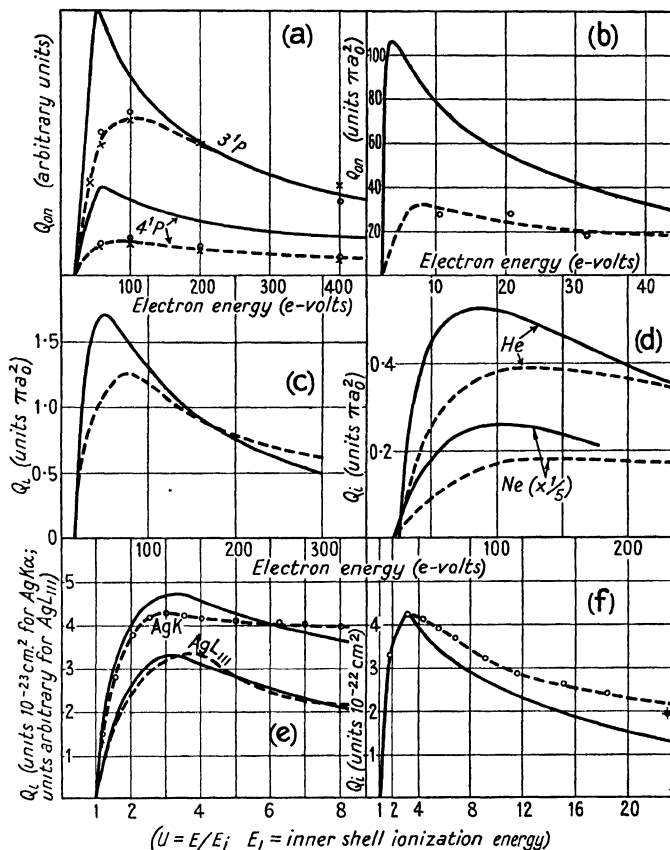


FIG. 80. Comparison of observed and calculated cross-sections for excitation.

— calculated; --- (experimental).

(a) Optically allowed transitions in helium. $\circ$ Thiemé; $\times$ Lees.

(b) Optically allowed transitions in sodium. $\circ$ Christhof (absolute values); --- Haft (relative values).

(c) Ionization of H_2 .

(d) Ionization of He and Ne.

(e) Inner-shell ionization for Ag K showing absolute cross-sections determined by Webster and collaborators and for Ag L_{III} showing relative cross-sections determined by McCue.

(f) Inner-shell ionization for Ni K. $\bullet$ cross-section calculated allowing for relativity.

is exactly similar to that for a $1S$ to $1P$ transition and it is therefore of interest to note here the observations of Mohr and Nicoll on the angular distribution of electrons scattered in mercury vapour after producing

the $6^1S-6^3P_1$ transition. At small angles the very steep angular distribution predicted by Born's approximation was found, but at large angles the scattering exhibited maxima and minima rather similar to those observed in the elastic scattering (see Chap. II, Fig. 54). This failure of Born's approximation to predict the angular distribution at large angles was also noted for helium (see p. 149), for which it is clear although less spectacular. It is a different type of failure from that responsible for the overestimated cross-sections at low electron energies (see § 3.6 below).

For incident electrons with energies close to the threshold it is no longer possible to neglect exchange. Although for optically allowed transitions the exchange integral g has the properties discussed in § 3.53, it is relatively so small as to be unlikely to produce a second maximum in the cross-section close to the excitation potential. Its inclusion increases the theoretical cross-section, thereby making the disagreement with experiment more marked at low energies.

3.522. Ionization of atoms from outer s -states. The evidence from measurements of ionization cross-sections is of particular interest in that reliable absolute values which could not be obtained with accuracy for excitation cross-sections are available. Once more the most important results are derived from the helium data. We shall again begin by comparing the observed results with values derived from Born's approximation, neglecting exchange.

The ionization cross-section for helium, calculated by Massey and Mohr,[†] is compared with the observed values (see Chap. II, § 2) in Fig. 80 (*d*). It will be seen that an exactly similar situation exists as for the $s-p$ excitation. At electron energies greater than 300 eV the absolute values are in good agreement, but at lower energies the theoretical predictions become gradually too great. The same conclusion results from a comparison of observed and calculated ionization cross-sections for molecular hydrogen (see Fig. 80 (*c*)). As in this case the molecule is treated as if it were composed of independent atoms, apart from the different ionization potential, too much weight should perhaps not be given to it. Nevertheless it reinforces the general conclusions.

The analysis of the angular distributions of electrons scattered after suffering different energy losses in producing ionization is somewhat more complicated than for the excitation of discrete states. After ionization two free electrons are produced. Although it is impossible to distinguish observationally between the scattered electron and the one ejected from the atom, for purposes of theoretical comparison the faster

[†] *Proc. Roy. Soc. A*, **140** (1933), 613.

of the two electrons may be regarded as the scattered one, an identification which is more accurate the greater the proportion of energy carried away by that electron. Mohr and Nicoll† (Chap. II, § 7.23) have observed a number of angular distributions of electrons of various energies resulting from ionizing collisions. Fig. 81 illustrates a comparison of

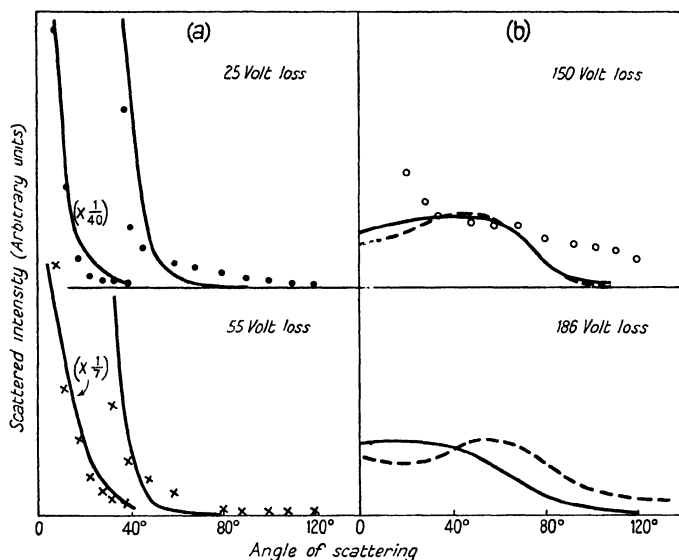


FIG. 81. Comparison of observed and calculated angular distributions of electrons resulting from ionizing collisions in helium, for electrons having an incident energy of 200 eV.

- (a) Electrons which have a large fraction of the incident energy (scattered electrons).
 (b) Electrons which have a small fraction of the incident energy (ejected electrons).

— calculated distribution for scattered electrons; --- calculated distribution for ejected electrons of the same energy.

their observations for He with the calculations of Massey and Mohr,‡ the identification of the electrons as scattered or ejected being as above. The angular distributions of the scattered electrons are very similar to those for the excitation of the 2^1P level and the agreement with the theory is much the same. For sufficiently slow incident electrons Born's approximation gives too little scattering at large angles. The energy below which this becomes perceptible is higher the greater the energy loss concerned. For the ejected electrons the distribution is much more nearly uniform in agreement with theoretical expectation.

† Ibid. A, **144** (1934), 596.

‡ Ibid. A, **140** (1933), 613.

No calculations have been carried out for the ionization of electrons from outer *s*-states of other atoms, but it is noteworthy that, for mercury, the angular distributions of the scattered electrons, of definite energy, resulting from ionizing collisions also behave similarly to those for excitation of the 6^3P_1 level (see Chap. II, Fig. 54). The distributions for the ejected electrons resemble the corresponding ones for helium, as would be expected theoretically.

No evidence is available concerning the importance of electron exchange in ionizing collisions. It has been suggested that some or all of the so-called 'ultra-ionization' potentials, observed for such atoms as mercury (Chap. II, § 2.5), may really be due to ionizing collisions in which electron exchange occurs. These would possess the sharp excitation function characteristic of such transitions. Superposed on the smooth ionization function they might give the observed irregularities.†

3.523. *Excitation of *s*- and *d*-states from *p*-states—Ionization of atoms with outer *p*-electrons.* The only atom with outer *p*-electrons for which detailed calculations for comparison with observation have been made is neon.‡ Although for an atom as complex as neon it is difficult to be sure that the wave functions used (Hartree self-consistent field functions) are sufficiently accurate, the comparison leads to conclusions in every way similar to those arrived at in §§ 3.521, 3.522. An example of the comparison of observed and calculated total cross-sections is given in Fig. 80 (*d*). Study of the angular distributions also supports the above conclusions.

3.524. *Inner-shell ionization.* The method of measurement of cross-sections for the ionization of inner shells has been discussed in Chap. II, § 3. As described there special efforts have been made to obtain accurate values of the cross-sections for *K*-shell ionization of silver and nickel and the absolute values of these cross-sections are known with an uncertainty of less than 5 per cent.

Calculations have been carried out for these and a number of other cases, using Born's approximation, by Burhop§, who used screened hydrogenic wave functions. Since most of the contribution to the matrix elements determining the cross-section comes from the neighbourhood of the *K* shell, the use of such wave functions is amply justified in this case. Comparison with the observed data reveals the rather

† Another possible explanation of the 'ultra-ionization' potentials is that they arise from double excitation of the mercury atom, the total excitation energy being greater than the ionization energy. The atom is then ionized in a subsequent radiationless transition (auto-ionization).

‡ Ledsham, in course of publication.

§ *Proc. Camb. Phil. Soc.* **36** (1940), 43.

surprising result that good agreement persists down to the lowest electron energies.

Fig. 80(e) shows that the theoretical and observed absolute values agree very well over the entire range from E_0 to about $5E_0$, where E_0 is the ionization energy. This is in sharp contrast to the ionization of outer electrons, but is largely confirmed from comparison of observed and calculated relative cross-sections for ionization of the L_{II} and L_{III} shells of gold† and the L_{III} shell of silver (see Figs. 80(e), 80(f)). At energies above $5E_0$ the rate of decrease of the observed cross-section with increase of energy is less than that calculated. However, at these energies relativistic effects would be expected to become important.

An approximate estimate of the magnitude of the relativistic effect‡ in the case of Ni K -ionization by 200 keV electrons has been made by using the relativistic relation between energy and momentum but otherwise keeping the wave functions occurring in the calculation of (47) unchanged. The effect is to increase the calculated cross-section by just about the amount required to bring it into agreement with the observed values. The relativistic correction for the Ni K -ionization cross-section is shown in Fig. 80(e). No calculations are, however, available of the cross-section using the more correct Dirac-Møller§ relativistic theory of the interaction of two electrons.

Similar approximate relativistic calculations have been made for the K -shell ionization of mercury by electrons of energy up to 800 keV. The relativistic correction factor to the theoretical cross-section at this energy comes out at about 2.7 and the resultant calculated cross-section is practically constant, or even increasing slightly in the range between 300 and 800 keV. No experimental evidence is available in this high energy range.

3.525. Summary for optically allowed transitions. The evidence we have discussed in §§ 3.521–4 above may be summarized as follows:

- (a) Born's approximation is valid in all cases when the electron energy is greater than $7E_0$, where E_0 is the excitation or ionization energy.
- (b) In the same energy range the angular distribution of the scattered and of the ejected electrons (in ionizing collisions) is also given correctly by Born's approximation.
- (c) At lower energies Born's approximation increasingly overestimates the cross-section in all cases of excitation or ionization

† The calculations were actually carried out for Hg L_{II} and Hg L_{III} shells, but no significant differences in the shape of the curves would be expected for gold.

‡ We are greatly indebted to Dr. A. Fundaminsky for making these calculations.

§ See *Theory of Atomic Collisions* (2nd edition), Chap. XV.

of outer shell electrons. The maximum error is of the order 2. Usually the inclusion of exchange (Born–Oppenheimer approximation) makes the discrepancy even larger.

- (d) At these energies deviations of the angular distribution from that given by Born's approximation are apparent at large angles of scattering. For heavier atoms maxima and minima appear which resemble those which occur in the corresponding elastic scattering. These deviations are distinct from those manifest in (c) which must, from their sense, arise from deviations at small angles.
- (e) For the ionization of inner shells, Born's approximation gives good results at all energies, when appropriate allowance is made for relativistic effects.

In considering the significance of these results it must be pointed out that in all the cases we have considered the effect of electron exchange is unimportant. Its inclusion leads if anything to slightly bigger discrepancies.

3.53. Transitions involving change of multiplicity. In these cases, as explained in § 3.3, excitation can only take place through electron exchange if the coupling between electron spin and orbital motion can be ignored, i.e. if L – S coupling conditions prevail.† For heavy atoms the coupling is more nearly of j – j type and direct excitation can occur to certain levels. This possibility will be further discussed below in connexion with the excitation of mercury atoms. We shall first suppose that excitation can only take place via electron exchange and examine whether the exchange transition amplitude of (63) is capable of giving a good description of the cross-section for the process.

A very important difference exists between the direct and exchange amplitudes f_n and g_n . Whereas the former is made up of small contributions from electrons with a wide range of quantized angular momenta about the atomic nucleus, in the latter a major contribution comes from collisions in which the incident electron possesses a very small angular momentum. Thus, for excitation of neutral atoms, if the transition is one in which the azimuthal quantum number of the active orbit changes from l to l' ; then the contributions from incident electrons with angular momenta greater than $(l+l')\hbar/2$ will certainly make a negligible contribution to the cross-section where it is at all large. This has two important consequences, one affecting the theory, the other the method of experiment.

† For a discussion of coupling between electronic angular momenta see White, *Introduction to Atomic Spectra* (McGraw-Hill).

‡ Or more correctly $\{(l+l')(l+l'+1)\}^{1/2}\hbar$.

The number of angular momenta which contribute appreciably to the cross-section is reflected in the form of the angular distribution of the scattered electrons. With many angular momenta, all giving small contributions, the angular distribution falls very steeply as the angle of scattering increases. This we have already seen in § 3.52 to be the case for optically allowed transitions. On the other hand, with the major contribution coming from very few and small angular momenta the angular distribution is very much more nearly uniform. It follows that misleading information about the relative magnitudes of the cross-sections for excitation of optically allowed and intercombination transitions will be obtained from experiments in which only electrons which have suffered small deviations in producing the excitation are studied (see Chap. II, § 8, and Chap. IV, § 5.2).

The theoretical importance arises from the possibility of applying the limit test of § 3.4 to check the validity of the approximate form for g_n . If the approximate expression (47) for f_n overestimates the cross-section, it is unlikely that even then the error, being spread over many angular momenta, will be so large that the contribution from any particular angular momentum $\{l(l+1)\}^{1/2}\hbar$ will exceed the maximum possible value $\pi(2l+1)/k^2$. With g_n , however, it is quite likely that over-estimation may lead to a prediction, coming from a single angular momentum $\{l(l+1)\}^{1/2}\hbar$, in excess of the upper limit. In fact, as we shall see, several cases exist in which this does occur.

According to the approximate expression for g_n , the strongest exchange transitions are those for which the azimuthal quantum number of the active orbit does not change. Thus, for helium, the strongest predicted exchange transitions are those to the n^3S terms. For these the situation is complicated by the necessity of using very accurate atomic wave functions to eliminate ambiguity as to whether the post or prior interaction should be used in (61) to give the better approximation (see § 3.3). Thus, for the strongest intercombination transition in helium, 1^1S-2^3S , the most recent calculations give a maximum cross-section, at 23 eV incident energy, of $0.2\pi a_0^2$ with the prior interaction and $0.65\pi a_0^2$ with the post interaction.† In this case it is only electrons with vanishing incident angular momentum which give an appreciable contribution. The maximum possible inelastic cross-section for 23 eV electrons is therefore $0.55\pi a_0^2$, so it is quite certain that in this case the post interaction, with the particular wave functions assumed, gives too large a cross-section. This does not provide evidence that the post interaction

† Bates, Fundaminsky, Leech, and Massey, loc. cit.

gives a good approximation. All that can be said is that no satisfactory theoretical estimate of the cross-section for this case exists. For other transitions in helium the limit test provides no information as the calculated cross-sections do not exceed the limit.

Calculations carried out for two other atoms fail to pass the test and in each case these are concerned with transitions in which the azimuthal quantum number of the active orbit does not change in the transition. Thus, Yamanouchi, Inui, and Amemiya† calculated the cross-sections for excitation of the lowest 1D and 1S terms of atomic oxygen from the ground 3P state. These terms arise from the same configuration as the ground state, so no change of azimuthal quantum number is involved. The major contributions to the cross-sections they obtain come from incident electrons with angular momentum $2\hbar$. The maximum values they give are many times greater than the upper limit for such electrons so no real meaning may be attached to them. A rather less marked but still quite definite failure occurs in the calculations, by Hebb and Menzel,‡ of the cross-section for similar excitation of the ion O^{++} . In this case the approximate theoretical values exceed the limit by a factor of about 2. A somewhat different case, in which the simple approximation gives an impossibly large cross-section over a certain energy range, is the excitation of the $^3\Sigma_u$ state of H_2 from the ground $^1\Sigma_g$ state (see Chap. IV, § 5.2). In the limit of widely separated atoms this corresponds to a transition with no change of azimuthal quantum number in either atom, but in the opposite limit of the united atom it corresponds to the transition 1^1S-2^3P in helium which involves a change of one unit in this number. It seems likely that, for purely atomic transitions, the approximate formulae for g_n (either with post or prior interaction) do not exceed the allowable upper limit when there is a change of azimuthal quantum number involved, but insufficient calculations have been carried out up to the present to establish this certainty.

Although we can be sure that the approximate formulae for g_n give incorrect results when these are greater than the allowable maximum, it remains to be considered under what circumstances, if any, they are satisfactory when they do not exceed this limit. It is also important to decide whether it is permissible to assume that, when the limit is exceeded, the true value of the cross-section does approach the limit—in other words, is there any correlation between an unduly large cross-section as given by evaluation of g_n and a large value of the actual cross-

† *Proc. Phys.-Math. Soc., Japan*, **22** (1940), 847.

‡ *Ap. J.* **92** (1940), 408.

section? An appeal to observation can throw light on these questions. It is only in this way that an answer to the first can be obtained, but we can hope also for further theoretical guidance eventually about the second.

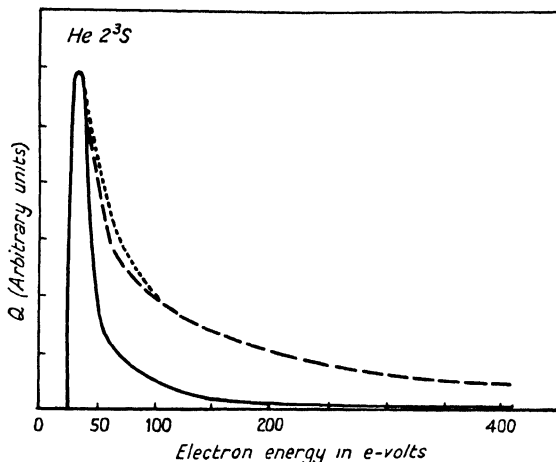


FIG. 82. Observed and calculated excitation cross-sections for the He 2^3S metastable level.

— calculated; ---- observed by Woudenberg and Milatz; observed by Dorrestein.

Unfortunately the available experimental results (see Chap. II, § 4) are hardly ever quantitative and provide little information about the absolute values of cross-sections for intercombination transitions. Furthermore, one of the atoms most thoroughly studied, mercury, is so complex that theoretical calculations involve the use of rather rough wave functions and the analysis is complicated by the strong departure from L - S coupling. As will be seen, no final conclusions can yet be drawn about many aspects of the questions.

The excitation function of the 2^3S metastable level of helium has been obtained by Woudenberg and Milatz† (Chap. II, § 4.44) and by Dorrestein‡ (Chap. II, § 5.4). Their results are compared in Fig. 82 with that calculated (assuming the prior interaction which gives a maximum cross-section less than the allowable limit). Qualitative agreement in the form of the variation of the cross-section with electron energy exists and this is a general feature. Both theory and experiment show that, for a transition brought about exclusively by electron exchange, the

† *Physica*, **8** (1941), 871.

‡ *Ibid.* **9** (1942), 447.

cross-section rises to a maximum at an energy very close to the excitation limit and then falls off rapidly as the energy increases. It would appear, however, that the theoretical cross-section falls off too rapidly at increasing electron energies. On the other hand, indirect evidence favouring the theory is provided from the measurements of Lees and of

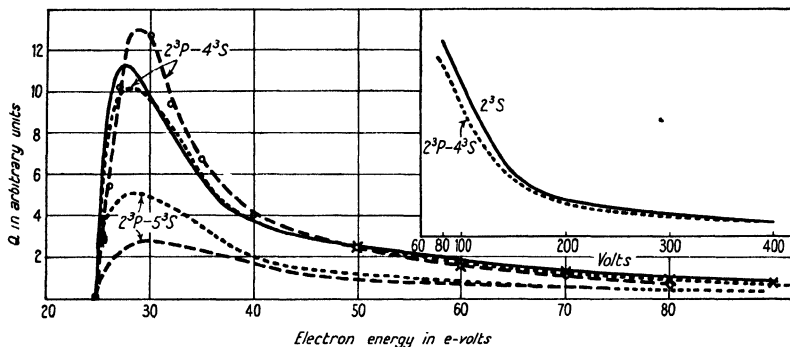


FIG. 83. Observed excitation curves for He 4^3S and 5^3S states compared with that calculated for the 2^3S state using the Born-Oppenheimer approximation.
 ——— calculated; - - - observed Lees; observed Thieme.

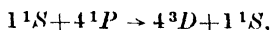
Thieme for the excitation functions of the 4^3S and 5^3S levels of helium (see Table IV). The rate of decrease of the cross-section with energy found by both authors for the 4^3S level is much the same and agrees quite closely with that calculated for the 2^3S excitation† over a wide energy range. This is illustrated in Fig. 83, in which the 4^3S curve of Thieme is normalized so as to agree with the calculated curve for electrons of 30 eV energy. Assuming the theory gives the correct result at this energy, it would appear to give about 10 per cent. too large a value at the maximum.

Evidence concerning the absolute magnitude of the cross-section for the excitation of the 2^3S level and for the position of the maximum is provided from the measurements of Maier-Leibnitz (Chap. II, § 5.2). According to these the cross-section at the maximum, which occurs at less than 0.5 eV above the threshold, is $0.055\pi a_0^2$. The theoretical maximum (with the prior interaction) occurs at 3.2 eV above the threshold and is over 3 times larger. Woudenberg and Milatz locate the maximum at rather more nearly the theoretical electron energy but the position in this regard is still not clear. The fact that Maier-Leibnitz found that the 2^3S excitation is strongest at low electron energies is in qualitative agreement with the theoretical prediction that exchange

† Massey and Mohr, *Proc. Roy. Soc. A*, **140** (1933), 613.

transitions involving no change of azimuthal quantum number are the strongest.

No similar comparison can be carried out for excitation of the 3^3D and 4^3D levels. This is because, in experiments such as those of Lees and of Thieme, the levels are populated to a considerable extent by processes other than direct impact excitation. Reactions such as



occur at a rate sufficient to mask direct impact production of 4^3D atoms unless the energy of the exciting electron beam is quite close to the excitation energy of the state concerned (see Chap. VII, § 8.2). Radiative transitions from the 4^3D to 3^3P states then mask also the direct production of excited 3^3P atoms.

A great deal of experimental work has been devoted to the study of the excitation of mercury by electron impact (Chap. II, §§ 4.42, 4.5). An interesting theoretical consequence of the failure of $L-S$ coupling in the mercury atom (see § 3.3) was first pointed out by Penney† and is in agreement with observation. In the mercury atom the 6^3P_1 level is not of purely triplet character but, due to spin-orbit interaction, contains an admixture of 6^1P_1 . On the other hand, the 6^3P_0 and 6^3P_2 are pure triplet levels. The excitation function for the latter two levels from the ground 6^1S state should therefore be of the usual intercombination type, falling rapidly after the maximum is reached at an energy close to the excitation energy. For the 6^3P_1 level the behaviour at the higher energies should, because of the 6^1P admixture, resemble that for an optically allowed transition, i.e. the excitation function should fall off as $E^{-1} \log E$. That this is so may be seen by reference to Fig. 84, in which the observed cross-section for the excitation of the 6^3P_1 levels is shown. It will also be seen that the theoretical results given by Penney, using quite crude wave functions for the mercury atom, give good agreement with the observed energy variation. The agreement in absolute magnitude is also surprisingly good. Penney predicts that for 6^3P_1 the maximum (see Chap. II, § 4.42) cross-section should be about 2×10^{-16} cm.² Bricout‡ obtained a value 2×10^{-16} cm.² by optical measurement. Arnot and Baines§ obtained 4.1×10^{-16} cm.² for the sum of the cross-sections for excitation of the three states $6^3P_{0,1,2}$, giving about 1.4×10^{-16} cm.² for the 6^3P_1 level alone.

(Good agreement has been claimed for other transitions in the mercury

† *Phys. Rev.* **39** (1932), 467.

‡ *J. Phys. Rad.* **9** (1928), 88.

§ *Proc. Roy. Soc. A*, **151** (1935), 256.

atom. Thus Yavorsky† has calculated cross-sections for the transitions 6^1S-7^3S , 6^3P-7^3S , $6^3P_1-6^3P_2$ in all of which electron exchange is important. For the first he claims fair agreement with the experiment of Hanle and Schaffernicht‡ (Chap. II, § 4.42), and for the others, which involve further excitation of excited mercury atoms, with the values derived by Fabrikant§ from a study of discharges in mercury vapour (see Chap. II, § 4.53).

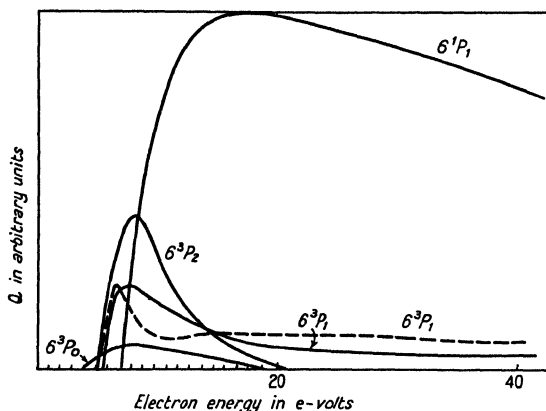


FIG. 84. Excitation functions for the $6^3P_{0,1,2}$ states of mercury compared with that for the 6^1P_1 state showing the effect of spin-orbit coupling for the 6^3P_1 state. The broken curve (---) illustrates the observed excitation function for the Hg line $\lambda 2537$ originating in the 6^3P_1 level.

It is difficult to decide how much weight should be given to the apparently marked success of the approximate formula as applied to the excitation of mercury atoms for which the approximate wave functions which must be used are so crude. The situation would be clearer if theoretical values obtained by use of both post and prior interactions were available. They may well be quite different, in which case the agreement for mercury would have to be regarded as fortuitous. On the other hand, no contradiction with the allowable limit arises in any of these cases. They at least suggest that, when there is no such contradiction and no ambiguity due to the post and prior interactions giving different results, the approximate formula for g_n gives results of semi-quantitative accuracy at all electron energies. This must be regarded for the present as an important hypothesis to verify or disprove by further investigation.

† C.R. (Doklady) U.R.S.S. **48** (1945), 175.

‡ Ann. der Physik, **6** (1930), 905.

§ C.R. (Doklady) U.R.S.S. **16** (1937), 263.

Summarizing the evidence concerning the excitation of intercombination transitions we may say that:

- (a) The evidence is not as definite as for optically allowed transitions.
- (b) The theory gives qualitatively the correct variation of the cross-section with electron energy and
- (c) probably, the correct absolute values at energies of the order four times the excitation energy.
- (d) The strongest intercombination transitions, according to the theory, are those for which there is no change in azimuthal quantum number. For these the approximate formula (63) gives too large a maximum cross-section in certain cases, but there is evidence that in some of these cases the actual cross-sections are comparatively large.

3.54. Optically forbidden transitions involving no change in multiplicity. In the preceding section we were concerned with transitions determined by the exchange amplitude g_n only, while in § 3.52 the effect of g_n could be ignored over most of the range of electron energy. We now consider transitions in which the amplitude g_n may be ignored at high energies but may be dominant at energies close to the excitation energy. These involve no change of multiplicity, but are optically forbidden because of violation of orbital angular momentum selection rules. They include, for example, such transitions as $1^1S \rightarrow n^1S$, $1^1S \rightarrow n^1D$, in helium.

The only detailed evidence concerning these transitions comes from the excitation of helium by electron impact. Referring to Table IV and Fig. 85 (a) it will be seen that there is quite good agreement over the entire incident energy range from 60 to 400 eV between theory and experiment for the excitation of the 4^1D and 5^1D levels of helium. This agreement applies not only to the variation with electron energy but also to the relative magnitude of the cross-section as compared with that for excitation of the 3^1P level.

For excitation of the 1^1S series the situation is not so clear as far as relative magnitudes are concerned, but the variation with incident electron energy seems to agree quite well, as may be seen from Fig. 85 (b). It is true that in this figure the calculated curve is for 3^1S and the observed curves are for 4^1S and 5^1S , but as both of the latter have the same shape it is probable that this does not depend on the total quantum number of the term.

At energies greater than 60 eV the contribution from g_n is negligible. For $s \rightarrow s$ transitions particularly it becomes important at energies close to the threshold. This is because the exchange amplitude is greatest

when there is no change of azimuthal quantum number and also because f_n is relatively small for s - s transitions (see Table VIII). The maximum cross-section should therefore occur at energies close to the threshold and be approximately $\frac{1}{3}$ of the maximum for the corresponding 3S state.

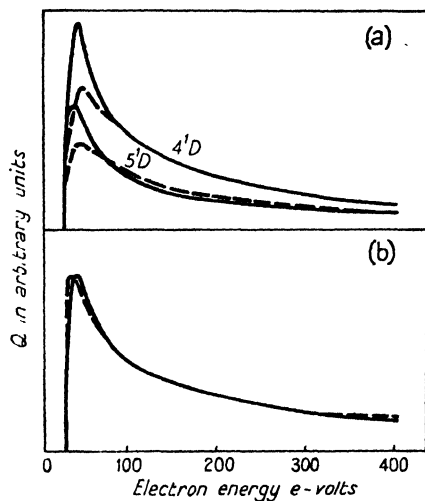


Fig. 85. Comparison of observed and calculated excitation functions for the 1S and 1D levels of helium.

- (a) 4^1D and 5^1D . Observed ----; calculated (Born's approx.) ———.
 (b) 4^1S and 5^1S . Observed ----; 3^1S calculated (Born's approx.) ———.

Evidence in support of this is provided from Maier-Leibnitz's observations (Chap. II, Fig. 34), in which the cross-section for the 2^1S excitation has a sharp maximum of about $0.027\pi a_0^2$, at an energy within 1 eV of the threshold. After falling to about half this value at an energy about 1 eV greater, there are indications that the cross-section begins to increase again. This might correspond to the contribution from direct excitation which has a theoretical maximum, at an energy of about 35 eV, of about $0.018\pi a_0^2$. On the other hand, the observed 'exchange' maximum is much sharper than theory would predict, just as for the 2^3S level.

There are no observational data available concerning the behaviour of D excitation cross-sections near the threshold. According to the Born-Oppenheimer approximation it is doubtful whether the exchange effect could produce a sharp maximum near the threshold in these cases as it appears to do for the S excitations.

The real behaviour of excitation cross-sections near the threshold is clearly not yet known with certainty. The optical and electrical methods

are far from consistent, either among themselves or with each other. Further experiments, in which electrons with well-defined energy are used, need to be carried out to clarify this question. It is important for many applications to have a definite answer.

The evidence concerning the excitation of forbidden transitions involving no change of multiplicity may be summarized as follows.

- (a) The theory is satisfactory for energies $> E_0$, say. E_0 is smaller the more strongly the transition is forbidden (roughly, as judged from the excitation of helium, E_0 is equal to $2\frac{1}{2}$ times the threshold for s - d and $1\frac{1}{2}$ times for s - s).
- (b) In this energy range the cross-sections are much smaller than for excitation of the corresponding optically allowed levels.
- (c) The behaviour of the cross-sections near the excitation threshold is not clear, but tentatively it appears that
- (d) exchange is probably important at energies within a few electron volts of the threshold for s - s transitions (and other transitions involving no change of azimuthal quantum number). It may give rise to a sharp second maximum so that, in the low energy range, an s - s excitation may be stronger than the corresponding s - p or s - d transitions when all involve no change of multiplicity.

3.55. Polarization of radiation excited by electron impact. It has been pointed out in Chap. II, § 6, that marked polarization effects, related to the direction of incidence of the electron beam, are observed for mercury lines excited by electron impact. Qualitatively this effect can be understood in terms of the relative probability that an electron will excite a particular magnetic substate of the upper state from which the line originates.† Penney† has calculated the polarization to be expected for the $\lambda 2537$ line of mercury for which the upper state is the 6^3P_1 level. He used the Born-Oppenheimer approximation (including exchange) to estimate the relative probability of excitation of the different substates of the 6^3P_1 level and, in determining the polarization, made allowance for nuclear spin. His results disagree completely with observation, giving a polarization of the wrong sign. This failure extends over a wide electron energy range and is rather surprising in view of the evidence in § 3.52, which suggests that the approximation gives good results when the electron energy is greater than 7 times that of the excitation threshold. It also runs counter to the admittedly rather surprising agreement obtained at considerably lower energies for excitation of mercury. In view of this it is very desirable that the theory should be re-examined to trace the source of the discrepancy.

3.6. *The physical significance of the departures from Born's approximation—interaction of elastic and inelastic scattering*

Although it is not possible to give a completely satisfactory theory when Born's approximation is invalid, it is nevertheless possible to

† See, for example, Skinner, *Proc. Roy. Soc. A*, **112** (1926), 642.

‡ *Proc. Nat. Acad. Sci.* **18** (1932), 231.

provide a qualitative explanation† of the observed departures from its predictions and even to give a semi-quantitative theory of certain aspects of these.

The basic assumption on which Born's approximation is derived is that there is only a very weak interaction between an incident electron and an atom so that the chance of a transition occurring in the atom during an impact is very small and the chance of two such transitions may be neglected. If, however, the incident electron is moving slowly so that it spends a considerable time in the neighbourhood of an atom, the chance of a transition may be so high that the possibility of two transitions occurring during the collision cannot be ignored. We may now see that, when this possibility is taken into account, a qualitative description of the observed deviations from the simple approximation may be obtained for the strongest transitions—those which are optically allowed.

If we allow for the possibility of 'double' collisions of an electron with a single atom, the following possibilities arise:

- (a) excitation of state B from the ground state A may be followed by the inverse deactivation from B back to A ;
- (b) after suffering an energy loss in producing excitation of the state B the electron may be diffracted by the static atomic field;
- (c) after diffraction an electron may give energy to the atom, leaving it finally in the state B .

The effect of a double process such as (a) is to lead to a reduction of the net inelastic scattered amplitude and an increase of the elastically scattered. Since in a collision involving energy loss by excitation of an allowed transition an electron suffers, on the average, only a slight deviation, the effect should be apparent in an increase in the intensity of elastic scattering at small angles above that predicted when elastic scattering is ignored.

In this way it is possible to account, both for the failure of Born's approximation in predicting too large a cross-section for excitation of optically allowed transitions at electron energies less than a few times the threshold, and for the excess of small angle elastic scattering in hydrogen and helium observed even for electrons with energies as high as 350 eV. Both effects should become more marked as the electron energy is decreased, as observed. Massey and Mohr‡ have verified that the explana-

† See Massey and Mohr, *Proc. Roy. Soc. A*, **140** (1933), 613; Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. XI, § 6.

‡ *Proc. Roy. Soc. A*, **146** (1934), 880.

tion of the excess small angle scattering is quantitatively valid. They evaluated the second approximation for the elastic scattering in Born's theory. This allows essentially for double collisions of the type (a).

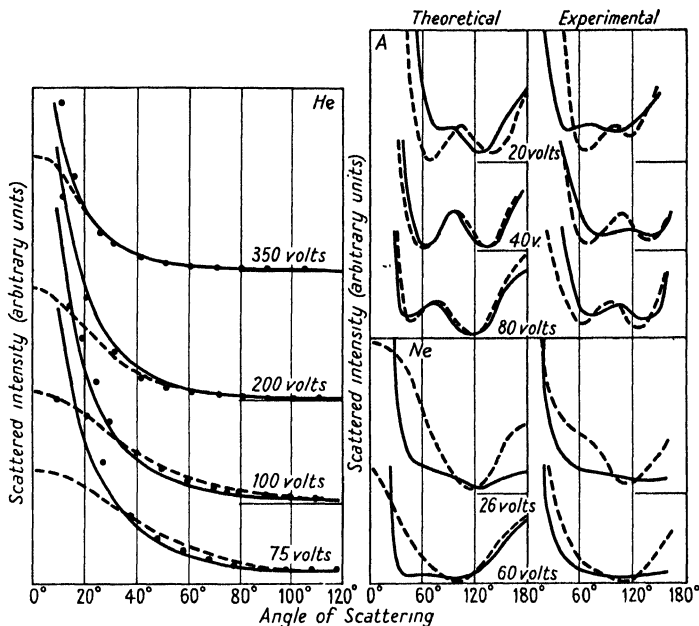


FIG. 86.

FIG. 87.

FIG. 86. Comparison of observed and calculated angular distributions for elastic scattering of electrons in He.

- calculated using Born's first approximation.
- · - · - calculated including Born's second approximation.
- observed values (see Chap. II, § 7.31).

The ordinates are adjusted so that calculated and observed results agree at 60° for 350-volt electrons.

FIG. 87. Comparison of observed and calculated angular distributions for electrons of different incident energies scattered elastically and inelastically in argon and neon.

- elastic; — inelastic.

Fig. 86 illustrates the satisfactory agreement they obtained with the observed excess scattering† in helium.

Although it has not so far proved possible to verify that the explanation of the inelastic cross-section anomaly is also quantitatively correct, it seems very probable that it is indeed an effect of back coupling between

† Arnot, *ibid.* A, **133** (1931), 615; Hughes, McMillen, and Webb, *Phys. Rev.* **41** (1932), 154.

inelastic and elastic scattering. Indirect evidence in support of this is afforded from a comparison of observed† and calculated total collision cross-section for electrons in helium. Referring to Table V it will be seen that, although, as we have emphasized in § 3.52, the theory gives too large a value for the sum of the inelastic cross-sections in the energy range tabulated, the total cross-section is given quite closely except at low energies where the calculated value becomes too small. This shows that the theory underestimates the elastic cross-section, as it must if our explanation is valid.

TABLE V

Comparison of Calculated and Observed Values for the sum of the Elastic and Inelastic (excluding Ionization) Cross-sections (in units πa_0^2) in He

<i>Electron energy</i>	<i>60 eV</i>	<i>100 eV</i>	<i>200 eV</i>	<i>400 eV</i>
Calculated	0.79	0.55	0.32	0.18
Observed	1.13	0.67	0.31	..

The 'observed' values are obtained by deducting the ionization cross-sections measured by Smith‡ from the total cross-section measured by Normand.§

If exchange is ignored the probability of an optically forbidden transition occurring during a collision is much smaller than for allowed transitions. We would therefore expect that double collisions of type (a) would be much less important in these cases. This does appear to be so. Thus for excitation of the *S* and *D* states of helium from the ground state Born's approximation, ignoring exchange, has a greater range of validity than for excitation of *P* states. At energies very close to the threshold the contribution from exchange becomes important, particularly for *s-s* or *p-p* transitions. It has been pointed out that in the latter cases the simple theory often gives an impossibly large value for the cross-section due to exchange. Here again double collisions are presumably effective in reducing the ultimate inelastically scattered amplitude considerably below the value given by the first approximation.

It is of interest also to compare the reduction in the inelastic cross-section when the time of collision is large with the much more marked effects occurring in inelastic collisions between particles of atomic dimensions. In such cases a transition may be energetically possible

† Ramsauer, *Ann. der Physik*, **66** (1921), 546; Brüche, *ibid.* **84** (1927), 279; Ramsauer and Kollath, *ibid.* **3** (1929), 536; Normand, *Phys. Rev.* **35** (1930), 1217.

‡ *Ibid.* **36** (1930), 1293.

§ *Ibid.* **35** (1930), 1217.

even though the velocity of relative motion of the colliding system is much less than the orbital velocity of the electron involved in the transition. The cross-section in such cases is very small, the conditions being nearly adiabatic. Such extreme conditions, which are discussed in Chap. VII, §§ 7, 8, and Chap. VIII, § 5.21, never arise in excitation by electrons, but the qualitative nature of the effect is the same.

The double processes (b) and (c) will superpose, on the steeply falling angular distribution of inelastically scattered electrons, maxima and minima characteristic of diffraction. Provided the incident electron energy is considerably in excess of the threshold, the wave-length of an electron will not be greatly changed when the electron loses energy in exciting the atom. Furthermore, an electron suffers no important deviation in producing an optically allowed transition. The diffraction pattern should therefore closely resemble that for the elastic scattering. This resemblance should become progressively less marked as the electron energy decreases. These effects are striking features of the observations (see § 7.32 and Figs. 53, 54 of Chap. II and § 3.521 above).

A semi-quantitative verification of this explanation has been given by Massey and Mohr,[†] who calculated the angular distributions for the scattering of electrons after exciting the resonance levels of neon and of argon respectively, allowing for the double processes (b) and (c). This they were able to do by replacing the plane wave functions $e^{ik\mathbf{n}_0 \cdot \mathbf{r}}$, $e^{-ik\mathbf{n} \cdot \mathbf{r}}$ in (39) by the so-called distorted wave functions $F_i(r, \theta)$, $F_f(r, \pi - \Theta)$. These are solutions of the wave equation for motion of electrons of energy $kh^2/2m$, $k_n^2 h^2/2m$ respectively in the static field of the atom in its normal and excited state. They have the asymptotic form for large r

$$F_i(r, \theta) \sim e^{ik\mathbf{n}_0 \cdot \mathbf{r}} + r^{-1} e^{ikr} f_i(\theta, \phi),$$

$$F_f(r, \pi - \Theta) \sim e^{-ik\mathbf{n} \cdot \mathbf{r}} + r^{-1} e^{ikr} f_f(\theta, \phi),$$

where the outgoing spherical waves arise from diffraction by the average atomic field in which the electron is moving. f_i and f_f are thus given by an expression of the form (19).

The agreement between these calculations and the experimental distribution is illustrated in Fig. 87 and is sufficiently close to leave little doubt of the correctness of the explanation. It is of interest to note that the inclusion of the effects (b) and (c) leads to an increase of the inelastic cross-section, an effect which must be more than compensated by the effect (a).

[†] Loc. cit.

3.7. Further description of available theoretical data

We have already had occasion in § 3.5 to refer to a number of theoretical calculations of cross-sections, but these have been selected with regard to the examination of the validity of Born's approximation. We now describe briefly the remaining available data and their probable ranges of validity in the light of the discussion of §§ 3.5 and 3.6.

3.71. Atomic hydrogen. Cross-sections for the following excitations have been calculated,† using Born's approximation (exchange neglected): from the ground $1s$ state to the $2s$, $2p$, $3s$, $3p$, $3d$ levels, and also from the $2p$ state to the $3s$, $3p$, and $3d$ states. The cross-section for ionization‡ has also been calculated to the same approximation.

The results are given in Table VI. While these may be too large at lower energies, Born's approximation probably gives sufficient accuracy for electrons of energy greater than seven times the excitation potential.

Extensive calculations have also been carried out with the Born-Oppenheimer approximation (exchange included), but in view of the doubtful accuracy of this approximation in the energy range near the threshold where exchange is important it has not been thought worth while to tabulate these results.

3.72. Single and double excitation of helium. Table VII gives differential and total cross-sections calculated§ for the excitation of different states of helium by electrons with energy of 100, 200, and 400 eV for which Born's approximation is likely to give sufficiently accurate results.

Values are also given for the excitation of a number of triplet states. These have been calculated§ using the Born-Oppenheimer approximation which is also likely to be reliable in the energy range concerned.

It will be noted that cross-sections for excitation of doubly excited states are included. These were calculated by Massey and Mohr|| in order to provide further evidence concerning the identification of the energy losses at 59.25 and 62.27 eV found by Priestley and Whiddington†† for electrons in helium. It appears from the calculations that the identification should be with the respective excitation of the $(2s2p)^1P$ and $(3s2p)^1P$ levels. The observed ratio of the scattered intensity at 10° of electrons which have excited the $(2s2p)^1P$ and 3^1P levels is of the

† Elsassor, *Zeits. f. Phys.* **45** (1927), 522; Bethe, *Ann. der Physik*, **5** (1930), 325; Goldstein, *Ann. de Physique*, **19** (1933), 305.

‡ Massey and Mohr, *Proc. Roy. Soc. A*, **140** (1933), 613.

§ *Ibid.*; Bates, Fundaminsky, Leech, and Massey, *Phil. Trans. Roy. Soc. A*, **243** (1950), 117.

|| *Proc. Camb. Phil. Soc.* **31** (1935), 604.

†† See Chap. II, § 8.3.

TABLE VII

Differential ($I_n(\theta) d\Omega$) and Total (Q_n) Cross-sections for Excitation of Various Levels of Helium by Electron Impact, calculated using the Born-Oppenheimer Approximation

Level	Electron energy (eV)	$I_n(\theta)$ in units a_0^2						Q_n in units πa_0^2
		0°	5°	10°	20°	30°	40°	
2^1S	100	0.126	0.120	0.103	0.049	0.0200	0.0 ₂ 63	0.0 ₂ 87
	200	0.155	0.126	0.087	0.024	0.0039	0.0 ₃ 7	0.0 ₂ 49
	400	0.166	0.120	0.087	0.005	0.0004	0.0 ₄ 3	0.0 ₂ 25
3^1S	100	..	..	..	..	..	..	0.0 ₂ 17
	200	..	..	..	..	..	..	0.0 ₂ 12
	400	..	..	..	..	..	..	0.0 ₃ 7
2^1P	100	7.8	4.4	1.78	0.32	0.056	0.013	0.107
	200	17.7	4.5	0.99	0.068	0.0 ₃ 88	0.0 ₃ 7	0.069
	400	39	2.6	0.33	0.009	0.0 ₃	0.0 ₄ 2	0.047
3^1P	100	1.84	1.20	0.45	0.103	0.021	0.0 ₂ 43	0.031
	200	4.5	1.33	0.24	0.027	0.0025	0.0 ₂ 28	0.021
	400	9.7	0.81	0.084	0.0035	0.0 ₃ 14	0.0 ₅ 8	0.013
4^1P	100	0.68	0.46	0.215	0.043	0.0 ₂ 92	0.0 ₂ 20	0.012
	200	1.71	0.52	0.131	0.011	0.0 ₂ 12	0.0 ₃ 13	0.0 ₂ 86
	400	3.70	0.33	0.048	0.0 ₁ 5	0.0 ₄ 6	0.0 ₅ 4	0.0 ₂ 61
5^1P	100	0.36	0.245	0.115	0.0235	0.0 ₂ 50	0.0 ₂ 10	0.0 ₂ 63
	200	0.91	0.278	0.070	0.0 ₂ 59	0.0 ₃ 57	0.0 ₂ 62	0.0 ₂ 46
	400	2.06	0.177	0.026	0.0 ₂ 8	0.0 ₄ 29	0.0 ₅ 18	0.0 ₃ 34
3^1D	100	0.0109	0.0098	0.0 ₂ 70	0.0 ₂ 28	0.0 ₃ 7	0.0 ₃ 14	0.0 ₃ 50
	200	0.0132	0.0106	0.0 ₂ 52	0.0 ₃ 86	0.0 ₄ 8	0.0 ₅ 7	0.0 ₃ 28
	400	0.0142	0.0094	0.0 ₂ 23	0.0 ₃ 11	0.0 ₅ 3	0.0 ₆ 1	0.0 ₃ 15
4^1D	100	0.0 ₂ 55	0.0 ₂ 51	0.0 ₂ 39	0.0 ₃ 15	0.0 ₃ 39	0.0 ₄ 8	0.0 ₃ 29
	200	0.0 ₂ 67	0.0 ₂ 55	0.0 ₂ 32	0.0 ₃ 48	0.0 ₄ 46	0.0 ₅ 41	0.0 ₃ 15
	400	0.0 ₂ 74	0.0 ₂ 49	0.0 ₃ 16	0.0 ₄ 63	0.0 ₅ 18	0.0 ₇ 8	0.0 ₄ 79
5^1D	100	0.0 ₂ 31	0.0 ₂ 28	0.0 ₂ 21	0.0 ₃ 87	0.0 ₃ 23	0.0 ₄ 49	0.0 ₃ 153
	200	0.0 ₂ 37	0.0 ₂ 31	0.0 ₂ 18	0.0 ₃ 28	0.0 ₄ 27	0.0 ₅ 24	0.0 ₄ 85
	400	0.0 ₂ 40	0.0 ₂ 28	0.0 ₃ 97	0.0 ₄ 47	0.0 ₅ 11	0.0 ₇ 45	0.0 ₄ 45
4^1F	100	0.0 ₄ 218	0.0 ₂ 270	0.0 ₃ 357	0.0 ₂ 267	0.0 ₅ 88	0.0 ₅ 20	0.0 ₅ 388
	200	0.0 ₁ 130	0.0 ₄ 288	0.0 ₃ 396	0.0 ₄ 108	0.0 ₆ 102	0.0 ₇ 74	0.0 ₆ 102
	400	0.0 ₅ 69	0.0 ₄ 370	0.0 ₄ 300	0.0 ₅ 142	0.0 ₇ 31	0.0 ₉ 94	0.0 ₈ 102
2^3P	100	0.0 ₂ 26	0.0 ₂ 25	0.0 ₂ 23	0.0 ₃ 17	0.0 ₃ 9	0.0 ₃ 4	0.0 ₃ 72
	200	0.0 ₃ 67	0.0 ₃ 59	0.0 ₃ 49	0.0 ₃ 23	0.0 ₄ 7	0.0 ₄ 1	0.0 ₄ 69
	400	..	..	..	..	..	..	0.0 ₅ 7
3^3P	100	0.0 ₃ 40	0.0 ₃ 38	0.0 ₃ 34	0.0 ₃ 24	0.0 ₃ 14	0.0 ₄ 7	0.0 ₃ 12
	200	0.0 ₄ 80	0.0 ₄ 76	0.0 ₄ 67	0.0 ₄ 40	0.0 ₄ 17	0.0 ₅ 5	0.0 ₄ 17
	400	..	..	..	..	..	..	0.0 ₅ 2
4^3P	100	0.0 ₃ 19	0.0 ₃ 104	0.0 ₄ 99	0.0 ₄ 75	0.0 ₄ 47	0.0 ₄ 25	0.0 ₄ 43
	200	0.0 ₄ 20	0.0 ₄ 19	0.0 ₄ 17	0.0 ₄ 11	0.0 ₅ 5	0.0 ₅ 2	0.0 ₅ 52
	400	..	..	..	..	..	..	0.06

TABLE VII (*cont.*)

Level	Electron energy (eV)	$I_n(\theta)$ in units a_0^2						Q_n in units πa_0^2
		0°	5°	10°	20°	30°	40°	
3^3D	100	..	..	..	..	..	..	0.0 ₆ 32
	200	..	..	..	..	..	..	0.0 ₆ 44
	400	..	..	..	..	..	..	0.0 ₇ 6
2^3S	100	..	..	..	..	..	..	0.0 ₃ 27
	200	..	..	..	..	..	..	0.0 ₇ 6
	400	..	..	..	..	..	..	0.0 ₄ 2
$(2s\ 2p)^1P$	200	0.041	0.030	0.0162	0.0 ₃ 39	0.0 ₃ 9	..	0.0 ₅ 06
	400	0.087	0.038	0.0114	0.0 ₃ 10	0.0 ₃ 1	..	0.0 ₅ 73
$(2s\ 3p)^1P$	200	0.0 ₃ 31	0.0 ₂ 23	0.0 ₃ 12	0.0 ₃ 26	0.0 ₄ 5	..	0.0 ₆ 68
	400	0.0 ₆ 65	0.0 ₂ 30	0.0 ₃ 8	0.0 ₄ 8	0.0 ₅ 5	..	0.0 ₄ 53
$(3s\ 2p)^1P$	200	0.042	0.029	0.0131	0.0 ₂ 18	0.0 ₃ 2	..	0.0 ₅ 53
	400	0.105	0.039	0.0 ₂ 82	0.0 ₃ 3	0.0 ₄ 1	..	0.0 ₄ 54

same order of magnitude as the calculated. There is evidence also that the angular distribution of electrons scattered after producing double excitation is rather less steep than for single excitation, as given by the theory. On the whole the evidence favours the interpretation of the energy losses as arising from double excitation even though the lifetime of these states towards auto-ionization is very short.†

3.73. Ionization of helium. The calculated total cross-section for ionization of helium has already been discussed in § 3.522 and illustrated in Fig. 80 (*d*). Calculated angular distributions for scattered and for ejected electrons are given in Fig. 81. It is also of interest to calculate the energy distribution of the ejected electrons. This is given in Fig. 88 for a number of incident energies, again employing Born's approximation without inclusion of exchange. Although the observed absolute magnitude of the cross-section is considerably smaller than given by the theory for the lower energy incident electrons (below 150 eV), it is likely that the calculated energy distribution is approximately correct in shape.

Referring to Chap. II, Fig. 55, it will be noted that there is a feature of the observed angular distributions of electrons of definite energy, scattered in ionizing collisions with light atoms, which we have not yet attempted to explain. This is the occurrence of a maximum which becomes less prominent as the energy of the incident electron decreases, in contrast to the diffraction effects already discussed. Its position depends only on the energies of the incident and outgoing electrons and not on the nature of the gas. Thus the maximum which appears at about

† Kiang, Ma, and Wu, *Chinese Journ. Physics*, **2** (1936), 117; Wu, *Phys. Rev.* **58** (1940), 1114.

40° for electrons of 200 eV incident energy which have lost 75 eV in ionizing hydrogen appears rather less clearly under the same conditions for helium.

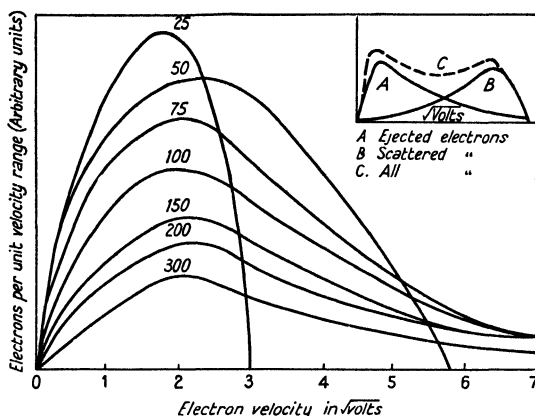


FIG. 88. Calculated energy distribution of electrons ejected in ionizing collisions of electrons with He atoms. The numbers marked on the curves refer to the voltages of the incident electrons.

The explanation of this effect was given by Mohr and Nicoll.[†] If the atomic nucleus were absent and the collisions were between two free electrons, the conservation of momentum would ensure a definite angle of scattering for an electron of given final energy. Thus if E_i is the incident energy, E_f the final energy, and E_0 the ionization energy, we would have for the angle of scattering θ ,

$$\cos \theta = (E_f + \frac{1}{2}E_0)/(E_i E_f)^{\frac{1}{2}}. \quad (64)$$

The presence of the atomic nucleus and the remaining atomic electrons obscures this effect to an extent which decreases with increase of the incident energy and decrease in atomic number. Mohr and Nicoll showed that the simple formula (64) does give the correct position of the maximum for hydrogen and also for the less definite maxima observed in other gases.

No calculations have been carried out for double ionization of helium.

3.74. Excitation of O and O⁺⁺. The calculations of Hebb and Menzel[‡] for the excitation of the transitions $^3P_0-^3P_1$, $^3P_0-^3P_2$, $^3P_0-^1D_2$, $^3P_0-^1S_0$ in O⁺⁺ and of Yamanouchi, Inui, and Amemiya[§] for the corresponding transitions in O have already been discussed in § 3.53, where it was

[†] *Proc. Roy. Soc. A*, **144** (1934), 596.

[‡] *Ap. J.* **92** (1940), 408.

[§] *Proc. Phys.-Math. Soc. Japan*, **22** (1940), 847.

pointed out that the maximum values they give exceed the permissible upper limit.

3.75. Excitation and ionization of neon, sodium, and mercury. Fundaminsky† has calculated cross-sections for transitions in which a p electron is excited to an s , p , and d orbital, using Born's approximation without exchange. The association of his results with actual transitions in neon is complicated by the fact that in this atom j - j coupling provides a better approximation than L - S coupling to the term values of all but the lowest states.

The ionization of neon has been studied in detail, using Born's approximation, without inclusion of exchange, by Ledsham.‡ His results for the total cross-section are illustrated in Fig. 80 (d).

Fundaminsky† has calculated cross-sections for the $3s$ - $3p$, $3s$ - $4s$, and $3s$ - $4p$ transitions for sodium, again without inclusion of exchange. These have been discussed in §§ 3.521 and 3.54. For mercury the transitions 6^1S - $6^3P_{0,1,2}$, § 6^1S_0 - 6^1P_1 ,|| 6^1S - 7^3S ,|| 6^3P - 7^3S ,|| 6^3P_1 - 6^3P_2 || have all been calculated and the comparison with observed excitation cross-sections has been discussed in §§ 3.521, 3.53.

3.76. Superelastic collisions of electrons in mercury. Experiments on superelastic collisions between electrons and metastable mercury atoms in the 6^3P_0 state have been described in Chap. II, §§ 4.53, 5.3. In these collisions the mercury atoms return to their ground 6^1S_0 state. Calculated cross-sections for the reverse transition from 6^1S_0 to 6^3P_0 have been described in § 3.53. From equation (50) it is seen that

$$Q_{n0}/Q_{0n} = k^2/k_n^2,$$

where Q_{n0} , Q_{0n} refer to the cross-sections for superelastic and inelastic collisions involving the states 0, n and kh , $k_n h$ are the momenta of the faster and slower electrons respectively. Applying this to superelastic collisions in mercury the calculated cross-section for de-excitation of the 6^3P_0 state by electrons of energy 2.8 eV is about 2×10^{-16} cm.² compared with the estimated value of 7×10^{-18} cm.² from the experiments of Latysheff and Leipunsky.†† Also the cross-section would be expected to increase indefinitely at low energies and not pass through a maximum value as observed by them. As pointed out in Chap. II, § 5.3, however, it appears likely that the measured cross-section was greatly under-estimated, so that this cannot be regarded as a definite disagreement with theory. In support of this view the values for this process deduced by Mohler‡‡ from Killian's§§ discharge data in mercury are 5.2×10^{-16} cm.² for electrons of mean energy 2.37 eV and 6.6×10^{-16} cm.² for electrons of mean energy 1.71 eV. These values are in much better accord with those expected on theoretical grounds.

3.77. Single and double inner-shell ionization. Calculations which have been carried out for single ionization of inner shells have been described in § 3.524.

R. D. Richtmyer||| has used Born's approximation to calculate the cross-section for the double inner-shell ionization of potassium in which

† Bates, Fundaminsky, Leech, and Massey, *Phil. Trans. Roy. Soc. A*, **243** (1950), 117.

‡ Thesis, London, (1951).

§ Ponney, *Phys. Rev.* **39** (1932), 467.

|| Yavorsky, *C.R. (Doklady) U.R.S.S.* **48** (1945), 175.

†† *Zeits. f. Phys.* **65** (1930), 111.

‡‡ Bureau of Standards, *J. Res.* **9** (1932), 493.

§§ *Phys. Rev.* **35** (1930), 1238.

||| *Ibid.* **49** (1936), 1.

electrons are ejected from a K and an L level, an effect which leads to emission of satellite lines (see Chap. II, § 3.4). In this way he estimated that the intensity of the $K\alpha$ satellites should be about 2 per cent. of that of the parent $K\alpha$ lines as compared with the measured relative intensity of 3 per cent. He showed further that the relative intensity should be

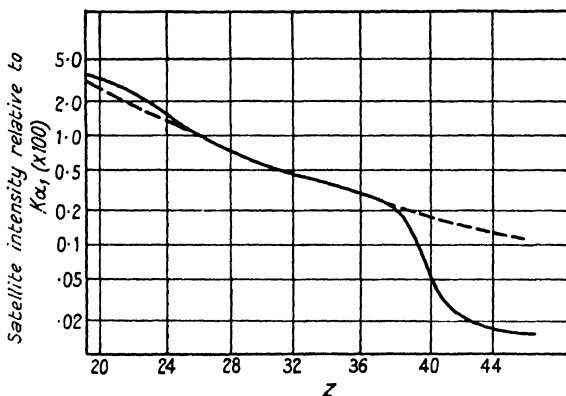


FIG. 89. Comparison of observed and calculated intensities of $K\alpha$ satellites for different atomic numbers.

— — — observed; - - - calculated.

approximately proportional to Z_{eff}^{-3} , where Z_{eff} is the effective atomic number in the neighbourhood of the L shell. Fig. 89 shows a comparison of the theoretical variation with the observations of Parratt† and of Shaw and Parratt.‡ Good agreement exists for atomic numbers below 40. At higher atomic numbers the observed satellite intensity becomes much too small.

3.8. Relative probabilities of different types of collision

In Table VIII the calculated relative probabilities of different types of collision of electrons with hydrogen atoms are given over an energy range from 100 to 10^4 eV throughout most of which Born's approximation is valid. For heavier atoms the relative importance of elastic scattering will be greater as this tends to increase as Z^2 , where Z is the atomic number, whereas the inelastic collision cross-sections increase more nearly as Z .

3.9. Angular distribution of the aggregate of all inelastically scattered electrons

In such experiments as those of Mohr and Nicoll (Chap. II, § 7.32) the angular distribution of electrons which have been scattered in producing

† *Phys. Rev.* **50** (1936), 1.

‡ *Ibid.* 1006.

a particular transition within the atom is investigated. It often happens, however, that information is required about the intensity of the total inelastic scattering in a particular angular range (see Chap. IV, § 1.1).

TABLE VIII

Relative Probabilities of Different Types of Collision of Electrons in Atomic Hydrogen

Type of collision	Energy of incident electrons (eV)				
	100	200	400	1,000	10,000
	Percentage of all collisions				
Elastic	12.2	10.2	9.8	8.7	6.5
Excitation of 2-quantum levels .	33.5	33.6	39.0	42.8	45.3
" " 3- " "	5.9	5.8	6.8	6.3	7.0
" " 4- " "	2.2	2.0	2.2	2.4	2.6
" " 5- " "	1.0	0.9	1.0	1.2	1.2
Excitation of higher-quantum levels	1.7	1.7	2.0	2.2	2.3
All discrete levels	56.5	44.0	51.0	54.8	58.4
Ionization	43.5	45.8	39.2	36.5	35.1
Total cross-section (units πa_0^2) .	2.45	1.50	0.79	0.37	0.049

TABLE IX

$vZ^{-\frac{1}{2}} \sin \frac{1}{2}\theta$ (v in $\sqrt{\text{volts}}$)	S
0.278	0.319
0.556	0.486
1.112	0.674
1.668	0.776
2.224	0.839
2.781	0.880
3.337	0.909
3.893	0.929
4.449	0.944
5.005	0.954
5.561	0.963

Morse† has shown that, if Born's approximation is valid for all important inelastic collisions, then the total intensity of inelastic scattering into the solid angle $d\Omega$ about a direction making an angle θ with that of incidence, of electrons of velocity v by an atom of atomic number Z , is given approximately by

$$I_{\text{in}}(\theta) d\Omega = \frac{e^4 Z}{m^2 v^4} \text{cosec}^4 \frac{1}{2}\theta S(vZ^{-\frac{1}{2}} \sin \frac{1}{2}\theta) d\Omega, \quad (65)$$

provided $\theta^2 \gg E_0/\frac{1}{2}mv^2$, where E_0 is the ionization energy of the atom. S is a function which may be calculated from the statistical model of the atom. It is given in Table IX as a function of $V^{\frac{1}{2}}Z^{-\frac{1}{2}} \sin \frac{1}{2}\theta$, where V is

† *Phys. Zeits.* **33** (1932), 443.

the energy of the electron in electron volts. An example of the use of this formula is given in Chap. IV, § 1.1.

For smaller angles of scattering an approximate representation of $I_{\text{in}}(\theta)$ similar to that given in § 2.44 for elastic scattering may be used.

It is
$$\pi I_{\text{in}}(\theta) = (B/\theta^2)(\hbar/mv)^2, \quad \theta_2 \leq \theta \leq \theta_3, \quad (66)$$

where the limiting angles θ_2 and θ_3 are given by

$$\theta_2 = \bar{E}/mv^2\gamma^2, \quad \theta_3 = (2\bar{E}/mv^2\gamma^2)^{\frac{1}{2}},$$

$\bar{E}$ being a mean excitation energy for the atom and $\gamma = (1 - v^2/c^2)^{-\frac{1}{2}}$. B is a constant depending on the size of the atom. It has been calculated by Marton and Schiff† for a number of atoms, the values they obtained being given in Table X together with estimated values of I . In most applications of this approximation $I_{\text{in}}(\theta)$ may be taken as negligibly small both for $\theta < \theta_2$ and for $\theta > \theta_3$ (see p. 186).

TABLE X

Values of Parameters B and $\bar{E}$ appearing in Approximate Formula for Inelastic Scattering Cross-section

Atom or ion	B	$\bar{E}$ (eV)	Atom or ion	B	$\bar{E}$ (eV)	Atom or ion	B	$\bar{E}$ (eV)
H	13.3	13.5	P	80	63	Sb	220	180
He	8.8	38	S	70	74	I ⁻	180	150
Li ⁺	3.4	98	C ⁻	76	77	Cs ⁺	120	230
C	35	44	A	55	110			
N	28	63	K ⁺	43	140			
O	23	83	Ca ⁺	33	180			
F ⁻	26	91	Cu ⁺	91	130			
Ne	18	130	Br ⁻	120	130			
Na ⁺	13	180	Rb ⁺	88	170			
Al ⁺⁺	7.5	300	Ag ⁺	200	170			

4. Miscellaneous subjects concerned with elastic and inelastic scattering of electrons by atoms

4.1. Pressure shift of the high-series terms of the alkali metals—Relation to low-velocity limit of the elastic cross-section of perturbing atoms

In Chapter I direct methods for measuring the elastic collision cross-section of atoms towards slow electrons were described. It was pointed out that these methods are very difficult to apply when the electron energy is so small as to be comparable with that at room temperature (≈ 0.03 eV). Information can be obtained about the low-velocity limit of the cross-section of a given atom by studying the effect of the presence

† *J. App. Phys.* **12** (1941), 759.

of such atoms, in sufficient concentration, in perturbing the highly excited terms of the alkali metal atoms.

If the valence electron of an alkali metal atom is excited to a state with principal quantum number $n \simeq 30$, the radius of its Bohr orbit is about $1,000a_0$. A sphere of this radius, at atmospheric pressure, encloses about 10^4 atoms. The valence electron moves very slowly through these atoms in a manner essentially similar to that of a very slow free electron through a gas. The associated wave-length is of the order $200a_0$. The presence of the foreign atoms will modify the energy of the excited state concerned for two reasons—the mean potential energy in which the valency electron moves will be modified, and the foreign atoms will be polarized by the charged core of the alkali atom.

To calculate† the change in the energy due to the modification of the mean field acting on the valence electron we start from the wave equation for the motion of that electron in the form

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(E - V - \sum_s v_s)\psi = 0. \quad (67)$$

V is the potential energy due to the alkali atom core and v_s that due to the s th perturbing atom. To obtain the average energy shift we consider the equation for the wave-amplitude ψ averaged over a region which, while containing many foreign atoms, is of dimensions small compared with the wave-length of the electron. Throughout such a region V will not vary appreciably and we have

$$\bar{\nabla}^2\bar{\psi} + \frac{8\pi^2m}{h^2}(E - V)\bar{\psi} - \frac{8\pi^2m}{h^2} \sum_s \bar{v}_s\bar{\psi} = 0, \quad (68)$$

where the bars denote the averaging process described.

We consider now the evaluation of $v_s\psi$. For this purpose it is convenient to take the origin of coordinates at the centre of the s th atom. We consider a region S enclosing this atom which is of dimensions large compared with the range of v_s but small compared with the distance between neighbouring atoms and hence with the electron wave-length. Throughout this region the negative potential energy V due to the alkali atom core may be regarded as constant and equal to V_s . The wave equation in the new coordinate system takes the form

$$\nabla^2\psi + \left(k_s^2 - \frac{8\pi^2m}{h^2}v_s\right)\psi = 0 \quad (69)$$

within the region S , k_s^2 being given by $2m(E - V_s)/h^2$. As v_s is negligible outside S it is only necessary to obtain ψ from (69).

The equation (69) is of exactly the same form as that concerned in any elastic scattering problem (see § 2.21). The potential energy v_s will produce distortion of the otherwise plane waves whose amplitude satisfies

$$\nabla^2\psi + k^2\psi = 0.$$

Employing the usual resolution into partial waves of different angular momenta

† The following treatment is due to Fermi, *Il Nuov. Cim.* **11** (1934), 157. See also Margenau and Watson, *Rev. Mod. Phys.* **8** (1936), 22.

it is clear that, for the long wave-lengths concerned, only the waves with zero angular momenta about the centre of the s th atom will be appreciably perturbed by v_s (see § 2.22). The others have such small amplitude near the centre of the s th atom that their contribution to $v_s\bar{\psi}$ is negligible.

The waves with zero angular momentum about the centre ($r = 0$) of the s th atom are spherically symmetrical about that centre so that, for our purposes, we may write

$$\psi = u(r)/r,$$

where

$$u \sim A \sin(k_s r + \eta_0),$$

η_0 being the phase shift produced by the field v_s of the perturbing atom (see § 2.2). Now k_s is very small and so also will be η_0 , apart from an integral multiple of π which is immaterial, so we may write

$$u \sim A k_s (r + \eta_0/k_s).$$

At these values of r , however, u must be nearly equal to $r\bar{\psi}$ so that $A = \bar{\psi}/k$.

The low-velocity limit of the elastic cross-section of a perturbing atom is $4\pi a^2$, where

$$a^2 = \eta_0^2/k_s^2.$$

We may therefore write

$$u \sim (r + a)\bar{\psi}, \quad (70)$$

where a is likely to be of the order of the gas kinetic radius of the perturbing atom.

To evaluate $\bar{v}_s\bar{\psi}$ we have now

$$\bar{v}_s\bar{\psi} = \frac{4\pi}{W} \int_0^R v_s u r dr,$$

where the upper limit R is large compared with the range of v_s but small compared with $1/k_s$, and $W = \frac{4}{3}\pi R^3$. Using (69)

$$\begin{aligned} \frac{4\pi}{W} \int_0^R v_s u r dr &= \frac{h^2}{2\pi m W} \int_0^R \left(\frac{d^2 u}{dr^2} + k_s^2 u \right) r dr \\ &= \frac{h^2}{2\pi m W} \left[r \frac{du}{dr} - u \right]_0^R + \frac{k_s^2 h^2}{8\pi^2 m} \bar{\psi}. \end{aligned}$$

As $u(0) = 0$ and at the upper limit (70) is valid we have

$$\bar{v}_s\bar{\psi} = -\frac{ah^2}{2\pi m W} \bar{\psi} + \frac{k_s^2 h^2}{8\pi^2 m} \bar{\psi}.$$

The second term on the right-hand side is negligible because $k_s R$ and $k_s a$ are both $\ll 1$.

If there are N perturbing atoms per unit volume we may obtain $\sum \bar{v}_s\bar{\psi}$ by replacing W by $1/N$. This gives, on substitution in (68),

$$\bar{\nabla}^2 \bar{\psi} + \frac{8\pi^2 m}{h^2} \left(E + \frac{ah^2 N}{2\pi m} - V \right) \bar{\psi} = 0. \quad (71)$$

The effect of the foreign atoms therefore gives an average decrease of the energy of the valence electron equal to $ah^2 N/2\pi m$, i.e. a frequency shift

$$\Delta\nu = -ahN/2\pi m,$$

where $4\pi a^2$ is the low-velocity limit of the elastic collision cross-section of a perturbing atom.

The sense of this effect depends on the sign of a . This is not fixed by the size of the elastic cross-section for the given perturbing atom. However, if the phase η_0 approaches its low-velocity limit $s\pi$ from above, a will be positive; if from below, negative. In the former case the cross-section will exhibit a minimum at a low electron energy so that a frequency shift towards the red should only occur from this effect if the perturbing atoms show a Ramsauer-Townsend effect with slow electrons (see § 2.31). Otherwise the shift is towards the violet.

The polarization energy is given by

$$\Delta E_p = -\frac{1}{2}\alpha\epsilon^2 \sum_s \frac{1}{R_s^4},$$

where R_s is the distance of the s th perturbing atom from the nucleus of the alkali metal atom. The sum over all perturbors is approximately given by

$$\sum \frac{1}{R_s^4} = 4\pi N \int_{R_0}^{\infty} \frac{R^2 dR}{R^4},$$

where the lower limit R_0 is the mean distance $(3/4\pi N)^{1/3}$ of a perturbing atom from the nucleus of the alkali metal atom. This gives a frequency shift,

$$\Delta\nu_p = -10(\epsilon^2/h)\alpha N^{1/3},$$

towards the red, which is usually small compared with that due to the first effect considered.

Measurements of the frequency shifts of the highest terms of the principal series of the spectra of the alkali metal atoms due to perturbation by various foreign gases have been carried out by a number of investigators.† The results are in good agreement with the theory and provide the only values at present available for the low-velocity limits of the elastic cross-sections of different atoms and molecules.

It is found that the shift of the highest terms is independent of the nature of the alkali atom and of the particular term concerned. The rare gases A, Kr, and Xe, which exhibit a Ramsauer effect, all produce a broadening which is strongly asymmetric towards the red, while He and Ne and Hg, which show no Ramsauer effect, all produce a broadening asymmetric towards the violet. Fig. 90 illustrates these results.

Table XI gives the values of the low-velocity limit of the elastic cross-section for different gases derived from the measured shifts

† Amaldi and Segrè, *Il Nuovo. Cim.* **11** (1934), 145; Füchtbauer, Schulz, and Brandt, *Zeits. f. Phys.* **90** (1934), 403 (Na and K). Füchtbauer and Gossler (*ibid.* **93** (1935), 648); Füchtbauer and Reimers (*ibid.* **95** (1935), 1) (Cs). Tsi-Zè and Shang-Yi, *Phys. Rev.* **51** (1937), 567.

together with the values obtained by direct measurement at the lowest electron velocity which has been used. The good agreement between the two sets of values for helium with the direct measurements of Wahlin† which have been carried out at very low electron energies, is satisfactory.

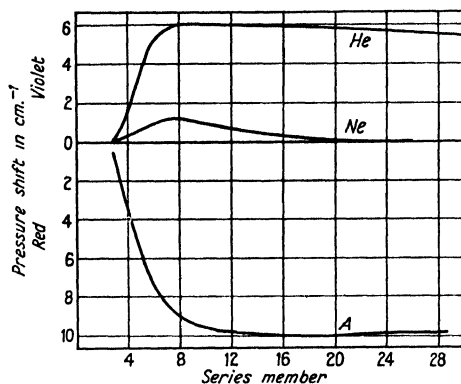


FIG. 90. Pressure shift of the C_4 principal series lines in helium, neon, and argon. The shift is towards the red or the violet according as the foreign gas does or does not exhibit a Ramsauer effect.

TABLE XI

Effective Cross-sections of Gases for Elastic Scattering of Electrons of Very Low Velocity

Gas	Q from pressure shift	Q measured directly	
		Electron energy eV	Q (units πa_0^2)
He	4.94 ⁽¹⁾ , 5.03 ⁽²⁾	0.03	4.88 ⁽³⁾
Ne	0.073 ⁽¹⁾ , 0.078 ⁽²⁾	0.2	1.0 ⁽⁴⁾
A	8.01 ⁽¹⁾ , 7.70 ⁽²⁾	0.03	0.83 ⁽³⁾
Kr	38.7 ⁽⁵⁾	0.6	6.38 ⁽⁶⁾
Xe	132 ⁽⁷⁾	0.2	18.4 ⁽⁶⁾
Hg	11.0 ⁽⁹⁷⁾	1	80-95 ⁽⁸⁾
N ₂	1.6 ⁽¹⁾	..	3.2 ⁽³⁾
H ₂	3.92 ⁽⁹⁾	..	7.8 ⁽³⁾

References

1. Fuchtbauer, Schulz, and Brandt, *Zeits. f. Phys.* **90** (1934), 403.
2. Tsi-Zè and Shaug-Yi, *Phys. Rev.* **51** (1937), 567.
3. Wahlin, *ibid.* **37** (1931), 260.
4. Normand, *ibid.* **35** (1930), 1217.
5. Fuchtbauer and Reimers, *Zeits. f. Phys.* **95** (1935), 1.
6. Ramsauer and Kollath, *Ann. der Physik*, **3** (1929), 536.
7. Fuchtbauer and Gössler, *Zeits. f. Phys.* **93** (1935), 648.
8. Brode, *Proc. Roy. Soc. A*, **109** (1925), 397.
9. Amaldi and Segre, *Nature*, **133** (1934), 141; *Il Nuovo Cimento*, **11** (1934), 145.

† *Phys. Rev.* **37** (1931), 260.

It is of interest to notice that for krypton, and especially for argon and xenon, the cross-section must still be increasing rapidly for electrons with energy less than $\frac{1}{2}$ eV. The large value $132\pi a_0^2$ found for the low-velocity limit in xenon indicates that resonance conditions are nearly approached in this case, i.e. the xenon atomic field is nearly strong enough just to introduce a stable bound state of Xe^- . For mercury, on the other hand, the limiting cross-section falls considerably below the directly measured value at the lowest electron energy ($\simeq 1$ eV).

4.2. *The theoretical limit to the resolution of an electron microscope†*

It is well known that, in principle, the resolving power of an electron microscope should exceed that of an optical microscope because of the much smaller wave-length which may be employed in the former. There are certain other aspects which must be taken into account in assessing the upper limit to the resolution which can be obtained with an electron microscope.

The first point arises from the fact that the scattering of fast electrons takes place mainly through very small angles, so the aperture angle α of the objective is very small. According to the Abbé theory, the minimum distance a between two objects in a self-luminous specimen, in order that they can be recognized as separate in the microscope image, is given by

$$a = 0.6\lambda/\sin \alpha, \quad (72)$$

where λ is the wave-length of the radiation concerned. Referring to § 2.44 it may be seen from (34) that, for elastic scattering, α may be taken as given effectively for an atom of atomic number Z by $\theta_1 = Z^{1/3}/180\beta\gamma$, where β is the ratio of the electron velocity v to that of light and $\gamma = (1-\beta^2)^{-1/2}$. The inelastic scattering gives a smaller limiting angle, as may be seen from § 3.9, so that we may estimate d by substituting θ_1 for α in (72). This gives

$$\begin{aligned} a &= 108h\gamma/mcZ^{1/3} \\ &\simeq 5a_0/Z^{1/3}. \end{aligned} \quad (73)$$

To this must be added the effective atomic radius for strong scattering which is of order $a_0/Z^{1/3}$. It appears then that for most atoms the limit imposed by the Abbé theory is between $\frac{1}{2}$ and $2 \text{ \AA}$.‡

The second point arises from the need to consider the contrast present in the image formed by an electron microscope. Whereas in an optical

† For general works on the electron microscope see Gabor, *The Electron Microscope*, Hulton Press, London, 1944.

‡ Schiff, *Phys. Rev.* **61** (1941), 721.

microscope contrast arises mainly from absorption in the specimen, in the electron instrument only a small contribution comes from this source. Instead, the contrast arises from phase changes in the electron waves in their passage through the specimen. If the specimen is very thin the incident plane electron waves will be coherent with the elastically scattered waves and the interference effects due to the phase shifts will lead to contrast. On the other hand, if the incident and elastically scattered waves are incoherent, contrast can still be produced by loss of electrons due to scattering through such large angles that they hit the aperture diaphragm of the objective. This scattering is also due to the phase shifts produced in the incident waves by the specimen. In either case the contrast depends on the atomic number of the scattering atoms and provides a more severe limitation than that obtained from use of the Abbé formula.

The contrast g may be defined as

$$g = \{I(\infty) - I(0)\}/I(\infty), \quad (74)$$

where $I(\rho)$ is the intensity in the image plane at a distance ρ from the centre of the image. We may suppose that it must be greater than 0.1 in order that an observable image can be registered on a photographic plate.

In the first (coherent)† case the scattered intensity is spread over a disk of radius a given by (73). If A is the amplitude of the incident plane wave and Q_0 the elastic scattering cross-section, the root mean square amplitude of the scattered wave within the disk will be $(A^2 Q_0 / \pi a^2)^{1/2}$. Hence, in (74), $I(\infty)$ may be taken as A^2 and $I(0)$ as $\{A \pm (A^2 Q_0 / \pi a^2)^{1/2}\}^2$, giving

$$g = 1 - \{1 \pm (Q_0 / \pi a^2)^{1/2}\}^2 \\ = 2(Q_0 / \pi a^2)^{1/2}.$$

According to (34)

$$Q_0 = 2\pi \int I(\theta) \sin \theta \, d\theta \\ \simeq 0.6\lambda^2 Z^4 \quad (75)$$

so that

$$g \simeq 0.008 \, Zc/v.$$

Hence, according to this, it should be possible in principle to observe, with 60 keV electrons, an atom with $Z > 7$.

When the contrast arises from incoherent scattering outside the diaphragm aperture we may write $I(0) = A^2(1 - Q'/\pi d^2)$, where d is the

† Schiff, loc. cit.; Zworykin, Morton, Ramberg, Hillier, and Vance, *Electron Optics and the Electron Microscope*, John Wiley & Sons, New York, 1945, Chap. 19, p. 729.

least resolvable separation and Q' is the cross-section for elastic scattering through angles greater than the aperture angle.† We now have, from (74),

$$g \simeq Q'/\pi d^2, \quad (76)$$

where Q' may be calculated from (34) in the same way as Q_0 and can be taken for present purposes as practically equal to Q_0 . This imposes a more severe limit than the previous case. With the same aperture as in that case and the theoretical value (73) for d it can be seen that even the heaviest atoms would barely be visible. With the resolution attainable in electron microscopes at the time of writing d is about 10^{-7} cm. For 60 keV electrons, this requires, according to (75), that Z should exceed 1600 if g is to be greater than 0.1. Even if the less rigid requirement $g > 0.02$ is taken values of $Z > 500$ are needed. This indicates that, even for atoms as heavy as gold, a cluster of less than 6 atoms would not be visible.

So far we have not considered the effect of lens aberrations on the performance of the microscope. Of these spherical aberration is the most important, particularly as, with present designs, it is not possible to correct for it. This limitation is unavoidable if, as at present, the electric and magnetic fields providing the lens systems are axially symmetrical, are free from sources and vortices in the neighbourhood of the optic axis, and do not vary with time. Although spherical aberration decreases the resolving power it does not necessarily decrease the contrast. This is because it produces an additional phase shift of the electron waves which adds to that caused by the specimen and may make non-absorbing specimens visible, even if no electrons are scattered outside the limiting aperture.

A discussion by Scherzer‡ indicates, however, that improvement of the resolving power by decrease of spherical aberration will improve the contrast in the image of an atom provided the limit of resolution d is above 1 Å. On the other hand, for a given value of d the contrast may be improved by the presence of some spherical aberration. For the details of this work we refer the reader to the original papers.

Although the situation is not yet sufficiently clear for definite predictions to be made as to the ultimate limit in performance of the electron microscope, it seems possible from the above considerations that at least the heaviest atoms might ultimately be rendered visible.

† Boersch, *Zeits. f. Naturforschung*, 2a (1947), 615; Zworykin *et al.*, loc. cit.

‡ *J. App. Phys.* 20 (1949), 20.

Marton and Schiff† have suggested a further application of electron scattering theory to the electron microscope. It is very difficult to determine the thickness of a specimen in a direction parallel to the optic axis of the instrument. Marton and Schiff proposed to determine this dimension from the intensity distribution in the image. If Q' is the total collision cross-section of the atoms of the specimen for scattering through angles greater than the aperture angle α , the intensity in traversing the specimen will be reduced by a factor $e^{-NQ'x}$ where x is the thickness of the specimen and N the number of atoms/c.c. within it (see Chap. I, § 2). Hence if I_0 is the intensity transmitted through the material supporting the specimen and I that through both material and specimen

$$x = \frac{1}{NQ'} \log I_0/I. \quad (77)$$

To determine Q' the approximate expressions (34) of § 2.44 and (66) of § 3.9 were used.

For a non-metallic specimen which is not too thick so that multiple scattering is negligible

$$Q' = Q'_0 + Q'_{in},$$

where Q'_0 and Q'_{in} are the respective contributions from elastic and inelastic scattering. Q'_0 has already been given in (75) above. Q'_{in} may be calculated from (66) of § 3.9 to give

$$\begin{aligned} Q'_{in} &= \int_0^\pi I_n(\theta) \sin \theta \, d\theta \\ &= \left. \begin{aligned} &B(h/mv)^2 \log(2/\theta_2), & \alpha < \theta_2, \\ &B(h/mv)^2 \log(2\theta_2/\alpha^2), & \theta_2 < \alpha < \theta_3, \end{aligned} \right\} \quad (78) \end{aligned}$$

The angles θ_2 and θ_3 are defined in § 3.9 and B is tabulated for different atoms and ions in Table XI.

For a metallic specimen a contribution Q'_f also arises from scattering by free electrons. Marton and Schiff show that, approximately,

$$\begin{aligned} Q'_f &= 8\pi\nu(\epsilon^2/mv^2\gamma)^2 \left\{ (3/4\alpha\theta_4) + (\alpha/16\theta_4^3) \right\}, & \alpha < 2\theta_4, \\ &= 4\pi\nu(\epsilon^2/mv^2\gamma\alpha)^2, & \alpha > 2\theta_4, \end{aligned} \quad (79)$$

where ν is the number of free electrons per atom and

$$\theta_4 = (h/mv\gamma)(3\nu N/8\pi)^{1/2},$$

the remaining symbols being as defined above.

Using these formulae x may be obtained from measurements of I_0/I and knowledge of the density of the specimen. Examples are given in Marton and Schiff's paper.

4.3. The effect of inelastic collisions on the velocity distribution of a swarm of electrons diffusing in an electric field

In Chap. I, § 5.2, the velocity distribution of electrons diffusing in a steady state through a gas at pressure p under the influence of a uniform electric field F was obtained on the assumption that the average energy of the electrons, while much greater than that of the gas atoms, was sufficiently small for inelastic collisions to be neglected. This is a serious

† J. *App. Phys.* **12** (1941), 759.

limitation in many applications such as to discharge phenomena. Approximate methods have therefore been developed to take into account the energy loss due to inelastic collisions. These are still restricted to electrons with mean energy somewhat less than the excitation energy, so that inelastic collisions affect mainly the high energy 'tail' of the distribution. The most detailed calculations have been carried out by Druyvestyn† for neon and by Smit‡ for helium.

The method used is essentially as follows. Referring to Chap. I, § 5.21, it will be seen that the velocity distribution function f in the case when inelastic scattering is ignored was obtained by equating the number $c d\gamma$ of representative points leaving the element $d\gamma$ ($= d\xi d\eta d\zeta$) of velocity space, due to the applied field F , to $(b-a) d\gamma$, where a is the number leaving and b the number entering the element per second due to collisions. If the mean energy is small compared with the energy of excitation we can ignore the contribution to b from inelastic collisions. The contribution to a will be $NQ_{in}vf$, where N is the number of gas atoms per c.c., and Q_{in} the cross-section for inelastic collisions when the electron velocity is v ($= (\xi^2 + \eta^2 + \zeta^2)^{1/2}$). If this term is included in (18) of Chap. I the equation (20)

$$(eF/m) \frac{\partial f_0}{\partial v} = -NQ_d v f_1,$$

is unchanged, but (21) is replaced by

$$(eF/3m) \frac{\partial (v^2 f_1)}{\partial v} = (mN/M) \frac{\partial}{\partial v} (v^4 Q_d f_0) - NQ_{in} v^3 f_0, \quad (80)$$

the notation being as in Chap. I, § 5.21. Q_{in} vanishes if $\frac{1}{2}mv^2 < E_a$, the excitation energy, so that for such values of v the form of the distribution is unaltered. For values of v such that $\frac{1}{2}mv^2 > E_a$ the term on the right-hand side of (80), representing the loss due to elastic scattering, may be neglected compared with that from inelastic collisions. Omitting this term we find§

$$\frac{\partial}{\partial v} \left(v \frac{\partial f_0}{\partial v} \right) = - \frac{3m^2}{e^2 F^2 l^2} \alpha v^3 f_0, \quad (81)$$

where $\alpha (= Q_{in}/Q_d)$ is a function of v and $l (= 1/NQ_d)$ is the mean free path for diffusion. Knowing α and l from observation and theory f_0 may therefore be determined, apart from two arbitrary constants, by solving this equation. The constants may be chosen so that f_0 joins smoothly at $v = (2E_a/m)^{1/2}$ and

$$4\pi \int_0^\infty f_0(v) v^2 dv = 1.$$

† *Physica*, 3 (1936), 65.

‡ *Ibid.* 643.

§ In terms of the energy distribution function $\rho(\epsilon)$ ($= f(v/m)$, where $\epsilon = \frac{1}{2}mv^2$, the equation may be written

$$\frac{d^2 \rho}{d\epsilon^2} = - \frac{3\alpha}{e^2 F^2 l^2} \rho,$$

use being made of the assumption $E_a \gg eFl$ which follows if the mean energy of the electrons is small compared with the excitation energy.

Fig. 91 illustrates a number of energy distributions $\rho(\epsilon)$ ($= vf(v)/m$) calculated by Smit† for different values of F/p in helium using the inelastic collision cross-sections given by Maier-Leibnitz (Chap. II, § 5.2).

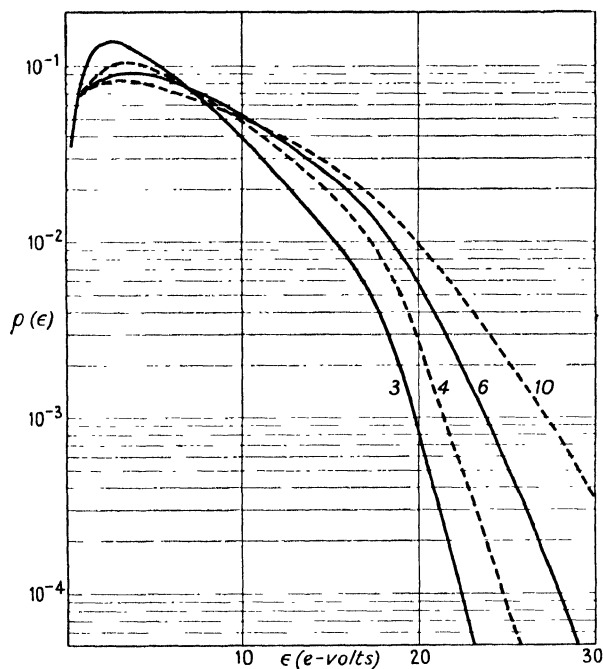


FIG. 91. Calculated energy distribution functions $\rho(\epsilon)$ for electrons in helium for different values of F/p including the effect of inelastic collisions. Values of F/p are indicated on the curves in volts/cm./mm. Hg.

† Loc. cit.

IV

ELECTRON COLLISIONS WITH MOLECULES

THERE are a number of additional effects of importance which arise when electrons collide with molecules instead of single atoms. In elastic scattering, interference occurs between the electron waves scattered from the different atoms and is apparent in the angular distribution of the scattered electrons. Considerable use has been made of this for studying molecular structure (see § 1.5). Inelastic collisions include the possibility of molecular dissociation and of the excitation of nuclear rotation and vibration. Molecular dissociation due to electron impact is usually a consequence of excitation of some electronic level of the molecule, but a great variety of possible modes of dissociation occur if the molecule is a complicated one. A detailed experimental study has been made for a number of molecules and much valuable information has been obtained.

1. Diffraction of fast electrons by molecules

If the separate atoms of a molecule are considered as separate scattering systems, interference will occur between the electron waves scattered by the individual atoms of a molecule. The nature of these effects will depend on the shape and size of the molecule. This raises the possibility of obtaining information about molecular structure by studying the scattering of electrons by the molecules concerned in the gas phase. Debye,[†] in 1915, developed the theory of the scattering of X-rays by gas molecules and initiated experimental work on the subject which had already begun to yield valuable results[‡] as early as 1927. Wierl[§] in 1931 was the first to use electrons for this purpose and since then a great deal of valuable work has been done using essentially his technique.|| Electron diffraction is now one of the most powerful methods of investigating molecular structure.

The theory of the elastic scattering of fast electrons by a molecule can be derived very simply from that for the separate atoms. We consider an electron beam of wave-length $\lambda = 2\pi/k$ incident on the molecule in the direction of the unit vector $\mathbf{n}_0$ which we shall take as the z-direction.

[†] *Ann. der Physik*, **46** (1915), 809.

[‡] Debye, *Phys. Zeits.* **28** (1927), 135; **31** (1930), 142 and 419; Debye, Bowillogua, and Ehrhardt, *ibid.* **30** (1929), 84.

[§] *Ann. der Physik*, **8** (1931), 521.

|| See § 1.5.

If we take the centre of the i th atom as origin, an incident wave of unit amplitude, with the corresponding scattered wave due to this atom, can be written

$$e^{ikz} + r^{-1}e^{ikr}f(\theta), \quad (1)$$

where r is the distance from the centre A_i of the atom and θ is the angle of scattering (see Fig. 92). Now if we change the origin to a point O

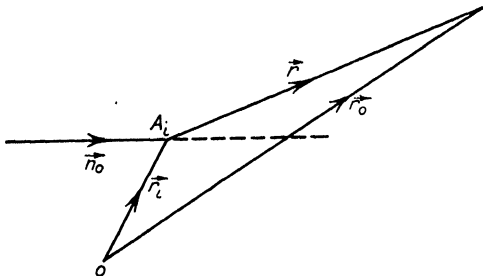


FIG. 92.

within the molecule, with respect to which the position vector of the centre of the i th atom is $\mathbf{r}_i$, (1) becomes

$$e^{ik(z_0 - z_i)} + \frac{e^{ik|\mathbf{r}_0 - \mathbf{r}_i|}}{|\mathbf{r}_0 - \mathbf{r}_i|} f_i(\theta),$$

where coordinates referred to O are distinguished by the suffix 0. If we reckon phase with reference to the new origin this becomes

$$e^{ikz_0} + \frac{e^{ik|\mathbf{r}_0 - \mathbf{r}_i|}}{|\mathbf{r}_0 - \mathbf{r}_i|} e^{ikz_i} f_i(\theta).$$

Further, since $\mathbf{r}_0$, the position vector of the point of observation, is very large compared with $\mathbf{r}_i$, we may write, approximately

$$|\mathbf{r}_0 - \mathbf{r}_i| = r_0 - \mathbf{n} \cdot \mathbf{r}_i,$$

where $\mathbf{n}$ is a unit vector in the direction of observation, i.e. in the direction of scattering. This gives for the scattered waves due to the i th atom

$$r_0^{-1} e^{ikr_0} e^{ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}_i} f_i(\theta). \quad (2)$$

Since this expression allows for the differences of phase between different scattering centres, we obtain the amplitude of the scattered wave due to the molecules by summing (2) over all atoms i , giving for the differential cross-section $I(\theta) d\Omega$,

$$\begin{aligned} I(\theta) &= \left| \sum_i e^{ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}_i} f_i(\theta) \right|^2 \\ &= \sum_i \sum_j f_i^* f_j e^{ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}_{ij}}, \end{aligned} \quad (3)$$

where

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j.$$

This formula is still incomplete, for it assumes a fixed orientation of the molecule relative to the electron beam. In practice, molecules of a gas will be oriented at random and the observed differential cross-section will be obtained from the average of (3) over all molecular orientations. This average may be calculated by considering each term of (3) separately.

Choosing $\mathbf{n}_0 - \mathbf{n}$ as polar axis, the average over all orientations of the vector $\mathbf{r}_{ij}$ will be

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi_{ij} \int_0^\pi \sin \theta_{ij} \exp\{isr_{ij} \cos \theta_{ij}\} d\theta_{ij},$$

where θ_{ij} , ϕ_{ij} are the polar angles of $\mathbf{r}_{ij}$ relative to $\mathbf{n}_0 - \mathbf{n}$ and

$$s = k|\mathbf{n}_0 - \mathbf{n}| = 2k \sin \frac{1}{2}\theta.$$

Evaluating the integrals gives

$$\bar{I}(\theta) = \sum_i \sum_j f_i f_j^* \frac{\sin sr_{ij}}{sr_{ij}}. \quad (4)$$

This expression is only valid if the effect of the molecular binding on the atomic fields can be neglected. This will be so for scattering of fast electrons which are practically unaffected by all but the inner atomic fields. For such electrons Born's approximation (Chap. III, § 2.43) may be employed to give

$$f_i(\theta) = \frac{2m\epsilon^2}{h^2} \frac{Z_i - F_i(\theta)}{s^2}$$

and
$$\bar{I}(\theta) = \frac{4m^2\epsilon^4}{h^4 s^4} \sum_i \sum_j (Z_i - F_i)(Z_j - F_j) \frac{\sin sr_{ij}}{sr_{ij}}. \quad (5)$$

F_i is the atom form factor defined in Chap. III, (31).

Before considering the practicability of using this result to explore molecular structure we must include the effect of inelastic collisions for, in any photographic technique, these will provide a background which will affect the contrast between diffraction maxima and minima. The total inelastic scattering can be regarded as incoherent and may therefore be built up as the simple sum of the contributions from different atoms. We have, then, for the total differential cross-section

$$\bar{I}(\theta) = \frac{4m^2\epsilon^4}{h^4 s^4} \left\{ \sum_i \sum_j (Z_i - F_i)(Z_j - F_j) \frac{\sin sr_{ij}}{sr_{ij}} + 4 \sum_i S_i \right\}, \quad (6)$$

where S_i is the function, discussed and tabulated in Chap. III, Table IX, which represents the total inelastic scattering from the atom.

To discuss the applicability of electron scattering to molecular structure determinations it is convenient to write the expression (6) in the form

$$\bar{I}(\theta) = \frac{K}{s^4} \left[\sum_i \{ (Z_i - F_i)^2 + 4S_i \} + \sum_i \sum_j' (Z_i - F_i)(Z_j - F_j) \frac{\sin sr_{ij}}{sr_{ij}} \right], \quad (7)$$

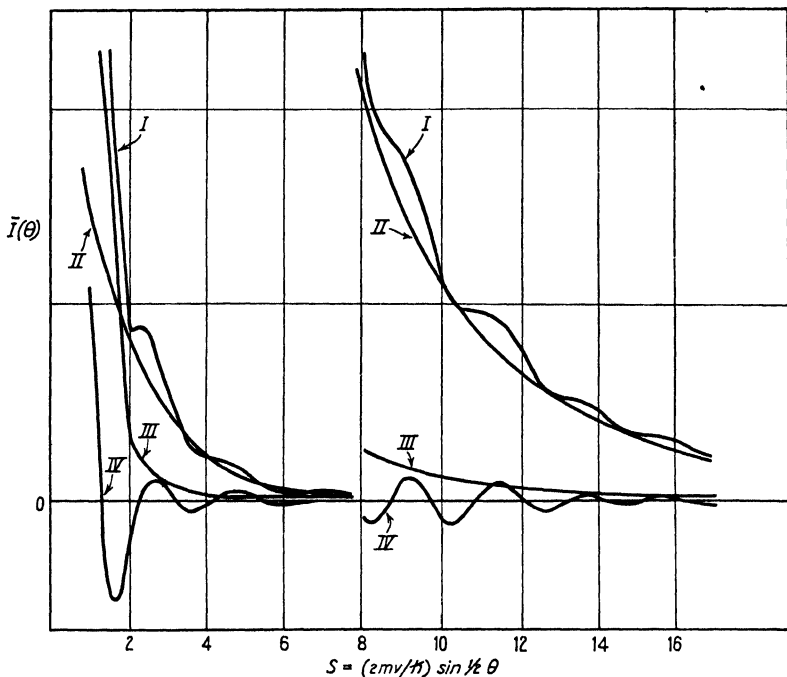


FIG. 93. Calculated angular distribution $\bar{I}(\theta)$ of electrons scattered in CCl_4 showing the diffraction effect due to the tetrahedral structure. The ordinate scale for $s > 8$ is increased 100 times.

Curve I represents the total scattered intensity $\bar{I}(\theta)$. Curves II, III, and IV show respectively the contributions to $\bar{I}(\theta)$ from elastic atomic scattering, inelastic atomic scattering, and from the interference effect.

where the first summation exhibits no diffraction effects. The terms sensitive to molecular structure arise from the second sum in which i and j are always different. The fluctuations with angle due to these terms are superimposed upon a background which decreases very rapidly with increase of angle, due to the factor s^{-4} . This leads to difficulty in accurate structure determination which has been largely overcome in various ways.

1.1. Application to carbon tetrachloride

To obtain a clear idea of the nature of the various terms contributing to $\bar{I}(\theta)$ it is instructive to consider a special case, that of carbon tetrachloride, which has been studied extensively. Using the tables of F_i and S_i together with the known tetrahedral structure of CCl_4 with the carbon—chlorine distance 1.76 Å and the chlorine—chlorine distance 2.87 Å, the curves of Fig. 93 may be derived. Curve I gives $\bar{I}(\theta)$ as a function of s , while curves II, III, and IV illustrate the respective contributions of the elastic atomic scattering $\sum_i (Z_i - F_i)^2/s^4$, the inelastic atomic scattering $4 \sum S_i/s^4$, and the structure-sensitive scattering

$$\frac{1}{s^4} \sum_i \sum_j' (Z_i - F_i)(Z_j - F_j) \frac{\sin sr_{ij}}{sr_{ij}}.$$

It will be seen that the decrease in the smooth background with increasing s is so rapid that the structure-sensitive terms are merely able to produce fluctuations and not true maxima and minima. This is clearly seen in the microphotometer records of diffraction patterns. Thus Fig. 94(a) reproduces records taken by Wierl for CCl_4 and C_6H_6 . The variation of intensity throughout the angular range observed is so great that, to obtain a measurable blackening at appreciable angles, such intensities must be used that at the small angles saturation of the plate or even reversal occurs. This subjectivity of the plate is exaggerated by visual observation of the diffraction photograph. The eye is very sensitive to rapid changes in intensity and enhances the contrast to give often the appearance of sharply defined rings of maximum and minimum intensity. This may be seen from Fig. 94(b) which reproduces patterns obtained by Wierl† for CCl_4 and C_6H_6 under the same conditions as that from which the microphotometer records of Fig. 94(a) were taken. Before discussing the technique of interpreting patterns such as these we shall describe the experimental methods employed in obtaining them.

1.2. Experimental methods

To obtain sharp diffraction patterns, a well-collimated electron beam, very homogeneous in velocity, is fired through a localized jet of gas, so that the scattering volume is very small, and the resulting scattering recorded in a short exposure on a photographic plate. Apparatus used, therefore, has remained of the same general form as that used by Wierl,† the essential features of which are illustrated in Fig. 95.

† Loc. cit.

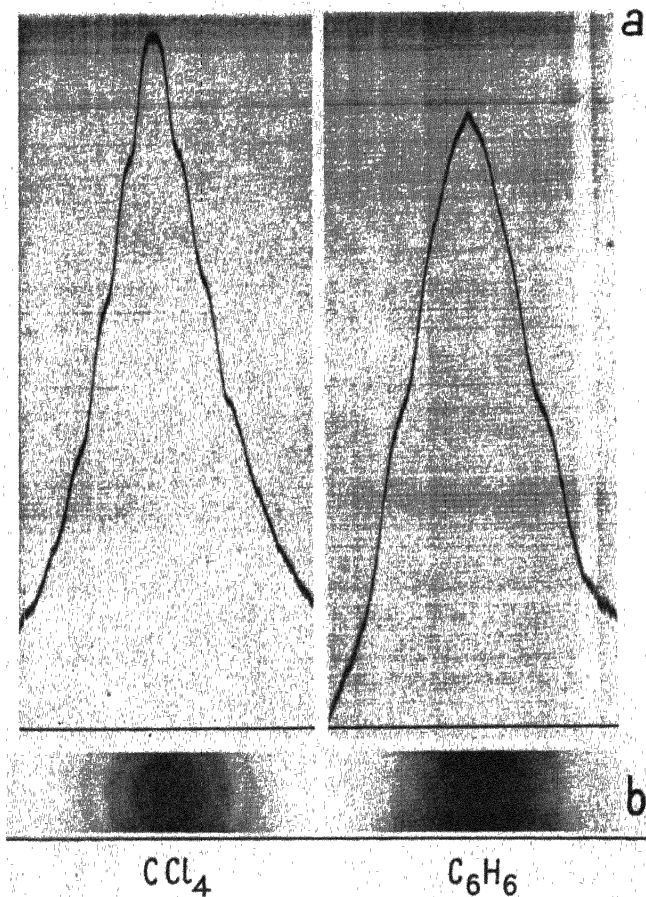


FIG. 94. Diffraction of electrons by CCl_4 and C_6H_6 as observed by Wierl using electrons of energy 43 keV. Fig. 94 (a) shows microphotometer records obtained under the same conditions as the photographs of Fig. 94 (b).

It consists essentially of three parts, the electron tube, the diffraction chamber, and the camera. The cathode-ray beam passing through a hole *A* in a water-cooled anode is collimated by passage for 10 cm. along a fine tube *B* of 0.1 mm. bore. This tube also provides the only gas connexion between the diffraction chamber *C* and the electron discharge

tube, so that a considerable pressure difference may be maintained between them. The gas or vapour enters the diffraction chamber through a 0.1 mm. hole in a conical jet *D*. This jet is so arranged as to intersect normally the electron beam issuing from *B*. The flow through *D* can be

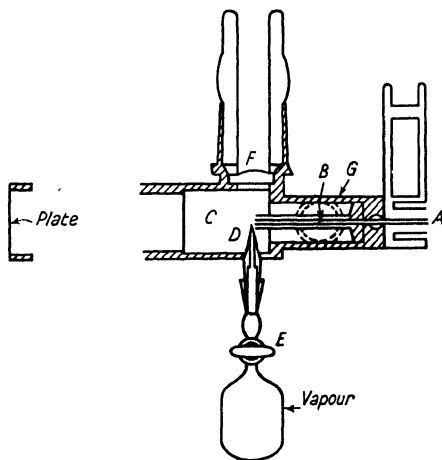


FIG. 95. Apparatus used by Wierl for investigating electron diffraction in gases and vapours.

shut off by means of a stopcock *E* between the jet and the main container of the material whose vapour is being investigated. The vapour is condensed on a liquid air-cooled surface *F* immediately above the jet *D*. The electrons scattered from the jet are recorded photographically by a plate 15 cm. from *D* which may be placed in position and exposed when required. A fluorescent screen for visual observation in effecting adjustments may be substituted for the plate. Pump connexions *G* are provided to maintain as low a pressure as possible in the diffraction chamber.

The electron energy employed is normally in the neighbourhood of 40,000 eV, corresponding to a wave-length of 6×10^{-2} Å. For precise determination of interatomic distances this wave-length must be known accurately. A convenient method of calibration of voltage measurements is to observe the diffraction of the electrons by a thin film of gold, the edge of the unit cell of which is known to be 4.070 Å. From the positions of the diffraction maxima the wave-length can then be determined with sufficient accuracy. To obtain the required homogeneity

in velocity of the electron beam the high voltage must be well regulated. A test of the homogeneity is the sharpness of definition of the rings obtained from a gold film. Alternatively, a magnetic field may be applied to the beam and its effect observed on the fluorescent screen.

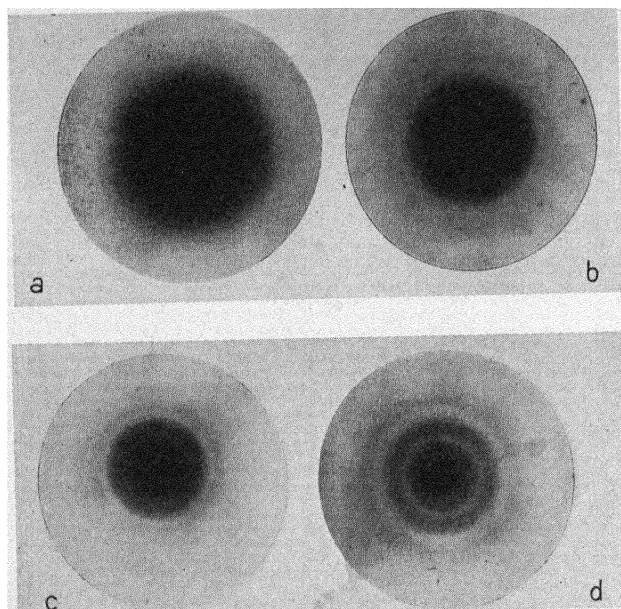


FIG. 96. Typical diffraction patterns obtained by Wierl for electron diffraction in (a) CS_2 , (b) CO_2 , (c) SiCl_4 , (d) GeCl_4 .

It is essential for good definition that the background pressure in the diffraction chamber should be as low as possible and modifications of Wierl's design have largely been directed towards improvements in this direction. Thus, in the apparatus used by Brockway and Pauling,[†] the jet issuing from a 0.3 mm. hole is directed into the opening of a high-speed pump connexion, the upper end of the nozzle being completely enclosed for about an inch, with a clearance of less than 0.5 mm. The electron beam passes about 2 mm. above the end of the nozzle through two holes in the pump connexion of only just sufficient size to clear the beam, allowing for the maximum angle of scattering. A separate pump

[†] Brockway, *Rev. Mod. Phys.* 8 (1936), 231.

connexion is also made to the diffraction chamber to evacuate it and the camera. Other modifications have been introduced by de Laszlo† and Cosslett.‡

In carrying out an experiment the container is brought to a temperature such that the vapour pressure of the substance is of order 100 mm. An exposure is carried out by releasing the film shutter during the time, about $\frac{1}{4}$ th sec., in which the stopcock is turned on to admit the vapour to the nozzle. If sufficient intensity is not secured with one exposure several successive exposures may be made at intervals of 10 or more seconds. In this way vapour is admitted to the diffraction chamber only when required for an exposure.

Fig. 96 illustrates a small selection of diffraction patterns obtained for different substances using apparatus of the general type described.

1.3. Analysis of diffraction photographs§

The methods employed to analyse the photographic patterns obtained can be classified as visual, photometric, and compensational respectively. In all cases the analysis proceeds by first assuming a structure and calculating the theoretical pattern to be expected for it. This is determined apart from a scale factor which must be adjusted by comparison with observed patterns. Even when a very good agreement is obtained with observation it is not completely certain that the assumed structure is correct.

In choosing this structure, guidance is usually provided from chemical and other data, but it is sometimes convenient to apply first a method which, in principle, determines the density distribution of the scattering material from the diffraction pattern. This involves replacement of the sum over all the atoms which appears in formula (7) by an integral in the following way. The product $f_i f_j$ of the scattering amplitudes (or electrons from protons) for the two atoms distant r_{ij} apart is replaced by $r^2 D(r) dr/s^4$ which represents the contribution from all volume elements at distances apart between r and $r+dr$. $D(r)$ is then essentially a function proportional to the chance of two atoms being at a distance apart between r and $r+dr$. We have then

$$\begin{aligned}\bar{I}(\theta) &= I(s) \\ &= C \int_0^\infty \frac{r^2 D(r)}{s^4} \frac{\sin sr}{sr} dr,\end{aligned}$$

C being a constant. This integral may be inverted to give

$$D(r) = C' \int_0^\infty s^6 I(s) \frac{\sin sr}{sr} ds. \quad (8)$$

Knowing $I(s)$, $D(r)$ is thus determined.

† *Proc. Roy. Soc. A*, **146** (1934), 672.

‡ *Trans. Far. Soc.* **30** (1934), 981.

§ A full account of the procedures employed in the analysis of the electron diffraction photographs is given in Brockway's article (*loc. cit.*). This article also contains a comprehensive list of references up to 1936.

In practice, the integral (8) is replaced by a sum over the separate diffraction rings

$$D(r) = \sum_k s_k^2 I_k \sin s_k r / s_k r, \quad (9)$$

s_k being the s -value of the k th ring and I_k the visually estimated intensity for that ring. The maxima of $D(r)$ represent distances between atoms in the molecule. In practice, only the atoms with strong scattering power are located accurately, but this is often of value in restricting the choice of assumed parameters.

The visual method takes advantage of the subjectivity of the eye in enhancing the contrasts. The eye is sensitive to the fluctuations to an extent determined largely by the ratio of the fluctuations to the background. The positions of the maxima and minima determined from the visual pattern are therefore compared with the corresponding maxima and minima in the ratio of the structure-sensitive scattering to the atomic scattering. Using also qualitative intensity comparisons, the validity of the assumed molecular structure is checked and the scale factor determined. In this procedure, allowance must be made for certain subjective effects which enter in the determination of the position of the visual maxima and minima. On the other hand, it has the great advantages of simplicity, the great number of maxima and minima which may be employed (the outermost are the most sensitive to the molecular structure), and the use of qualitative intensity comparisons.

In using the microphotometer record of the pattern, comparison must be made between the positions of the fluctuations in the calculated total scattering curve and in the record. The accuracy of this method seems to be comparable with that of the visual one, but it has the disadvantage of employing a relatively small number of comparison points, excluding the outer portions of the pattern, and requiring rather laborious numerical calculations.

Compensation methods attempt to introduce some procedure to compensate for the rapid decrease of background intensity with s . Maxwell, Hendricks, and Mosley† compared theoretical and experimental intensity curves (derived from accurate photometric methods) each multiplied by s^2 . This converts the fluctuations into real maxima and minima. Cosslett‡ performed the compensation photographically by preparing a compensating plate whose density distribution represented the complement of the smooth background along a radius of the diffraction pattern. A third plate was exposed through the negative and compensating plate together, giving a record with pronounced maxima and minima. These were compared with the theoretical curves representing the departure from the smooth background. Finally, Debye§ introduced a compensating device which can be used to effect the compensation in taking the original negative.

1.4. General remarks on the method

In principle, electron diffraction has an advantage over that of X-rays for exploring the structure of molecules because the atomic nuclei, which do not scatter X-rays, make a major contribution to the electron scattering. The diffraction effects observed with electrons should therefore serve more nearly to locate the nuclei of the molecular atoms.

† *J. Chem. Phys.* **3** (1935), 699.

§ *J. Chem. Phys.* **9** (1941), 55.

‡ Loc. cit.

The accuracy of the method depends very largely on the scattering power of the atoms concerned. For a given structure the atomic separations of such atoms as chlorine can be determined with an error of less than 1 per cent., whereas for light atoms such as carbon it is not likely to be less than 5 per cent. and hydrogen atoms cannot be located at all. This limitation also affects the accuracy of structure determination. Thus, to determine the bond angle in a triatomic molecule such as ClO_2 , the O—O separation must be determined accurately. The scattering power of the chlorine is so much greater than that of the oxygen that only the Cl—O distances can be derived with accuracy and change of the bond angle from 60° to 180° does not markedly affect the theoretical intensity curve. Despite these limitations the method has proved of very great value as it may be used in conjunction with other evidence to obtain information about the structure of a great number of molecules. This may be seen from the list of molecules which have been investigated.†

1.5. *Results obtained by electron diffraction observation*

A remarkably large number of molecules, both organic and inorganic, have been studied by electron diffraction. It is not possible here to discuss the results in detail. A comprehensive table of results obtained for more than 500 substances investigated up to the end of 1949 has been given by Allen and Sutton.†

2. Diffraction of electrons of medium speed by molecules

In the preceding section the formula (4), in which the contribution of the molecular binding to the scattering is ignored, is applied to the scattering of such fast electrons that the amplitude f_i for scattering by the i th atom is given accurately by Born's approximation. It is to be expected, however, that the neglect of the molecular binding may still be unimportant for electrons of medium energy for which the amplitude f_i is not given correctly by Born's approximation and must be calculated from the Faxén-Holtmark formula (20) of Chapter III.

In this section we shall discuss the scattering of electrons with these medium energies. Experimental and theoretical work in this direction has been concerned with the study of the angular distribution of electrons elastically scattered by various molecules and of the fine structure of X-ray absorption edges in molecular gases. In the latter the electron ejected by the absorption of the X-ray quantum is diffracted by the surrounding atoms.

† *Acta Crystallographica*, **3** (1950), 46.

2.1. Angular distribution of elastically scattered electrons

The first application of the formula (4), in which the amplitudes f_i were calculated from the static field of the atom by using Faxén and Holtsmark's expression

$$f_i = \frac{1}{2ik} \sum_l (e^{2i\eta_l} - 1)(2l+1)P_l(\cos \theta), \quad (10)$$

where the phases η_l are as discussed in Chap. III, § 2.2, was made by Bullard and Massey.† They calculated the angular distribution of

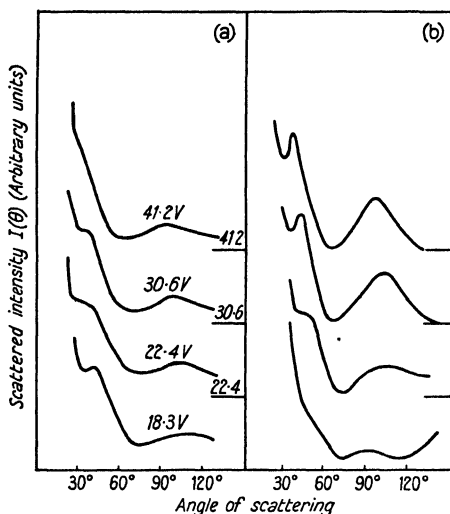


FIG. 97. Comparison of observed and calculated angular distributions of electrons of medium energy scattered in CCl_4 vapour. (a) observed; (b) calculated.

electrons in the energy range 30–780 eV scattered in nitrogen and found reasonable agreement with observation.‡ Some of the most interesting calculations on these lines have been those carried out by Hill and Woodcock§ for the carbon tetrahalides. Neglecting the small contributions from the carbon atom, the scattered intensity becomes, in these cases,

$$I(\theta) = I_h(\theta) \left(1 + \frac{3 \sin x}{x} \right),$$

where $I_h(\theta)$ is the scattered intensity for a single halogen atom and $x = 2kd \sin \frac{1}{2}\theta$, d being the distance between halogen atoms.

† *Proc. Cambridge Phil. Soc.* **29** (1933), 511.

‡ Arnot, *Proc. Roy. Soc. A*, **133** (1931), 615; Bullard and Massey, *ibid.* 637; Mohr and Nicoll, *ibid.* **138** (1932), 469.

§ *Ibid.* **155** (1936), 331.

Fig. 97 illustrates $I(\theta)$ calculated from this formula for CCl_4 compared with observed distributions.[†] The agreement between this theory and observation is remarkably good, even for electrons with energies as low as 18 eV. Similar agreement was found for CF_4 , but for CBr_4 only a rough qualitative correspondence was found with the observed curves. As the approximation depends on the assumption that the electron distribution in the molecular atoms is not disturbed by the binding and that scattering of an electron does not occur more than once within the molecule, it is not surprising that the agreement is not good for a molecule containing such large atoms as bromine which must overlap considerably. The surprising thing is rather that the agreement should be so close for CCl_4 .

A discussion on these lines has also been given by Hughes and McMillen[‡] of their results on the scattering of electrons by CH_4 , C_2H_4 , and C_2H_2 . They found it to be useful in providing a qualitative description of the relative scattering in these cases.

An alternative procedure was introduced by Frye[§] to analyse the results of electron scattering measurements in gaseous bromine. Assuming the formula

$$I(\theta) = |f_a(\theta)|^2 \left(1 + \frac{\sin x}{x} \right),$$

where $f_a(\theta)$ is the amplitude scattered by a free bromine atom, he first obtained $|f_a(\theta)|$ and then derived the values of the phases in the formula (10) which gave the best agreement with the observed angular distributions in the electron energy range from 15 to 121 eV. These 'observed' phases are not very different from those estimated by Shaw and Snyder^{††} from Holtsmark's calculated phases for krypton (see Chap. III, § 2.31 and Fig. 64). Frye went further and derived an atomic field for bromine which would give the 'observed' phases.

2.2. The fine structure of X-ray absorption edges in molecular gases

X-radiation of quantum energy greater than that of the K electrons of the atoms of a gas may be absorbed by the gas in ejecting a K electron by the photo-electric effect. The absorption coefficient of a monatomic gas, due to this effect, falls off steadily as the frequency increases beyond the long wave-length limit. It was found, however, by Hanawalt^{‡‡} in 1931 that, if the gas is polyatomic, the variation of the absorption

[†] Hill and Woodcock, loc. cit.

[§] Ibid. **60** (1941), 586.

^{††} *Phys. Rev.* **57** (1940), 881.

[‡] *Phys. Rev.* **44** (1933), 876.

^{||} Arnot, *Proc. Roy. Soc. A*, **144** (1934), 360.

^{‡‡} Ibid. **37** (1931), 715.

coefficient with the quantum energy may be more complicated. Within an energy range of a few hundred electron volts extending from the long wave-length limit, the absorption coefficient may exhibit a series of maxima and minima. This may be seen by reference to Fig. 99(a), which illustrates the effect for germanium tetrachloride.†

The theoretical explanation of the maxima and minima was first given by Kronig,‡ who showed that they arose by diffraction of the photo-electron ejected from the central atom, by the surrounding atoms. This effect may be discussed in a very similar way to the treatment of electron scattering in the preceding section.

Let A be the central atom and B one of the surrounding atoms so that $AB = r'n'$. The absorption coefficient is proportional to the square of the magnitude of the mean dipole moment associated with the electronic transition, i.e. to $|\mathbf{M}|^2$ where

$$\mathbf{M} = e \int \psi_0(x, y, z) \mathbf{r} \psi_f^*(x, y, z) d\tau.$$

$\mathbf{M}$ is the dipole moment $e\mathbf{r}$ averaged over the wave functions ψ_0, ψ_f of the initial and final states. ψ_0 is the spherically symmetrical wave function for a K electron of atom A . If the electron is ejected in the direction of the unit vector $\mathbf{n}_0$ then, in the absence of the surrounding atoms, ψ_f has the form of a plane wave together with a scattered spherical wave. The latter arises from the distortion of the plane wave $e^{ik\mathbf{n}_0 \cdot \mathbf{r}}$ by the field of the atom A , k being as usual the wave number of the ejected electron.

When an atom such as B is present it also produces a distortion of the plane wave by introducing a spherical wave system centred round B . As viewed from A that part of this spherical wave system which travels in the direction BA , i.e. of $-\mathbf{n}'$, will appear as a second incident plane wave $qe^{-ik\mathbf{n}' \cdot \mathbf{r}}$, q being an amplitude factor depending on the strength of the scattering from B . This plane wave will also be modified by the atomic field of A , so that we may write

$$\psi_f = \psi_f^a(x, y, z) + q\psi_f^b(x, y, z). \quad (11)$$

$\psi_f^a(x, y, z)$ includes the incident plane wave $e^{ik\mathbf{n}_0 \cdot \mathbf{r}}$ and the corresponding scattered wave. $q\psi_f^b(x, y, z)$ includes the apparent plane wave $qe^{-ik\mathbf{n}' \cdot \mathbf{r}}$, incident by scattering from B , and the corresponding scattered wave. $\psi_f^b(x, y, z)$ will differ from $\psi_f^a(x, y, z)$ only in that its axis of symmetry will be the vector $-\mathbf{n}'$ instead of $\mathbf{n}_0$.

We have now, dropping the superscript a ,

$$\mathbf{M} = \mathbf{M}_1 + q^*\mathbf{M}_2,$$

where

$$\mathbf{M}_1 = e \int \psi_0(x, y, z) \mathbf{r} \psi_f^*(x, y, z) d\tau,$$

$$\mathbf{M}_2 = e \int \psi_0(x, y, z) \mathbf{r} \psi_f^*(x_1, y_1, z_1) d\tau.$$

To relate $\mathbf{M}_1$ and $\mathbf{M}_2$ choose the direction $\mathbf{n}_0$ as the x -direction and let $\mathbf{n}'$ lie in the plane of x and y . We then have (see Fig. 98)

$$M_{1y} = M_{1z} = 0,$$

$$x = x_1 \cos\vartheta - y_1 \sin\vartheta, \quad y = x_1 \sin\vartheta + y_1 \cos\vartheta, \quad z = z_1.$$

† Coster and Klammer, *Physica*, **1** (1934), 889.

‡ *Zeits. f. Phys.* **75** (1932), 468. See also Petersen, *ibid.* **80** (1933), 258 and Diss. Groningen, *Arch. Néerland*, **14** (1933), 165.

Changing the axes for the calculation of $\mathbf{M}_2$ to x_1, y_1, z_1 we have, since $\psi_0(x, y, z)$ (being spherically symmetrical) $= \psi_0(x_1, y_1, z_1)$,

$$M_{2x} = \cos\vartheta M_{1x}, \quad M_{2y} = \sin\vartheta M_{1x}, \quad M_{2z} = 0,$$

and

$$|\mathbf{M}|^2 = |\mathbf{M}_1|^2 \{1 + (q + q^*) \cos\vartheta + |q|^2\}.$$

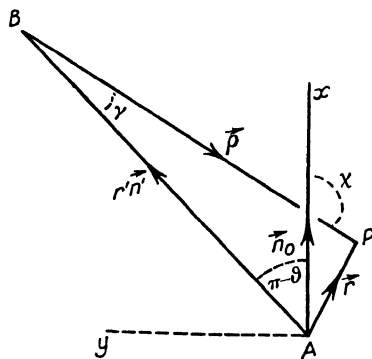


FIG. 98.

To complete the calculation it is necessary to sum over all surrounding atoms B and average over all orientations of the molecule relative to the direction of ejection. We then have, finally,

$$\frac{\chi_m}{\chi_a} = 1 + \frac{1}{2} \sum_B \int_0^\pi \{(q_B + q_B^*) \cos\vartheta + |q_B|^2\} \sin\vartheta_B d\vartheta_B, \quad (12)$$

where χ_m, χ_a are the respective absorption coefficients of molecule and atom.

It remains to calculate q_B . As in the preceding sections we assume that each atom scatters independently and make no allowance for multiple scattering back and forth between the different atoms. Referring to Fig. 98 we take B as origin so that the incident plane wave with the corresponding wave scattered by B is given, at a point P , by

$$\psi = e^{ikn_0 \cdot P} + \rho^{-1} e^{ik\rho f(\chi)},$$

assuming that $k\rho$ is large compared with unity. Writing now $P = r - r'$, where $r \ll r'$, we have

$$\psi = e^{ikn_0 \cdot r} e^{-ikn_0 \cdot r'} + \frac{e^{ik|r-r'|}}{|r-r'|} f(\vartheta - \gamma).$$

Since $r \ll r'$ we may expand

$$|r - r'| \simeq r' - n' \cdot r,$$

giving

$$\begin{aligned} \psi &\simeq e^{ikn_0 \cdot r} e^{-ikn_0 \cdot r'} + r'^{-1} e^{ikr'} e^{-ikn' \cdot r} f(\vartheta) \\ &= e^{-ikn_0 \cdot r'} [e^{ikn_0 \cdot r} + (r')^{-1} f(\vartheta) \exp\{ikr'(1 + \cos\vartheta)\} e^{-ikn' \cdot r}]. \end{aligned}$$

Apart from the constant phase factor $e^{-ik\mathbf{n}_0 \cdot \mathbf{r}}$ this is of the form of two plane waves $e^{ik\mathbf{n}_0 \cdot \mathbf{r}} + qe^{-ik\mathbf{n}' \cdot \mathbf{r}}$, where

$$q = (r')^{-1} \exp\{ikr'(1 + \cos \vartheta)\} f(\vartheta). \quad (13)$$

$f(\vartheta)$ may be calculated by the method of partial cross-sections (equation (10)), if the field of the atom B is known.

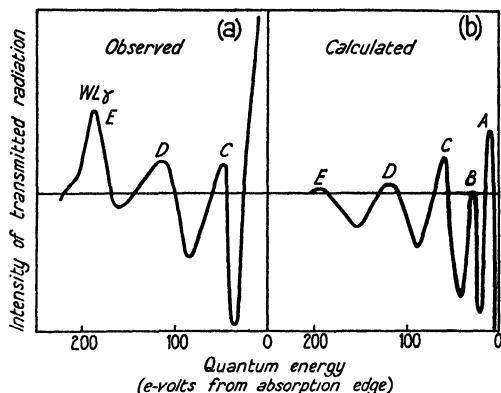


FIG. 99. The structure on the short wave-length side of the K absorption edge of GeCl_4 . (a) observed; (b) calculated.

The resolution of the spectrograph would not have enabled the peaks A and B of the calculated curve to be resolved. The positions of peaks C and D agree well in the two curves. The calculated peak E is masked by the WL_γ line.

The most detailed calculations on these lines have been carried out by Hartree, Kronig, and Petersen† for GeCl_4 . $f(\vartheta)$ was calculated for chlorine using the self-consistent field for that atom obtained by the Hartree method (see Chap. III, § 2.1), the various phases appearing in the expression for $f(\vartheta)$ being evaluated by numerical integration of the appropriate differential equations (see Chap. III, § 2.23). Assuming that the GeCl_4 molecule is tetrahedral in shape with the distance of each chlorine atom from the central atom $2.10 \text{ \AA}$, quite good agreement with observation was found, as may be seen by reference to Fig. 99.

Shaw and Snyder‡ have used Kronig's theory to calculate the fine structure of the X-ray absorption by gaseous bromine, for which measurements are available.§ In this case a considerable sensitivity is found particularly with regard to the behaviour of the η_1 phase at low electron energies. They used phases derived from Holtmark's calculations for krypton (see Chap. III, Fig. 64). An alternative procedure is to use the phases derived by Frye from Arnot's observations on electron

† *Physica*, **1** (1934), 895.

§ Shaw, *ibid.* 877.

‡ *Phys. Rev.* **57** (1940), 881.

scattering in bromine (see § 2.1). Fig. 100 illustrates the comparison between the observed absorption coefficients and those calculated using Frye's phases. General but not detailed agreement will be noted.

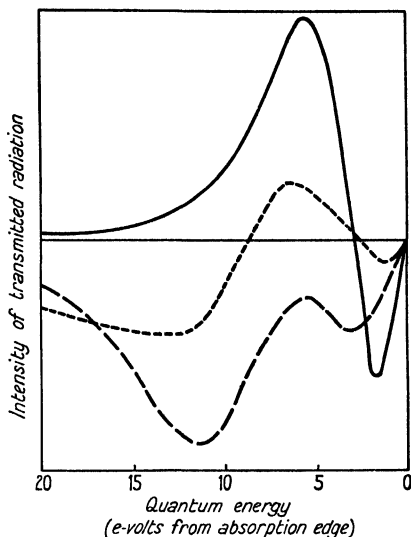


FIG. 100. The structure on the short wave-length side of the K absorption edge of Br_2 .

——— observed; ——— calculated from equation (12) using the phases by derived Frye for electron scattering by Br ; - - - - calculated using phases of Shaw and Snyder for krypton, adjusted appropriately.

In principle this method provides another means of investigating molecular structure, but in practice it is limited by the rather laborious calculations which have to be carried out in analysing each case. The only polyatomic molecule apart from GeCl_4 to which it has been applied is AsCl_3 .†

3. Scattering of slow electrons by molecules

We now consider the scattering of electrons which have energies comparable with those of molecular binding and wave-lengths of the same order or greater than interatomic separations. The scattering effects observed with these electrons should depend considerably on the modifications of the electron distributions with respect to the various atoms within the molecule by the valence forces. The experimental results establish that this is so in many cases, but it is very difficult to develop a satisfactory theory which would enable one to work back from

† Coster and Klammer, loc. cit.

the observed scattering to the charge distribution in the molecule. Some progress has been made in this direction but, as will be seen from § 3.2, a great deal more theoretical work is yet required.

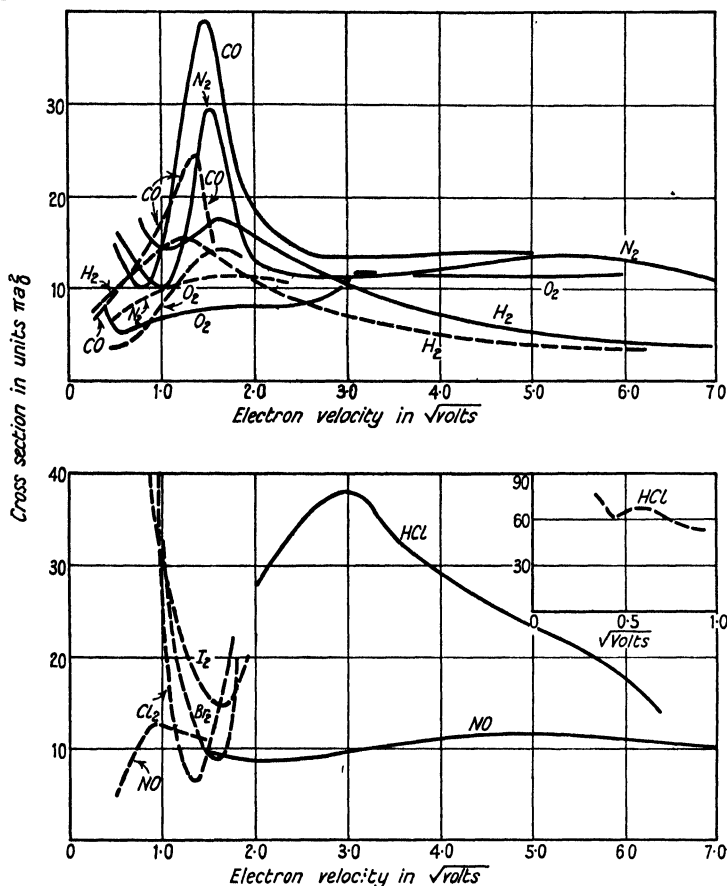


FIG. 101. Total collision cross-sections of diatomic molecules for slow electrons.

(a) H_2 , N_2 , O_2 , CO . (b) Cl_2 , Br_2 , I_2 , HCl , NO .

— values obtained by the Ramsauer method; --- values obtained by the Townsend method.

The values obtained by the Townsend method represent diffusion cross-sections, averaged over a range of energies, at different mean energies.

3.1. Observed cross-sections

The methods of Ramsauer and of Townsend have been applied to the determination of the total cross-sections of a number of molecules towards slow electrons.

The diatomic molecules which have been investigated are hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, carbon monoxide, nitric oxide, and hydrogen chloride.† The observed cross-section velocity curves for these molecules are illustrated in Fig. 101.‡ (When curves have been given by more than one investigation, averaged results are given.) Results obtained by the Townsend method, which refer to mean diffusion cross-sections only (see Chap. I, § 8), are denoted by broken lines, those obtained by the Ramsauer method by full-line curves.

The total cross-sections for a number of organic series of molecules have been measured in an attempt to observe correlations with the nature of the chemical binding. Thus Fig. 102(a) exhibits the contrast between the behaviour of ethane, ethylene, and acetylene,§ while Fig. 102(b) shows the similarity of behaviour in the paraffin series from methane (CH_4) to butane (C_4H_{10}).|| It is also of interest to note the remarkable similarity in behaviour between methane†† and argon. This may be seen by reference to Fig. 103. The detailed structure of a hydrocarbon does not seem to exert any important influence—isomers behave in very nearly the same way as may be seen in Fig. 102(c), where results are given for the normal and isomeric forms of butane and pentane.‡‡ Even isomers which differ very considerably in structure, such as ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) and methyl ether ($(\text{CH}_3)_2\text{O}$),§§ do not seem to behave very

† H_2 : Ramsauer, *Ann. der Physik*, **64** (1921), 513; Townsend and Bailey, *Phil. Mag.* **44** (1923), 1033; Rusch, *Phys. Zeits.* **26** (1925), 748; Brode, *Phys. Rev.* **25** (1925), 636; Brüche, *Ann. der Physik*, **81** (1926), 537 and **82** (1927), 912; Normand, *Phys. Rev.* **35** (1930), 1217; Ramsauer and Kollath, *Ann. der Physik*, **4** (1930), 91.

O_2 : Brose, *Phil. Mag.* **50** (1925), 536; Brüche, *Ann. der Physik*, **83** (1927), 1065; Ramsauer and Kollath, *ibid.* **4** (1930), 91.

N_2 : Ramsauer, *ibid.* **64** (1921), 513; Townsend and Bailey, *Phil. Mag.* **42** (1921), 873; Brode, *Phys. Rev.* **25** (1925), 636; Brüche, *Ann. der Physik*, **81** (1926), 537 and **82** (1927), 912; Normand, *Phys. Rev.* **35** (1930), 1217; Ramsauer and Kollath, *Ann. der Physik*, **4** (1930), 91; Fisk, *Phys. Rev.* **51** (1937), 25.

Cl_2 : Bailey and Healey, *Phil. Mag.* **19** (1935), 725; Fisk, *Phys. Rev.* **51** (1937), 25.

Br_2 : Bailey, Makinson, and Somerville, *Phil. Mag.* **24** (1937), 177.

I_2 : Healey, *ibid.* **26** (1938), 940.

CO : Skinner and White, *ibid.* **46** (1923), 630; Brode, *Phys. Rev.* **25** (1925), 636; Brüche, *Ann. der Physik*, **83** (1927), 1065; Normand, *Phys. Rev.* **35** (1930), 1217; Ramsauer and Kollath, *Ann. der Physik*, **4** (1930), 91.

NO : Skinner and White, *loc. cit.*; Brüche, *Ann. der Physik*, **83** (1927), 1065.

HCl : Brüche, *ibid.* **82** (1927), 25; Bailey and Duncanson, *Phil. Mag.* **10** (1930), 145.

‡ The curves for Cl_2 are given in Fig. 107 on a different scale.

§ Bannion and Bröse, *Phil. Mag.* **6** (1928), 817; Brüche, *Ann. der Physik*, **2** (1929), 909 and **4** (1930), 387.

|| Brüche, *ibid.* **4** (1930), 387.

†† Brode, *Phys. Rev.* **25** (1925), 636; Brüche, *Ann. der Physik*, **83** (1927), 1065 and **4** (1930), 387; Ramsauer and Kollath, *ibid.* **4** (1930), 91.

‡‡ Brüche, *ibid.* **5** (1930), 281.

§§ Schmieder, *Zeits. f. Elektrochem.* **36** (1930), 700.

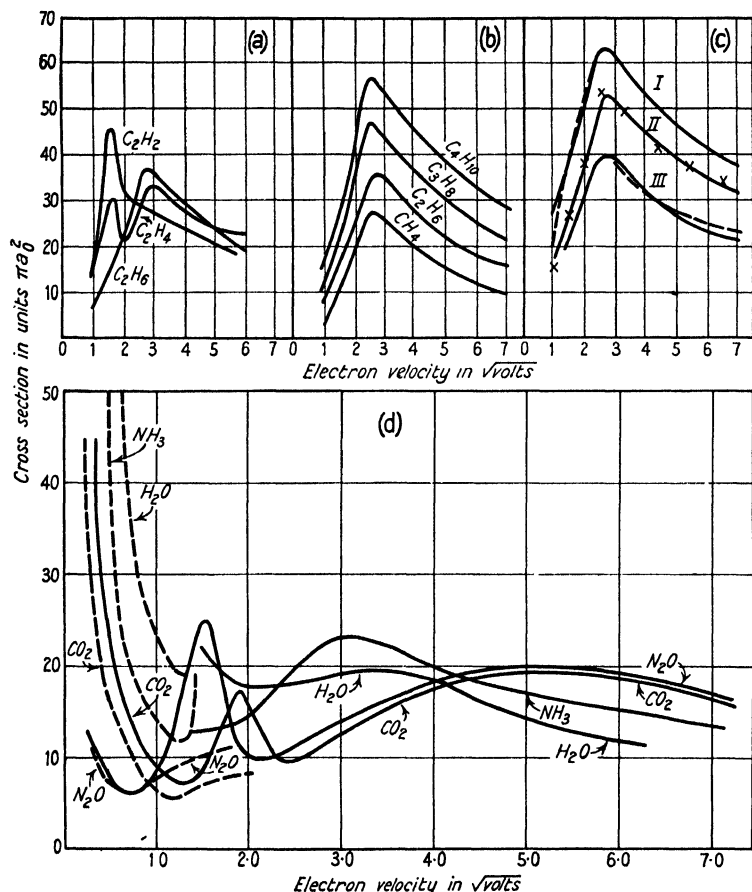


FIG. 102. Total collision cross-sections for slow electrons scattered by
 (a) C_2H_2 , C_2H_4 , C_2H_6 (Ramsauer method).
 (b) molecules of the paraffin series CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} (Ramsauer method).
 (c) normal pentane (C_3H_{12}) curve I — (Ramsauer method)
 iso-pentane (C_3H_{12}) ,, I ———— ,, ,,
 normal butane (C_4H_{10}) ,, II ———— ,, ,,
 iso-butane (C_4H_{10}) ,, II × × × × ,, ,,
 methyl ether ($(CH_3)_2O$) ,, III ———— ,, ,,
 ethyl alcohol (C_2H_5OH) ,, III ———— ,, ,,
 (d) H_2O , NH_3 , CO_2 , N_2O . ———— Ramsauer method.
 ----- mean diffusion cross-section from the Town-
 send method.

differently towards slow electrons (see Fig. 102(c)). Other groups of related organic molecules which have been investigated are the singly

substituted methanes CH_3F , CH_3OH , CH_3NH compared with CH_4 ; $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_3\text{CH}^\dagger$ and CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 .[‡]

Finally in Fig. 102 (*d*) results obtained for H_2O , NH_3 , CO_2 , and N_2O ,[§] all of which possess dipole moments, are illustrated.

In general the behaviour of the different molecules presents a range of variation in character and magnitude similar to that for the atoms. Before discussing the extent to which the details can be interpreted theoretically we shall describe the observations which have been carried out on the angular distribution of electrons scattered elastically by molecules.

The methods described in Chap. II, § 7, for observing the angular distribution of slow electrons scattered elastically by molecules have also been applied to a number of molecular gases—the diatomic molecules H_2 , N_2 , CO , Br_2 , and I_2 , the hydrocarbons CH_4 , C_2H_6 , C_2H_4 , and C_2H_2 , the inorganic hydrides PH_3 and H_2S , carbon dioxide, the carbon tetrahalides CF_4 , CCl_4 , and CBr_4 and also CH_2Br_2 .|| Of these, the results for PH_3 and H_2S have already been described in Chap. III, § 2.42, as being roughly representative of those expected for the P and S atoms respectively, and those for CF_4 , CCl_4 , and CBr_4 have been discussed in § 2.1 of this chapter.

The angular distribution curves for hydrogen resemble those for helium in exhibiting no marked maxima and minima. Those for nitrogen and carbon monoxide reveal very close similarity at all electron energies.

[†] Schmieder, *Zeits. f. Elektrochem.* **36** (1930), 700.

[‡] Holst and Holtsmark, *Kong. Norsk. Vid. Selskab.* **4** (1931), 89.

[§] H_2O and NH_3 : Brüche, *Ann. der Physik*, **1** (1929), 93; Bailey and Duncanson, *Phil. Mag.* **10** (1930), 145.

CO_2 : Skinker, *ibid.* **44** (1922), 994; Brüche, *Ann. der Physik*, **83** (1927), 1065; Ramsauer and Kollath, *ibid.*, **4** (1930), 91.

N_2O : Skinker and White, *Phil. Mag.* **46** (1923), 630; Brüche, *Ann. der Physik*, **83** (1927), 1065; Ramsauer and Kollath, *ibid.* **7** (1930), 176.

|| H_2 : Bullard and Massey, *Proc. Roy. Soc. A*, **133** (1931), 637; Arnot, *ibid.* 615; Ramsauer and Kollath, *Ann. der Physik*, **12** (1932), 837; Mohr and Nicoll, *Proc. Roy. Soc. A*, **138** (1932), 469; Hughes and McMillan, *Phys. Rev.* **41** (1932), 39; Webb, *ibid.* **47** (1935), 384.

N_2 : Bullard and Massey, *loc. cit.*; Arnot, *loc. cit.*; Mohr and Nicoll, *loc. cit.*

CO : Arnot, *loc. cit.*; Ramsauer and Kollath, *Ann. der Physik*, **12** (1932), 529 and *Phys. Zeits.* **32** (1931), 867.

Br_2 , I_2 , and CH_2Br_2 : Arnot, *Proc. Roy. Soc. A*, **144** (1934), 360.

CH_4 : Bullard and Massey, *loc. cit.*; Arnot, *Proc. Roy. Soc. A*, **133** (1931), 615; Mohr and Nicoll, *loc. cit.*; Hughes and McMillan, *Phys. Rev.* **44** (1933), 876.

C_2H_6 : Childs and Woodcock, *Proc. Roy. Soc. A*, **146** (1934), 199.

C_2H_4 and C_2H_2 : *ibid.*; Hughes and McMillan, *Phys. Rev.* **44** (1933), 876.

PH_3 and H_2S : Mohr and Nicoll, *loc. cit.*

CO_2 : Arnot, *Proc. Roy. Soc. A*, **133** (1931), 615; Mohr and Nicoll, *loc. cit.*

CF_4 , CCl_4 , and CBr_4 : see references, p. 200.

An interesting feature of the results for methane is noticed on comparison with argon (see Fig. 103). For electrons with energies greater

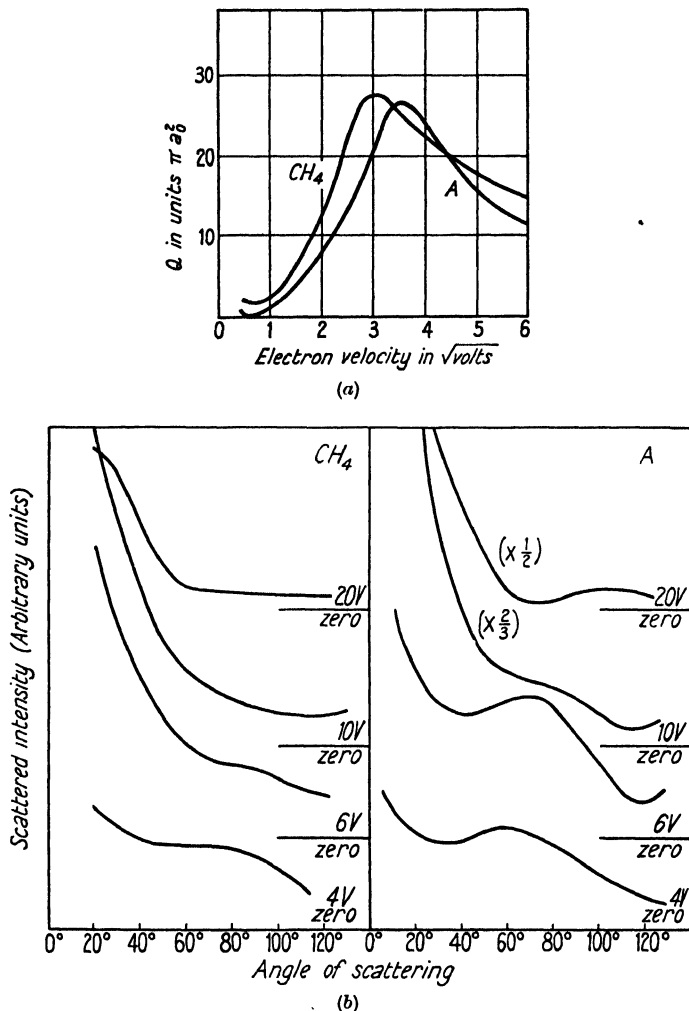


FIG. 103. Comparison of scattering of slow electrons in A and CH₄.
 (a) Total collision cross-section (Ramsauer).
 (b) Angular distribution.

than 20 eV there is no resemblance, but for slower electrons there is quite a distinct similarity between the two sets of angular-distribution

curves which becomes more marked as the electron energy decreases (see Fig. 103).

3.2. *Theory of scattering of slow electrons by molecules*

In order to obtain a theory of the elastic collisions of slow electrons with molecules as satisfactory as that for atoms it would be necessary to extend the Faxén-Holtmark method (Chap. III, § 2.41) to scattering by fields which no longer possess spherical symmetry. Even if this could be done the theory would be hampered by the greater ignorance of molecular as compared with atomic fields. Despite these difficulties it has, however, proved possible to extend the Faxén-Holtmark theory to a sufficient extent by approximate methods to obtain some interesting results for certain molecules.

Whereas the Schrödinger equation for the motion of electrons in a spherically symmetrical field of force can always be solved in principle, the corresponding problem for an axially symmetrical field is, in general, insoluble. However, by using spheroidal coordinates it is possible to obtain solutions for certain forms of axially symmetrical field which are likely to be rather similar to the actual fields of diatomic molecules. Stier† and, later, Fisk‡ have taken advantage of this to develop a theory of the elastic scattering of slow electrons by diatomic molecules which is a direct generalization of the Faxén-Holtmark method of partial cross-sections (see Chap. III, § 2.4) which deals so successfully with the spherically symmetrical fields of atoms.

The total angular momentum of the incident electron about the centre of the molecule is no longer a constant of the motion. On the other hand, the component of the angular momentum in the direction of the nuclear axis is constant and is therefore quantized, the allowed values being $m\hbar$, $m = 0, 1, 2, \dots$. The incident wave may therefore be resolved into partial waves for which $m = 0, 1, 2, \dots$, etc. With the particular fields for which the Schrödinger equation is separable in spheroidal coordinates a further resolution may be made for a given value of m , as follows. When the two foci of the spheroidal coordinate system (the two nuclei) are allowed to come together (the united atom limit) the resolution in terms of the total angular momentum quantum number $l + m$ is again possible as the system is once more spherically symmetrical. In the spheroidal case a partial wave denoted by m, l is one in which the axial angular momentum is $m\hbar$ and the total angular momentum in the united atom limit is $\{(l+m)(l+m+1)\}^{\frac{1}{2}}\hbar$. For each such partial wave a phase-shift η_{lm} is introduced by the scattering field. The total elastic

† *Zeits. f. Phys.* **76** (1932), 439.

‡ *Phys. Rev.* **49** (1936), 167.

scattering cross-section Q_0 , averaged over all orientations of the molecular axis, becomes

$$Q_0 = \sum_{m,l} q_{ml},$$

where

$$\begin{aligned} q_{ml} &= \frac{2\pi}{k^2} \sin^2 \eta_{ml}, & m = 0, \\ &= \frac{4\pi}{k^2} \sin^2 \eta_{ml}, & m \neq 0, \end{aligned}$$

and k is as usual equal to $mv/\hbar$, where v is the electron velocity. Associated with each partial wave is an angular distribution function. This depends, for a fixed orientation of the molecular axis, on the angles specifying the directions of the incident and scattered electrons with respect to the molecular axis. If θ is the angle between the direction of the scattered electron and the molecular axis and ϕ an azimuthal angle specifying the plane containing the molecular axis and the direction of scattering while ω , α are similar angles defining the direction of incidence, then under these conditions the scattered intensity $I(\vartheta)$ is found to be

$$I(\vartheta) = k^{-2} \left| \sum_{m,l} (e^{2i\eta_{ml}} - 1) S_{ml}(kd, \cos \theta) S_{ml}(kd, \cos \omega) \cos m(\phi - \alpha) \right|^2 \quad (14)$$

with $\cos \vartheta = \cos \theta \cos \omega + \sin \theta \sin \omega \cos(\phi - \alpha)$.

The first few functions $S_{ml}(c, \cos \theta)$ for $m, l = 0, 0; 1, 0; \text{ and } 0, 1$ for a series of typical values of c are shown in Fig. 104.

It will be noticed that in contrast to the scattering by a spherically symmetrical field S_{ml} , and thence the angular distribution of the scattered electrons, depends on the energy of the electrons through kd where d is the nuclear separation.

As pointed out above the expression (14) refers to a fixed molecular orientation and accordingly must be averaged over all possible orientations.

As $k \rightarrow 0$, i.e. for slow electrons, all the partial cross-sections tend to zero except q_{00} which tends to a finite value. The corresponding angular function S_{00} also tends to a constant value as $k \rightarrow 0$, so the averaged angular distribution tends to become spherically symmetrical for sufficiently slow electrons just as for atoms.

In carrying out detailed calculations, involving determination of the phases η_{ml} , it is necessary to confine oneself to axially symmetrical scattering potentials which permit the separation of the spheroidal coordinates in the wave equation. It has, nevertheless, been possible to choose forms which provide a satisfactory representation of the observed

scattering by many molecules. In the first detailed study on these lines Stier† used for the potential of the molecular field

$$V = -2Z\epsilon^2 d^{-1} \rho f(\rho)/(\rho^2 - \mu^2), \quad (15)$$

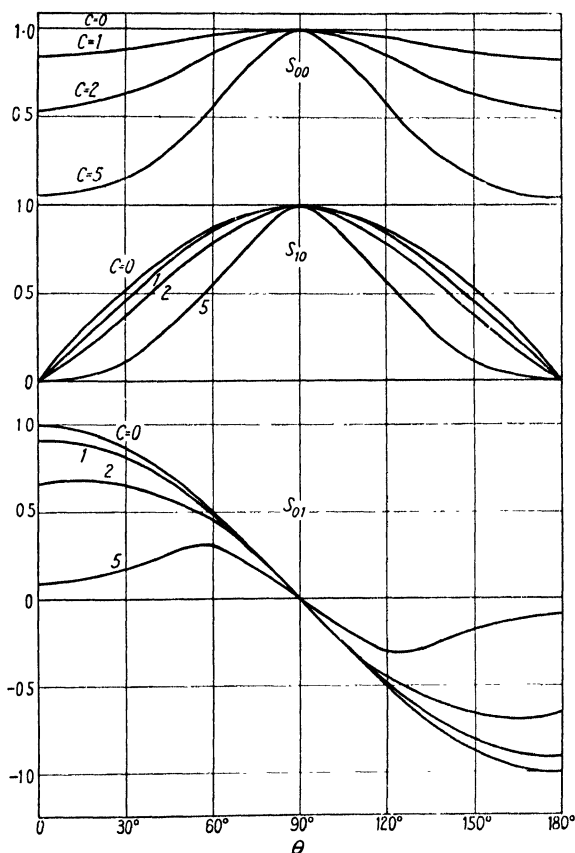


FIG. 104. The functions $S_{ml}(c, \cos \theta)$ for $m, l = 0, 0; 1, 0; 0, 1$; and $c = 0, 1, 2, 5$.

where $\rho = (r+p)/d$, $\mu = (r-p)/d$. Z is an effective nuclear charge and r, p refer to the distances from the centres of the two atoms in the molecule. $f(\rho)$ was taken to be of the form

$$\begin{aligned} f(\rho) &= (\rho - \rho_0)^2 / (\rho_0 - 1)^2, & \rho < \rho_0, \\ &= 0, & \rho > \rho_0. \end{aligned}$$

† Loc. cit.

Two parameters Z and ρ_0 are thus available for adjustment of theory to agree with observation. Choice of the values $\rho_0 = 3.46$, $Z = 4.08$ gave good agreement with observed cross-section curves for electrons of energy less than 10 eV.

The most extensive calculations have been carried out by Fisk,[†] who was guided by the method of Morse and Allis for dealing with scattering by atoms (see Chap. III, § 2.35). He also took V in the form (15) but with

$$f(\rho) = 1 - \frac{\rho_0(\rho-1)}{\rho(\rho_0+1)}^2,$$

and studied the variation of η_{ml} , and hence of the q_{ml} , with two parameters β and x exactly analogous to those introduced by Morse and Allis for atoms. Thus $\beta^2 = \frac{1}{4}Zd\rho_0$ and $x = \rho_0 kd$. Throughout the work ρ_0 was taken to be 2, as it was found that the results were rather insensitive to values of ρ_0 between 1.75 and 3.0. While x is proportional to the electron velocity, β depends only on the molecular field. For a fixed x the partial cross-sections exhibit a periodic behaviour with β .

The method was applied to hydrogen, nitrogen, oxygen, and chlorine. For hydrogen only the 0, 0 partial wave is affected if the electron energy is below 10 eV and good agreement is obtained with the observed total cross-section if β is taken to be 0.6 (see Fig. 105 (a)). The results for nitrogen and oxygen are of considerable interest in revealing the power and limitations of the method. Fig. 105 (b) and (c) illustrates the good agreement obtained and the contributions from the partial cross-sections. The small increase in β from 1.32 to 1.35 in going from nitrogen to oxygen has a very pronounced effect in removing the sharp maximum for 2.25-volt electrons in nitrogen which is due to the 1, 0 partial wave. The angular distribution at this maximum derived from averaging

$$[S_{10}(kd, \cos \theta) S_{10}(kd, \cos \omega) \cos(\phi - \alpha)]^2$$

is compared with the observations in Fig. 106. The form of the observed distributions perhaps approximates more closely to that derived from the function S_{01} (Fig. 104), and it is of interest to notice that Stier, with his representation of the nitrogen field, did in fact interpret the sharp maximum for 2.25 eV electrons as arising from the 0,1 partial cross-section and not the 1, 0 as did Fisk. Stier's theoretical cross-section and its analysis is compared with observation in Fig. 105, and the good agreement of his angular distribution with the observed may be seen from Fig. 106. By reducing the value of β from 1.3 to about 1.0 in Fisk's nitrogen field a similar analysis to Stier's could be obtained, the 0,1

[†] Loc. cit.

partial cross-section becoming the most important one. The sensitivity in going from nitrogen to oxygen would presumably remain at this lower value of β .

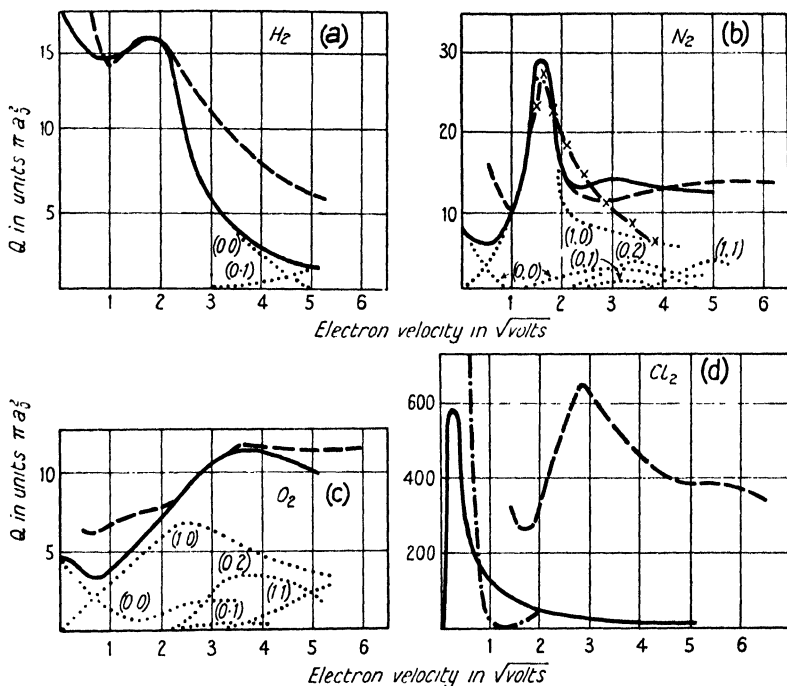


FIG. 105. Comparison with experiment of Fisk's calculations of the total collision cross-section of slow electrons in (a) H_2 , (b) N_2 , (c) O_2 , (d) Cl_2 . The dotted lines represent the contribution from the various partial cross-sections.

— — — experimental values; — — — Fisk's calculated curve; — × — × Stier's calculated curve for N_2 ; — · — · observed values for Cl_2 obtained by Bailey and Healey.

It is of interest to compare the molecular fields of nitrogen used by Stier and by Fisk with that derived by Hund† by an approximate statistical method. Such a comparison is exhibited in Fig. 107.

The agreement obtainable by Fisk's theory in the above cases does not appear when applied to chlorine—the observed total cross-section is very much greater than the theoretical over the range of electron energies investigated (see Fig. 105(d)). The reason for this is not clear and further investigation is called for.

† *Zeits. f. Phys.* **77** (1932), 12.

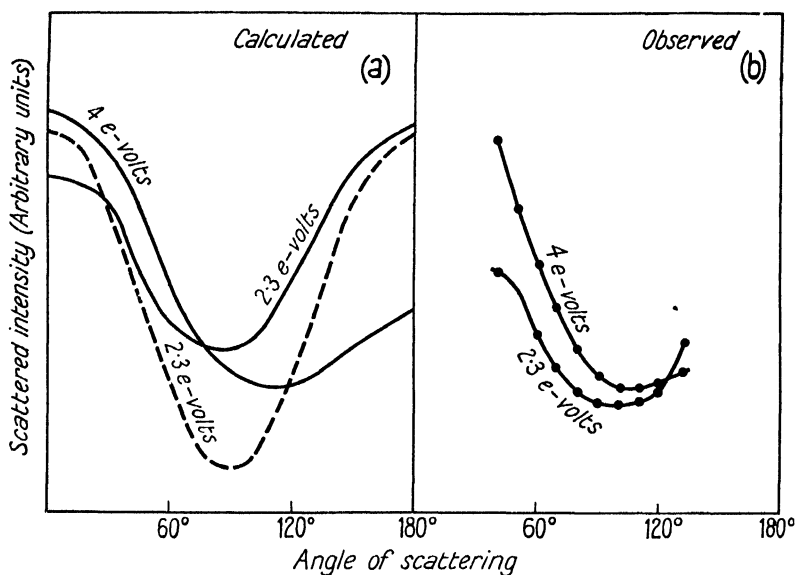


FIG. 106. Comparison of observed and calculated angular distribution of slow electrons scattered in N_2 .

(a) Calculated: ——— Stier (2.3 and 4 eV); --- Fisk (2.3 eV).

(b) Observed: —•—•— (2.3 and 4 eV).

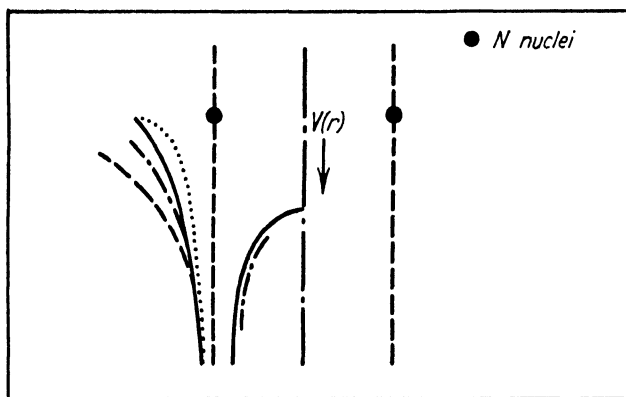


FIG. 107. Variation along the nuclear axis of the molecular field of N_2 used by Stier and by Fisk compared with that calculated by Hund using a statistical method. Between the nuclei the Stier and Fisk fields coincide with the Coulomb field.

——— Fisk; Stier; —•—•— Hund; ---- Coulomb.

One further type of molecular scattering problem is amenable to approximate theoretical treatment. This arises when the molecule possesses such a high degree of symmetry that its scattering field is nearly spherically symmetrical. An interesting illustration is provided by methane. The remarkable resemblance between the observed behaviour of methane and of argon towards slow electrons has already been stressed in § 3.1. Close similarity between the mean field outside the molecule and that of the atom at these distances must be responsible. This can only be represented by taking into account the highly symmetrical average field in which the outer electrons move in methane. Buckingham, Massey, and Tibbbs† have calculated a spherically symmetrical average field for the methane molecule by first averaging the field due to the protons over a sphere and then applying the usual self-consistent field method of Hartree. They calculate the phases for scattering of electrons by this spherically symmetrical field, in the usual way (Chap. III, § 2.23), and find that close similarity in behaviour to argon would indeed be expected for electrons with energies less than about 20 eV. For such electrons the calculated first- and second-order phases are about the same for both, while the zero-order phase for argon exceeds that for methane by π . As these are the only important phases the scattering effects should be much the same for both. The fact that the zero-order phase for methane is less by π than that for argon means that methane can be regarded as filling the place in the series xenon, krypton, and argon which one might have thought would be occupied by neon (see Chap. III, §§ 2.31, 2.32). Thus the occurrence of the Ramsauer-Townsend effect in methane arises because the molecular field is just strong enough to introduce exactly two extra half waves into the low-energy partial waves with zero angular momentum, whereas the argon field introduces exactly three, krypton four, and xenon five.

It is probable that much interesting information about the outer fields of molecules could be derived from a systematic study of the elastic scattering of slow electrons in conjunction with approximate theories, but a much wider range of molecular types would have to be investigated than have been examined up to the time of writing.

4. Inelastic collisions of electrons with molecules—Electronic excitation

4.1. *Introductory—Quantum states of diatomic molecules*

The problem of describing the quantum states of even a diatomic molecule seems at first sight to be a very complicated one. Allowance

† *Proc. Roy. Soc. A*, **178** (1941), 119.

must be made for nuclear vibration and rotation as well as for the motion of the electrons relative to the nuclei which alone is important for atoms. Very considerable simplification is introduced, however, by the relatively great mass of the nuclei compared with that of the electrons. Even for the lightest molecule, hydrogen, this mass ratio is 1,850. As a result, in all molecules the electrons are much more mobile than the nuclei and are usually able to adjust themselves to changing nuclear motion without sufficient disturbance to produce a transition in their own state of motion. For any fixed nuclear separation R of a molecule AB we can derive a set of electronic energy levels $\epsilon_n(R)$, $n = 1, 2, \dots$, with corresponding wave-functions $\phi_n(\mathbf{r}, R)$, $\mathbf{r}$ representing the aggregate of electronic coordinates relative to the centre of mass of the nuclei. In the limit of infinitely large nuclear separation R , $\epsilon_n(R)$ will simply become the sum of the energies of two definite states, either of the atoms A and B , of the ions A^+ and B^- or of the ions A^- and B^+ . It is important to note, however, that more than one molecular electronic level may tend to the same limit at infinite separation. Thus, while the energy of the ground electronic level of a molecule will tend to that of the two atoms in their ground states, there may be other molecular levels which tend to this same limit.

When we allow the nuclei to move, we now assume that the electronic motion adjusts itself so that, when the nuclear separation is R , the energy of the system due to the electronic motion is $\epsilon_n(R)$. The nuclei, of charge Z_1e , Z_2e respectively, can then be regarded as moving in a field of force of potential $\eta_n(R) = \epsilon_n(R) + Z_1Z_2e^2/R$. The plot of $\eta_n(R)$ against R is therefore referred to as the potential energy curve for the molecule in the n th electronic state. Its form determines the nature of the nuclear motion. The two most important cases which arise are illustrated in Fig. 108.

In Fig. 108(a) the potential energy curve has a minimum at $R = R_0$, which is therefore an equilibrium separation for the nuclei. As $R \rightarrow \infty$ the curve tends asymptotically to a point representing the sum of the energies U'_A , U''_B of the two states A' , B'' of the atoms A , B . If we now suppose the nuclei moving under the influence of this potential the quantum states of the nuclear motion will consist of a discrete series of vibrational levels such as at ab , cd in Fig. 108(a), converging to a limit at the electronic energy possessed by the system when at infinite nuclear separation. Above this limit there will be a continuum of unclosed nuclear states representing a dissociated molecule in which the nuclei have various amounts of kinetic energy of relative motion. These

nuclear levels are illustrated in Fig. 108 (a). The total energy of the molecule in the particular electronic state corresponding to a will be given by

$$\epsilon_n(R_0) + v_{ns},$$

where v_{ns} is the energy of the nuclear motion.

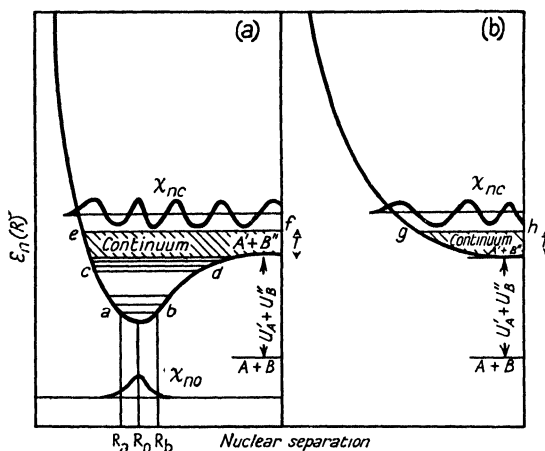


FIG. 108. Types of potential energy curves and vibrational wave functions χ for a diatomic molecule.

(a) Typical curve for a bound state.

(b) Typical curve for a repulsive state.

Corresponding to this energy the nuclear wave function will have the form

$$\Psi_{ns}(R, \mathbf{r}) = \psi_n(R, \mathbf{r})\chi_{ns}(R). \quad (16)$$

Here $\psi_n(R, \mathbf{r})$ is the electronic wave function defined for each nuclear separation and χ_{ns} is the wave function for the nuclear motion. The wave function χ_{n0} for the lowest vibrational state is very small in regions outside the classically allowed motion, i.e. for values of $R < R_a$ or $R > R_b$ in Fig. 108 (a), and has the general form illustrated in that figure. For higher vibrational levels the vibrational wave functions χ_{ns} are also small outside the classically allowed region but have s nodes within that region.

A state lying within the continuum of nuclear levels no longer represents a stable molecule, but the wave function can still be written approximately in the form (16). The function χ_{nc} representing the nuclear motion in this case will consist of modulated plane waves in the classically allowed region, falling rapidly to zero at closer nuclear separations, as illustrated diagrammatically in Fig. 108 (a).

A state in the nuclear continuum represented in Fig. 108(a) by *ef* corresponds to two atoms A' , B'' moving with relative kinetic energy T . If, in particular, the potential energy curve is that for the ground electronic level, the two atoms will be in their normal states. It is important to note also that, if the level of the curve for infinite nuclear separation is the energy of two ions A^+ , B^- , a state such as *ef* would correspond to these two ions moving with the relative kinetic energy T .

In the second type of potential energy curve, illustrated in Fig. 108(b), there is no minimum so that an effective repulsive force exists between the atoms (AB , $A'B''$, A^-B^+ or A^+B^-) at all separations. No stationary nuclear states and no stable molecule can result under these conditions—the electronic state is said to be repulsive. The state of affairs is much the same as for curves of Type *a* when the nuclear motion lies in the continuum, so the wave function can be written again in the form (16) with χ_{nc} as illustrated in Fig. 108(b). A state represented by *gh* in Fig. 108(b) has an exactly similar significance to that of *ef* in Fig. 108(a).

Exactly similar considerations apply to molecular ions such as AB^+ or AB^- . The only difference is that at infinite nuclear separation the potential energy curves tend asymptotically, for AB^+ , to normal and excited states of A and B^+ or A^+ and B , and for AB^- to those of A and B^- or A^- and B .

For stable molecules the ground electronic state gives a potential energy curve of Type *a*. There are molecules such as He_2^+ in which the ground electronic state gives a repulsive curve of Type *b* whereas some of the excited electronic levels give stable curves. At best such molecules can only be metastable since eventually they must make a transition to the ground repulsive state.

In the above discussion we have made no mention of molecular rotation. Each of the vibrational levels we have indicated in Fig. 108(a) are in reality composed of rotational levels the presence of which can lead to many important energy transfers within a molecule. As we shall have no occasion to discuss these effects in special detail the reader is referred to books on molecular spectra such as Kronig, *Band Spectra and Molecular Structure*† or Herzberg, *Molecular Spectra and Molecular Structure*‡ for detailed discussion of molecular energy levels.

It must be remembered, furthermore, that the above treatment, useful as it has been found to be, is, nevertheless, an approximation. The effects neglected, involving the interaction of electronic and

† Cambridge University Press, 1930.

‡ New York, Prentice Hall, 1939.

nuclear motion, can be regarded as small internal perturbations capable of producing transitions between different electronic states defined as above. Important instances of this will be discussed in later sections.

4.2. *Electronic transitions in diatomic molecules—The Franck–Condon principle*

An electronic transition in a molecule may result from the influence of an internal perturbation or of an external one, as in electron impact or in absorption or emission of radiation. The question which immediately arises concerns the way the nuclear separation behaves in the transition. The answer to this follows again from the great ratio of nuclear to electronic mass and is summarized in the Franck–Condon principle which states that, in an electronic transition, the nuclear separation and velocity of relative motion alter to a negligible extent—the transition takes place so quickly that the nuclei have no time to move an appreciable distance. This leads to a number of possible consequences of an electronic transition which depend on the shapes of the potential energy curves of the initial and final electronic states. These are best studied in terms of potential energy diagrams, as illustrated in Fig. 109 for upward electronic transitions in a molecule AB .

In all three cases represented in Fig. 109, curve I is the potential energy curve for the initial electronic state, while curves IIa, IIb, IIc represent three distinct possibilities for the potential energy curve of the upper state. The nuclear separation in the ground vibrational level will effectively lie between the limits a and b in all cases. Hence, according to the Franck–Condon principle, it must still lie within these limits after the transition. Referring to Fig. 109 the final state of the molecule will therefore be represented by points lying between c and d on the upper curves. The three cases which are illustrated then correspond to the following consequences:

Case (a): the final state always lies within the region of the discrete vibrational levels of the upper potential energy curve. The transition always results then in a stable electronically excited molecule possessing also some degree of vibrational excitation.

Case (b): the region in which the final state must lie includes some part of the continuum as well as some discrete vibrational levels of the upper potential energy curve. A certain proportion of the transitions will therefore lead to dissociation of the molecule while others will produce stable excited molecules.

When dissociation occurs the molecule will split into two atoms

quantity. This is the minimum energy necessary to remove an electron from the normal molecule without change of nuclear separation. (Referring to Fig. 109, in which the upper state is taken to be one of AB^+ , the vertical ionization energy is represented by bd in all three cases.) According to the Franck-Condon principle this will be the usual state of affairs in any actual transition. As the equilibrium separation of normal molecule and molecular ion need not be the same it is obvious that the vertical ionization energy will not normally be the difference in energy of the normal states of molecule and molecular ion (thus in Fig. 109 (b), while bd represents the vertical ionization energy, ef represents the difference in the energy of the normal states).

It must be remembered that the above treatment is only an approximation, though a very good one, so there may be a small but finite chance of ionization of the molecule if it receives energy less than the vertical ionization energy, i.e. in Fig. 109 (b) a transition from b to e is theoretically possible but would be associated with a very low probability. This may result in a certain indefiniteness in molecular ionization potentials, depending on the sensitivity of the detecting apparatus. Owing, however, to the small chance of finding the nuclei at a separation represented by f in Fig. 109 (b), the probability of ionization appreciably below the vertical ionization potential is usually negligible (see, however, pp. 232, 246).

4.22. Energetic relations in dissociative transitions. Consider a transition from the ground state of a molecule AB to an upper electronic state. Take as the zero of potential energy the energy of the two normal atoms A, B . If D_{AB} is the dissociation energy of AB , $T_{\min}$ the minimum energy of relative motion of the resulting atoms $A'B''$ (or ions $A+B^-$ or A^-B^+) after the transition, U'_A, U''_B the total excitation energy of these atoms then, according to the Franck-Condon principle, the minimum energy $E_{\min}$ necessary to produce the transition is given by

$$E_{\min} = U'_A + U''_B + D_{AB} + T_{\min}, \quad (17)$$

as may be seen from Fig. 109 (c) in which $T' = E_d$.

This formula applies equally well to ionization of the molecule, leading to production, say, of excited atoms A' and ions B^+ . Its importance lies in the possibility of obtaining information about D_{AB} or the nature of the products A', B^+ by measurement of $E_{\min}$ and T . In any such measurement it is usually only possible to determine the kinetic energy T^+ of the ions B^+ . If M_A, M_B are the respective masses of the atoms A and B , then it follows from the conservation of momentum that

$$T = (1 + M_A/M_B)T^+. \quad (18)$$

Applications of these relations will be described in §§ 5.4, 6.3–5 of this chapter.

4.23. Energy distribution of atoms or ions in a dissociative transition.

In an electronic transition which can lead to dissociation, the resulting atoms or ions may have relative kinetic energy lying within a finite range. It is of interest and importance to have some means of estimating

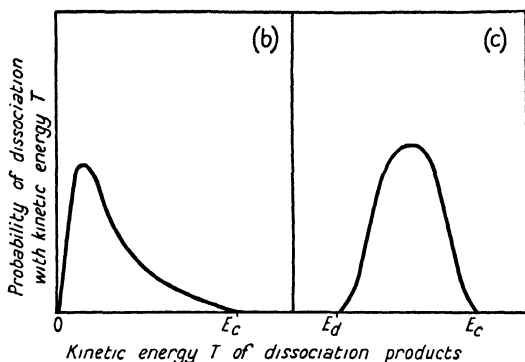


FIG. 110. Kinetic energy distribution of products of dissociation by electron impact: (b) when the final state has a potential energy curve similar to IIb of Fig. 109; (c) when the final state has a potential energy curve similar to IIc of Fig. 109.

the probability that the energy will have any particular value in this range. This probability is determined mainly by the chance that the nuclear separation should have any particular value in the classically allowed range. Thus, referring to Fig. 109 (c), the chance that the transition be from l to m is determined mainly by the probability that the nuclear separation in the initial state be R_l . This probability is given by the value of $\chi_{00}^2(R_l)$, χ_{00} being the vibrational wave function appearing in (16). Using this function as weighting factor, the energy distributions of the atoms or ions resulting from transitions of the respective types (b) and (c) take the forms illustrated in Fig. 110. A characteristic difference may be noted in that, in the former case, illustrated in Fig. 110 (b), where atoms or ions with zero kinetic energy may be produced, the distribution curve falls off more or less sharply on the low-energy side, whereas in case (c), where the atoms or ions formed have always some finite kinetic energy, the distribution curve is more nearly symmetrical as illustrated in Fig. 110 (c). Use has been made of this difference to obtain information about the processes involved (see § 6.21).

4.24. Downward transitions. Similar considerations to the above apply to downward transitions. These may result in production of a stable molecule or lead to dissociation, depending on the nature of the potential energy curve for the lower state and the nuclear separation involved.

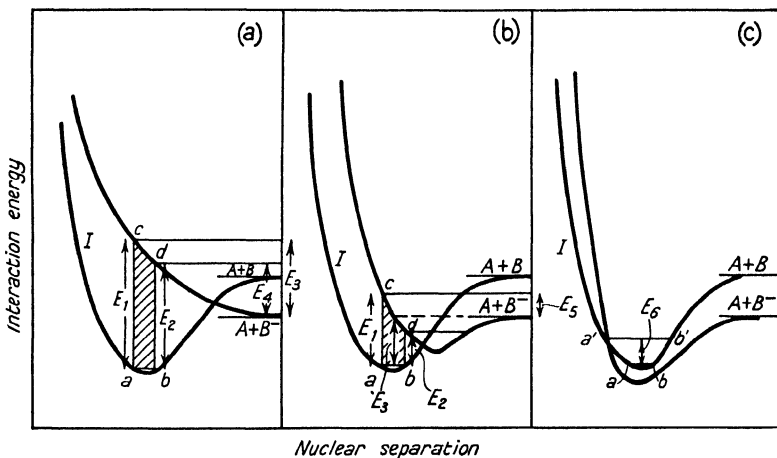


FIG. 111. Potential energy curves illustrating three possible ways in which negative ions may be formed from a molecule AB by electron capture.

4.3. The formation of negative ions from molecules by electron impact

There are two ways in which stable negative ions may be formed as a result of electron impact with a molecule, one in which the electron is captured and the other in which it simply breaks up the molecule into a positive and a negative ion. We shall consider these possibilities separately.

4.31. Negative ion formation by electron capture. If an electron is captured by a neutral molecule a transition can be regarded as taking place between two electronic levels of the negative molecular ion. In the initial state one of the electrons occupies an unbound orbital and the potential energy curve is just that of the neutral molecule in its initial state. The position of the upper potential energy curve relative to the lower determines the consequences of the capture. Three situations may arise, as illustrated by the potential energy curves of Fig. 111.

In all three cases (a), (b), and (c) curve I is the potential energy curve

of the initial state of the neutral molecule AB while the second curve in each case represents that for the state of the negative molecular ion into which the electron is captured. At infinite nuclear separation these upper curves tend to the energy of certain states of A and B^- . If, as is often the case, these are the normal states, then the upper curve will tend, at infinite separation, to an energy value less than curve I by the electron affinity of B .

In cases (a) and (b), according to the Franck-Condon principle, the transitions will be confined within the shaded areas $abdc$, i.e. the final state will lie on the upper potential energy curve between c and d .

In case (a) the final state will therefore have an energy in excess of that at infinite nuclear separation. As a consequence the negative molecular ion formed will break up into an atom A and ion B^- with total kinetic energy lying between E_3 and E_4 . The threshold electron energy will be nearly equal to E_2 and the probability of the capture will fall rapidly again when the electron energy exceeds E_1 .

On the other hand, in case (b), some of the possible final states fall where the energy is less than that at infinite separation. Dissociation will only occur if the electron energy lies between E_1 and E_3 and the kinetic energy shared between A and B^- will range correspondingly from zero to E_5 . Transitions produced by capture of electrons with energies between E_2 and E_3 will produce vibrationally excited molecular ions AB^- . Unless such an ion loses its surplus energy in some other way first, it will release the captured electron and revert to the neutral molecule in the ground state by a process the reverse of that which led to its formation. Alternative ways of getting rid of the surplus energy, leading to a stable molecule AB^- , are by radiation or by a superelastic impact. Radiation through vibrational transitions occurs very slowly and can usually be ignored, but stabilization by impact may be important if the pressure is not too low.

The rate of formation of stable AB^- by electron capture followed by collision stabilization will be proportional to the pressure at low pressures but, owing to saturation, may become independent of pressure at higher pressures. Thus, if τ be the average time taken for the vibrationally excited molecule AB^- to be relieved of its excess energy by impact with a gas molecule and θ the time before spontaneous dissociation of the molecule, $1/\tau$ is proportional to the gas pressure, θ independent of it. If, at time $t = 0$, we have an excited molecule AB^- , the chance that it will not have dissociated in time t will be $e^{-t/\theta}$. The chance that it will be relieved of its excess energy by impact in a time between t and $t+dt$

is $e^{-t/\tau} dt/\tau$, so the total probability of the ion being stabilized by collision before it breaks up will be

$$\begin{aligned}\rho &= \int_0^{\infty} \exp\left\{-t\left(\frac{1}{\tau} + \frac{1}{\theta}\right)\right\} dt/\tau \\ &= \theta/(\theta + \tau) \\ &= p/(p + p'),\end{aligned}$$

where p is the gas pressure and p' a critical pressure for which $\theta = \tau$. Hence if p is large enough ρ becomes independent of it. Because of this result it is unsafe to assume that if the rate of formation of a particular molecular negative ion is independent of the pressure in a particular pressure range it will remain so at still lower pressures.

Case (c) represents a situation in which collision stabilization must occur if a stable molecular negative ion is to result. With the potential energy curves related as in Fig. 111 (c) no transition can occur with appreciable probability unless the neutral molecule is first excited to a vibrational level such as $a'b'$. Once excited to this state the chance of capture of an electron will be high. The following sequence of events may therefore be imagined. The incident electron first excites the neutral molecule to the vibrational level $a'b'$ and is thereupon captured into an excited vibrational state of the molecule AB^- . Left to itself this molecule will break up again by the inverse process, but it can be stabilized by impact in the same way as the excited molecules AB^- discussed under case (b). This process will only be possible if the electrons have energies very close to E_6 of Fig. 111 (c).

A slight variant of case (c) would be if the incident electron first excited the molecule to a new electronic state with such vibrational excitation that the electron could then be captured into a vibrationally excited level of some electronic state of AB^- .

Summarizing these possibilities we have:

Case (a). Electrons with energies between E_1 and E_2 are captured and molecular dissociation results, giving atoms A and ions B^- with kinetic energies lying between E_3 and E_4 . This process we call dissociative attachment.

Case (b). Electrons with energies between E_1 and E_3 are captured, again leading to molecular dissociation into atoms A and ions B^- with kinetic energies lying between 0 and E_5 . Electrons with energies between E_2 and E_3 are also captured, giving rise to vibrationally excited molecular ions AB^- . In the absence of collision stabilization, i.e. at low

pressures, these ions will be transitory and in a short time of order 10^{-8} sec. will revert to the initial neutral molecule with release of an electron. At higher pressures, however, stable molecular ions AB^- will be formed.

Case (c). Electrons with energies in the neighbourhood of E_6 are captured giving rise to vibrationally excited molecular ions AB^- which will be transitory unless the pressure is high enough for stabilization to occur.

Normally the energy ranges $E_1 \rightarrow E_2$, etc., will be of the order of a few electron volts and would be expected to be somewhat larger in case (a) owing to the steepness of the repulsive part of the potential energy curve. It will be seen also that E_2 , the minimum electron energy necessary to produce dissociative attachment, cannot be zero unless the electron affinity of B is greater than the dissociation energy D_{AB} of the ground state of the molecule AB . Except for the halogen molecules this is rarely true, so negative ions formed by capture of very slow electrons will normally be molecular ions AB^- formed as described above. Since they will only be stabilized if the pressure is sufficiently high, it is unlikely that they will be formed in any appreciable quantity in low-pressure experiments.

4.32. Determination of dissociation energies and electron affinities. The relation (17) applies to dissociative attachment as well as to other collisions in which dissociation occurs. The sum $U'_A + U''_B$ in (17) becomes $-E_u$ where E_u is the electron affinity of B , if both the products A and B^- are in their ground states. Hence, from an experimental study of the relation between the energy of the incident electron and the kinetic energy of the ion B^- , either the dissociation energy of AB or the electron affinity of B may be determined. It must be remembered, however, that the products may be in excited states and there may be doubt about their identification. This somewhat restricts the value of the method, but it remains a very valuable one. Applications of it to a study of the electron affinity of O and the dissociation energy of CO will be described in § 6.4.

4.33. Dissociation into positive and negative ions. A molecule AB may be excited by electron impact into an electronic state which dissociates, not into neutral atoms, but into ions A^+ and B^- , either in their normal or excited states. The process only differs essentially from other excitation processes leading to dissociation in the nature of the dissociation products. Once more the relation between the electron energy E and the kinetic energy T of the resulting ions is of the form (17). If the ions

A^+ and B^- are in their normal states $U'_A + U''_B$ becomes $I - E_a$, the difference between the ionization energy I of A and the electron affinity E_a of B .

Apart from the nature of the dissociation products, the difference between this process of negative ion production and that involving capture is manifest in the variation of probability with electron energy. The capture process is important only in a narrow energy range of a few electron volts, whereas the probability of the non-capture one will vary with energy in much the same way as any electronic excitation process, viz. will increase to a maximum at an energy a few times the threshold value and then fall off gradually for increasing energies (see Chap. II, Fig. 24(a)). Examples of non-capture production of negative ions will be discussed in §§ 6.3, 6.4.

5. Electronic excitation of molecular hydrogen by electrons

The potential energy curves of the low electronic states of the hydrogen molecule and molecular ion H_2^+ are known rather more fully than for any other molecules. They exemplify almost all the effects discussed above so that the effects of electron impact in producing electronic excitation with a variety of possible consequences have been quite extensively investigated experimentally. Very good confirmation, both of the predicted forms of the potential energy curves and of the consequences of the excitation derived from use of the Franck-Condon principle as above, has been provided. We shall therefore devote some space to a detailed description both of the expected effects and the experiments which have confirmed them.

5.1. Predicted effects

Fig. 112 illustrates the potential energy curves for the more interesting electronic states of the hydrogen molecule, which lie within 20 eV of the ground state, while Fig. 113 illustrates on a reduced scale some states up to 50 eV above that state, including particularly the most interesting states of the ionized molecule.

Referring first to Fig. 112, curve I is that for the ground electronic state of the molecule with equilibrium nuclear separation 0.76 Å and dissociation energy 4.4 eV. In the ground vibrational state the classical range of the nuclear separation is between M and N . This ground electronic state is a singlet ($^1\Sigma_g$). The lowest triplet state ($^3\Sigma_u$) is a repulsive one, represented by curve II of Fig. 112. In the limit of large nuclear separation the molecule in this state tends to two normal hydrogen atoms, just as for the ground state. This repulsive state is of special

interest because its existence was predicted by Heitler and London[†] at the introduction of their quantum theory of valency. The result that an electron pair (two electrons with opposite spins) gives rise to a bonding

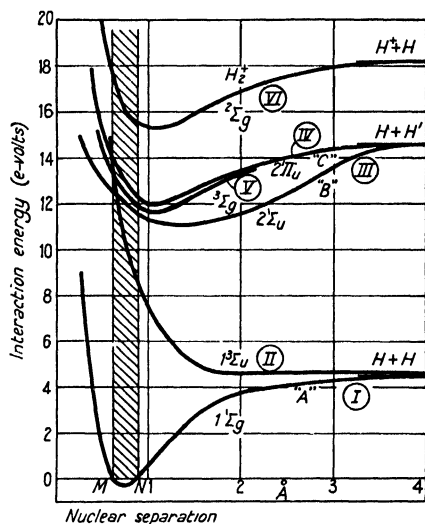


FIG. 112. Potential energy curves for electronic states of H_2 and H_2^+ lying within 20 eV of the ground state.

effect, whereas two electrons of parallel spins tend rather to oppose bonding, was generalized by them to a theory of the electron pair bond, now extensively employed in quantum chemistry. Curves III and IV represent two well-known stable singlet excited states—the so-called *B* ($^1\Sigma_u$) and *C* ($^1\Pi_u$) states respectively. Curve V represents the lowest stable triplet state ($^3\Sigma_g$) and curve VI the ground $^2\Sigma_g$ state of the molecular ion H_2^+ . According to the Franck–Condon principle, transitions from the ground state due to electron impact must occur vertically within the shaded region in Fig. 112.

We would therefore expect the following effects as the energy of the exciting electrons increases. No appreciable electronic excitation should occur until the electron energy reaches 8.8 eV when excitation of the repulsive $^3\Sigma_u$ triplet state begins. This will result in dissociation of the molecule into two normal atoms each with 2.2 eV kinetic energy. Further increase will make possible excitation of the B and C states which will be followed by emission of ultra-violet light as radiative transitions occur from them back to the ground state. At 11.8 eV excitation of the

† *Zeits. f. Phys.* **44** (1927), 455.

stable triplet state (curve V) can occur. This will result also in dissociation, for radiative transitions can take place from this state only to the lower triplet state, which is repulsive. Apart from the possibility of excitation of other electronic levels of the molecule, the next result of increasing the electron energy will be to produce stable H_2^+ ions when it exceeds the vertical ionization energy 15.4 eV.

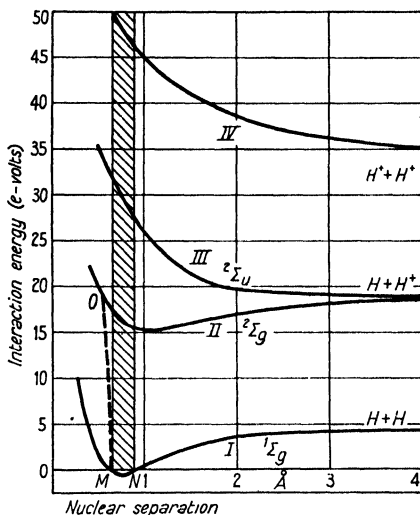


FIG. 113. Potential energy curves for higher energy states of H_2^+ .

To follow the further effects of increasing the electron energy it is convenient to refer to Fig. 113. Here curves I and II are those for the normal $1\Sigma_g$ states of the molecule and $2\Sigma_u$ of the molecular ion H_2^+ . Curve III is that for a repulsive $2\Sigma_u$ state of H_2^+ dissociating into normal H and H^+ . The existence of this state is of interest in connexion with the other current theory used in quantum chemistry, that known as the molecular orbital method. Instead of thinking in terms of electron pairs, the properties of the molecule are built up as the sum of those of the individual electrons. Whether a particular electron contributes a bonding or antibonding effect depends on the symmetry of its wave function in the nuclear coordinates. This is exemplified in the simplest form in the two curves II and III of Fig. 113 for H_2^+ , for in II the wave function of the single electron in the molecular ion is symmetric in the nuclear coordinates, in III antisymmetric. Finally, curve IV represents the Coulomb repulsion of two protons.

As in Fig. 112 the probable transitions must take place vertically within the shaded area. Hence, when the electron energy reaches 28 eV, excitation of the unstable state of H_2^+ , represented by curve III, begins. This will produce a hydrogen atom and a proton, each with 5 eV kinetic energy. Increased energy of the incident electrons can increase this energy up to about 7 eV by making possible excitation from initial nuclear separations nearer to M in Fig. 113. Eventually, when the bombarding energy reaches 46 eV, excitation to H_2^{++} , i.e. to two protons, can occur. These protons will have energies ranging from 7 to 10 eV.

It will be noted, however, that, although all transitions to the $2^3\Sigma_g$ level of H_2^+ which correspond to the Franck-Condon principle lead to stable H_2^+ , a transition such as MO in Fig. 113 would lead to H_2^+ excited above dissociation. This transition would represent a comparatively weak violation of the Franck-Condon principle and might be expected to occur to a detectable extent for the lightest molecule H_2 . The onset potential is 18 eV and the protons produced will have a very small kinetic energy—the smaller this kinetic energy the more nearly is the Franck-Condon principle obeyed. It should therefore be possible to distinguish proton production by this transition from that due to excitation of the unstable state, not only by the onset potential but by the proton energy (see § 5.4).

A summary of these effects is provided in Table I.

TABLE I

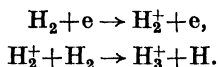
Onset energy (eV)	State excited†	Predicted effects
8.8	H_2 $1^3\Sigma_u$ (lowest triplet state)	Dissociation into normal H atoms with 2.2 eV kinetic energy.
11.5	H_2 $2^1\Sigma_u(B)$	Ultra-violet radiation due to radiative transitions from B to ground state.
11.8	H_2 $2^3\Sigma_g$	Dissociation into normal H atoms accompanied by emission of continuous spectrum due to radiative transitions from $2^3\Sigma_g$ to the repulsive $1^3\Sigma_u$ state.
12.6	H_2 $2^1\Pi_u(C)$	Ultra-violet radiation due to radiative transitions from C to ground state.
15.6	H^+ $^3\Sigma_g$ (ground state)	Ionization without dissociation.
18	H_2^+ $^3\Sigma_g$	Production of slow protons from dissociation into normal H and H^+ . (Transition weakly violating the Franck-Condon principle.)
28	H_2^+ $^3\Sigma_u$ (repulsive state)	Dissociation into normal H and H^+ , each with 5 eV kinetic energy.
46	H_2^{++} (repulsive)	Dissociation into two protons with 10 eV kinetic energy.

† For a summary of the notation for electronic states of diatomic molecules see Herzberg, *Molecular Spectra and Molecular Structure*, New York, Prentice Hall (1950).

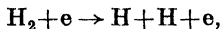
We shall now consider these processes separately in detail.

5.2. Dissociation into normal H atoms due to electronic excitation of triplet states

It was remarked as early as 1925 by Blackett and Franck† that the intensity of excitation of the Balmer lines of atomic hydrogen by passage of an electron stream through hydrogen at low pressures was approximately proportional to the pressure. This indicated that dissociation resulted directly from impact of a molecule with an electron and was not mainly due to a series of processes such as:



In 1927 the work of Glockler, Baxter, and Dalton‡ and of Hughes and Skellet§ established the existence of a direct dissociative collision process



and their results were confirmed two years later by Dorsch and Kallmann.||

The principle of the experimental method used was the same in all three cases. An electron beam of definite and controllable energy was fired through gaseous hydrogen and the production of atomic hydrogen detected in some way. The method of detection differed in the three investigations. The two earlier groups of workers used a stationary mass of hydrogen at a pressure of the order 0.1 mm. Hg and dissociation became manifest by a falling pressure. In Glockler, Baxter, and Dalton's method the pressure fall was secured by oxidizing the inner walls of the copper cylinder containing the hydrogen. Any atomic hydrogen formed reduced this oxide, forming water vapour which was condensed on a liquid-air trap. Hughes and Skellet froze the atomic hydrogen out directly on the glass walls of the hydrogen container which was a glass tube coated internally with a conducting film of evaporated tungsten and immersed in liquid air. In both experiments the pressure fall was observed with a hot wire gauge. Both found that the onset potential for dissociation was between 11.4 and 11.5 eV. As this is more than 4 volts less than the ionization potential of the molecule it is clear that the phenomenon is in no way dependent on ionization. In addition Hughes and Skellet made a special study of the variation of dissociation rate with pressure from which they derived strong evidence in favour of the process being a primary one.

† *Zeits. f. Phys.* **34** (1925), 389.

§ *Phys. Rev.* **30** (1927), 11.

‡ *J.A.C.S.* **49** (1927), 58.

|| *Zeits. f. Phys.* **53** (1929), 80.

The method used by Dörsch and Kallmann differed from that of the earlier workers in that the dissociation was produced in a stream of hydrogen gas and the presence of atomic hydrogen detected by blackening of a deposit of lead chloride due to the reaction



This increased the sensitiveness of detection and indications of the occurrence of dissociation by electrons with energies somewhat below 11.5 eV (down to 8.0 eV) were observed. On the other hand, a special search was made to determine whether electrons with energy just sufficient to produce dissociation by excitation of 4.4 eV vibrational energy in a normal molecule were in fact capable of transferring this energy on collision. It was found that the chance of such an occurrence was less than 3×10^{-6} per collision. The effectiveness of the electron beam in producing dissociation was found to increase considerably as the energy rose from 10 eV up to the ionization energy.

Reference to the most accurate potential energy curves available for the $1^1\Sigma$ and $1^3\Sigma$ states of H_2 of Fig. 112 shows that, according to the Franck-Condon principle, the vertical excitation energy for dissociation would be 8.8 eV but the form of the vibrational wave function χ_{11} would make the probability very small until the energy exceeded this value quite substantially. The onset potential of 11.4 eV found in the early work is thus explicable.

Further evidence concerning the dissociative triplet excitation has been obtained from experiments in which a swarm of electrons with a distribution of velocities has been used to produce the excitation. The most detailed and thorough investigation on these lines is that of Poole,[†] who determined the energy efficiency of atom production in the positive column of a striated glow discharge in hydrogen as a function of the ratio F/p of the field strength in the positive column to the gas pressure. This function may be related to the cross-section Q_{diss} for the dissociative collisions and its variation with energy E by making use of the theory of electron diffusion discussed in Chap. I, § 5.

If $f(E) dE$ is the number of electrons with energies between E and $E + dE$, the number of dissociations produced per second is

$$N \int_0^{\infty} Q_{\text{diss}}(E) v f(E) dE,$$

where v is the velocity of an electron of energy E and N is the number of molecules/c.c. In this time the work done on the swarm will be eFu ,

[†] *Proc. Roy. Soc. A*, **163** (1937), 404, 415, and 424.

where u is the drift velocity, which equals the distance traversed in the direction of the field in one second. The number η of dissociations produced, per unit energy, is therefore given by

$$\eta = \frac{N}{\epsilon F u} \int_0^{\infty} Q_{\text{diss}}(E) v f(E) dE. \quad (19)$$

As $f(E)$ and u are determined by the ratio F/p and N is proportional to p it follows that η is a function of F/p . From data available from electron diffusion experiments (see Chap. I, §§ 6, 7) in hydrogen, u and the mean random velocity c may be obtained. If $f(E)$ is assumed to be Maxwellian, the formula can be used to calculate η if $Q_{\text{diss}}(E)$ is known. It is important to remember, however, that the formula only applies when the gas is predominantly molecular. If a large atomic concentration is built up it cannot be applied without modification.

In Poole's experiments, hydrogen was allowed to stream at an adjustable rate through a tube in which a striated glow discharge was maintained. Atomic hydrogen, formed by the electrons in the positive column of the discharge, passed, together with the outflowing molecular hydrogen, into a calorimeter in which it recombined, the heat of recombination being measured. From this and the known binding energy of H_2 the rate at which atomic hydrogen reached the calorimeter could be derived. The power input into the positive column was obtained from the discharge-tube current and the potential drop down the column. From these measurements a quantity μ was obtained giving the number of dissociated molecules received as atoms at the calorimeter per unit of energy supplied to the positive column. This is not equal to the quantity η appearing in (19), for the degree of dissociation in the positive column was considerable and atoms were lost by wall recombination before reaching the calorimeter. To derive η , experiments were conducted at a fixed pressure, for a series of values of hydrogen flow rates U and power input W . In the limit of vanishing W and infinitely large U the proportion of atomic hydrogen tends to vanish and there is no time for wall recombination to occur before the calorimeter is reached. Hence, by extrapolating μ to vanishing W and $1/U$, η could be found at each pressure.

The general arrangement of the apparatus is illustrated in Fig. 114. Hydrogen passed through the capillary flowmeter F from which it was saturated with water vapour. It entered the discharge tube at two points K and L in the neighbourhood of the electrodes E and passed out through the side tube A to the calorimeter J and thence to the pump.

By means of a device for varying the pumping speed it was possible to adjust conditions to maintain a constant pressure at different flow rates. The glass walls of the discharge tube and calorimeter and of the side tube were coated with metaphosphoric acid to poison them for recombination. To secure permanent effectiveness of this coating the

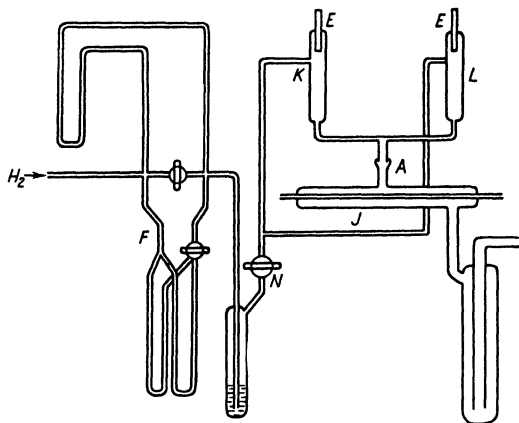


FIG. 114. Apparatus used by Poole to study dissociation of H_2 by electron impact.

water-vapour content of the hydrogen is important. Although recombination was not reduced to a negligible value by this arrangement it remained constant to a degree unattainable otherwise. The calorimeter consisted of a glass tube enclosing a concentric platinum-coated copper tube through which water passed at an adjustable rate. The gas from the positive column entered through a centrally placed side tube and the hydrogen atoms recombined on the walls of the copper tube. In equilibrium the rate of heat input due to the recombination could be determined from the water flow and the temperature difference between inlet and outlet measured by two thermocouples. The glass tube of the calorimeter was 25 mm. bore and 42 cm. long, while the copper tube was of external diameter 5.5 mm., thickness 0.75 mm., and 65 cm. long. Water-flow rates from 4 to 55 c.c./min. were employed.

The discharge-tube voltage was 5,000 volts D.C., the hydrogen pressure employed varied from 0.4 to 1.35 mm. Hg, the flow rates from 700 to 6,000 c.c./sec., and the discharge currents up to 100 mA. The results obtained are illustrated in Fig. 115 as a function of F/p .

A rough idea of the size of the cross-section corresponding to these observed values of the energy efficiency may be obtained as follows. Since the electronic excitations responsible for the dissociation are of the intercombination type (they are transitions from singlet to triplet states), the cross-section is only likely to be large for electron energies close to the excitation potential (see Chap. II, § 4.4, 5 and

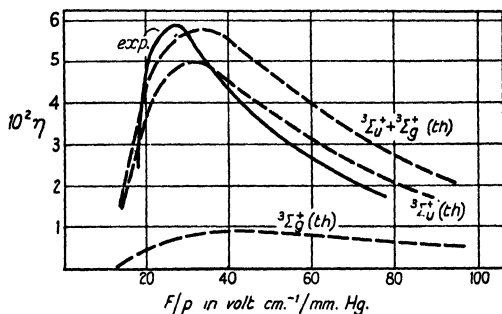


FIG. 115. Energy efficiency η of dissociation of H_2 by electrons, as a function of F/p . The full line shows the experimental results of Poolo. The 'theoretical' curves - - - have been calculated with the assumption (20) taking S as $0.45\pi a_0^2$.

Chap. III, § 3.53). We write then for the cross-section $Q(^3\Sigma_u)$ for the excitation of the lowest triplet state by electrons of energy V

$$\left. \begin{aligned} Q(^3\Sigma_u) &= S, & V_e < V < 2V_e \\ &= 0, & V > 2V_e \end{aligned} \right\} \quad (20)$$

where V_e is the excitation energy and S is a constant. A similar assumption may be made for the excitation of the $^3\Sigma_g$ state. As a further rough approximation the constant value assumed for the cross-section in this case in the range $V_e < V < 2V_e$ may be taken as $\frac{1}{2}S$. Using the values 9.5 V and 12.0 V for the excitation potentials of the two states, and assuming a Maxwellian distribution of velocities about the mean random velocity c corresponding to the value of F/p concerned, quite good agreement is obtained with the observed results if S is taken as $0.45\pi a_0^2$ (see Fig. 115).

Evidence that slow electrons may suffer an energy loss of 9.5 eV in hydrogen has been given by Jones and Whiddington† using the apparatus described in Chap. II, § 8.1 in which a velocity analysis was made of an initially homogeneous electron beam after passage, without appreciable deviation, through the gas. They found that the proportion of electrons suffering this loss was a maximum at about 16 eV incident energy and fell off very rapidly at high energies. At its maximum the probability of the loss was 0.25 of that due to the excitation of the C state (see Table II), requiring 12.6 eV. Electrons in producing the latter excitation (which is of the optically allowed type, see Chap. III, § 3.51) suffer little

† *Phil. Mag.* **6** (1928), 889.

deviation, whereas those producing the triplet excitations are distributed much more nearly uniformly after impact. Hence, in experiments such as those of Jones and Whiddington a much larger proportion of collisions in which *C*-state excitation occurs will be observed than for those leading to triplet excitation. The observations are therefore not incompatible with a cross-section as large as that estimated from Poole's experiments.

The same energy loss has also been detected by Ramien† using the Hertz diffusion method described in Chap. II, § 5.2. The loss first became apparent for electrons with initial energy a little over 9 eV and became more probable as this energy increased to 11.7 eV, the maximum used in the experiments. At this energy the cross-section was about 1/40 of the total collision cross-section ($12\pi a_0^2$, see Fig. 101) giving Q_{diss} as about $0.3\pi a_0^2$.

Finally, Kruithof and Ornstein‡ in the course of an investigation of the optical excitation functions of certain hydrogen molecular and atomic lines (see Chap. II, § 4) obtained a curve giving the variation of the probability of impact dissociation of the molecule as a function of electron energy in the range 14–50 eV. This curve exhibits a steep rise as the energy falls from 18 eV just as would be expected if the dissociation is due to excitation of a triplet state of the molecule.

The method used to obtain the dissociation curve was as follows. Dissociation proceeds by electron impact and recombination takes place on the walls of the experimental chamber so that, in equilibrium at pressure p , if m is the degree of dissociation,

$$Ap \frac{1-m}{1+m} = p^2 \frac{4m^2}{(1+m)^2}, \quad (21)$$

where A is proportional to the rate of dissociation per molecule by impact. From (21)

$$1 + 4p/A = 1/m^2. \quad (22)$$

By observing the variation of the intensity of a molecular line with pressure A may therefore be determined at each electron energy.

The theoretical evaluation of Q_{diss} is still in a somewhat unsatisfactory state. As an intercombination transition the variation of Q_{diss} with electron energy is likely to have the characteristic form exhibited in Chap. II, Fig. 24 (*b*), for the excitation of the 3S levels of helium. Calculations of Q_{diss} have been carried out using the Born–Oppenheimer approximation which gives a sharp maximum of the cross-sections for the $^3\Sigma_u$ excitation at 16 eV and for $^3\Sigma_g$ also at a few eV above the vertical excitation energy. The ratio of the two cross-sections at the

† *Zeits. f. Phys.* **70** (1931), 353. See also § 7.

‡ *Physica*, **2** (1935), 611.

maximum is about 3:1, but no reliability can be attached to this because the calculated absolute values near the maxima are clearly too large (see Chap. III, § 3.4). There seems no doubt, however, that electrons in the energy range 10–15 eV are able to produce dissociation of hydrogen molecules into normal atoms quite effectively without appreciable production of H_2^+ (see § 5.4). This is of practical importance in the design of proton sources (see § 5.5).

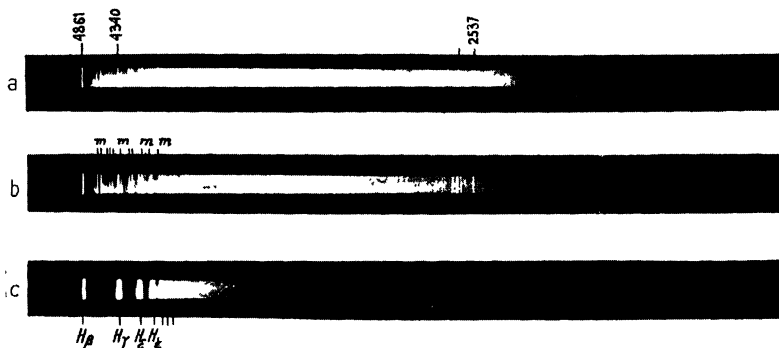


FIG. 116. The H_2 continuous spectrum, photographed by Vencov. The exciting electron energy is least in (a) which shows the continuous molecular spectrum. In (c), a higher electron energy favours production of the continuous atomic spectrum. Case (b) is intermediate.

It remains to consider the other manifestation of the excitation of the $^3\Sigma_g$ state—the continuous spectrum of molecular hydrogen. Considerable success has been attained in understanding the details of this spectrum even though it is not possible to predict the absolute value of the cross-section for excitation of the initial state concerned.

5.21. The continuous spectrum of molecular hydrogen. It has been shown that a consequence of the excitation of the $^3\Sigma_g$ state of molecular hydrogen should be the emission of a continuous spectrum due to transitions from the $^3\Sigma_g$ state to the unstable $^3\Sigma_u$ state. The existence of a continuum, stretching approximately over the wave-length range from 4,000 to 2,000 Å, in the emission spectrum of molecular hydrogen had long been known and, until Winans and Stueckelberg† provided the correct explanation in 1928, aroused much speculation as to its origin. Fig. 116 illustrates three spectrograms obtained by Vencov‡ on which the continuum appears clearly. Since 1928 the intensity

† *Proc. Nat. Acad. Sci.* **14** (1928), 867. See also Finkelburg, *Zeits. f. Phys.* **62** (1930), 624.

‡ *Ann. de Physique*, **15** (1931), 131.

distribution in the continuum under controlled excitation conditions has been studied in very considerable detail.† In particular, in 1931 Finkelburg and Weizel‡ showed that the threshold electron energy for excitation of the spectrum was 11.8 eV, in good agreement with the predicted value. James, Coolidge, and Present§ have also worked out the theory of the intensity distribution, and good agreement has been obtained with experiment, particularly with the most recent observations of Coolidge.||

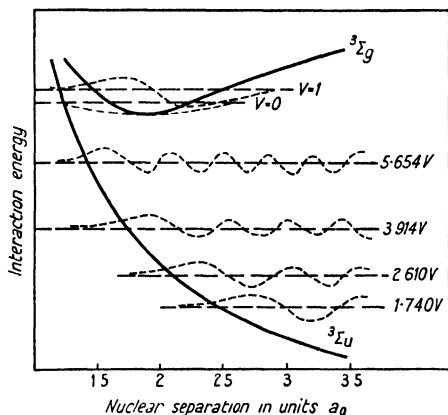


FIG. 117. Potential energy curves of the ${}^3\Sigma_u$ and ${}^3\Sigma_g$ states of H_2 as calculated by Coolidge, James, and Present. The continuous spectrum is produced by transitions ${}^3\Sigma_g \rightarrow {}^3\Sigma_u$. The broken lines show the wave functions for the two lowest vibrational states of the ${}^3\Sigma_g$ level and for four states of different kinetic energy associated with the repulsive ${}^3\Sigma_u$ level.

A complete theory of the intensity distribution involves not only the calculation of the relative probability of a radiative transition from each vibrational level of the upper ${}^3\Sigma_g$ state to different states of unquantized nuclear motion associated with the unstable lower ${}^3\Sigma_u$ state, but also the determination of the relative population of excited molecules in each vibrational state. The second part is the more difficult to carry out accurately for any given experimental conditions so, as explained below, Coolidge|| arranged the conditions of his experiments to minimize the contribution from excited vibrational levels of the ${}^3\Sigma_g$ state.

The first part of the calculation may be carried out in the usual way. The relative probabilities of different transitions are determined by the overlap of the appropriate nuclear wave functions, of the form illustrated in Fig. 117.

The functions may be calculated from the known potential energy curves for the two electronic states. Fig. 118 illustrates the results obtained for the relative

† Hukumoto, *Tohoku Univ. Sci. Rep.* **19** (1930), 773; Chalonge, *Compt. Rend.* **192** (1931), 1551, *Ann. de Physique*, **1** (1934), 123; Finkelburg, *Phys. Zeits.* **34** (1933), 529.

‡ *Zeits. f. Phys.* **68** (1931), 577.

§ *J. Chem. Phys.* **4** (1936), 187.

|| *Phys. Rev.* **65** (1944), 236.

probability of transitions from the ground vibrational level of the upper $^3\Sigma_g$ state to the lower level, involving emission of radiation over the wave-length range shown. Similar curves have been obtained by James and Coolidge† for other initial vibrational levels of the $^3\Sigma_g$ state. To complete the calculation they suppose that the excitation function for any particular level of the upper state increases linearly

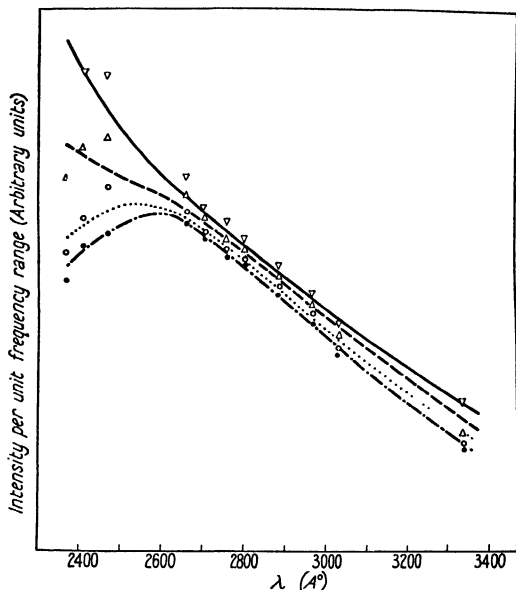


FIG. 118. Comparison of calculated and observed distributions of intensity in the H_2 continuous spectrum excited by electron impact. The vertical excitation potential is 11.72 eV. The curves show the calculated intensity distribution for electrons of energy Δ_0 eV above the vertical excitation potential. — $\Delta_0 = 0.5$; - - - $\Delta_0 = 0.3$; . . . $\Delta_0 = 0.1$; - · - $\Delta_0 = -0.1$. The points show the observed intensity distributions for electrons corresponding to different values of Δ_0 : ∇ , 0.55; Δ , 0.35; $\circ$, 0.15; $\bullet$, -0.05. The possibility of excitation for negative Δ_0 arises from the small but finite spread in electron energies due to the filament temperature (1,100° K).

with the excess of the electron energy above that just sufficient to produce the transition and that the constant of proportionality varies, for different vibrational levels of the upper $^3\Sigma_g$ state, as the square of the overlap integral between the nuclear wave functions of the initial state (the ground vibrational state of the $^1\Sigma_g$ ground electronic level), and of the final state.

To test the results of this theory in detail Coolidge excited the spectrum in streaming hydrogen at a pressure of 0.015 mm. of mercury by a 25 microampere beam of electrons of nearly homogeneous energy, emitted from an indirectly heated oxide-coated cathode. Elaborate precautions were taken to secure clean

† Loc. cit.

conditions. The radiation was analysed by photographic comparison with a rocalibrated standard mercury arc and the use of a small Hilger quartz spectrograph, great care being taken to ensure accurate photometry in spite of the extremely weak source. To minimize the effects of inaccurate estimation of the relative population of different vibrational levels of the upper state, an extensive series of measurements was made in which the mean electron energy was very close to the vertical excitation energy of the ground vibrational level, 11.72 eV. Correction was then made for the small amount of excitation of higher vibrational levels due to the energy spread of the electron beam, determined from measurement of the filament temperature (1,100° K). The close agreement obtained between theory and observation, under such conditions, is illustrated in Fig. 118.

This work has also been extended to deuterium for which slightly different results are expected. While the electronic potential energy curves are the same as for hydrogen, the vibrational states are changed by the increase in nuclear mass. The accord between theory and experiment is equally close in this case.

There seems little doubt from this and earlier work that the continuous spectrum does arise in the manner suggested and the close verification of the theory is gratifying. Much less attention has been paid to the investigation of the excitation function for the $^3\Sigma_g$ state for different electron energies. As a multiplicity change is involved the general form of this function should be typical of such transitions (see previous section). Apart from some early observations of Finkelburg,[†] which favoured this, the only detailed experimental work which has been carried out on this aspect is due to Lunt, Meek, and Smith[‡] using the electron swarm method. They observed the relative energy efficiency η_{ex} of excitation of the continuous spectrum, as a function of F/p , for a steady discharge in streaming hydrogen. This is related to the cross-section $Q_{\text{ex}}(E)$ for excitation of the upper state by electrons of energy E in the same way as is η to Q_{diss} in (19). The observed variation is consistent with an excitation function of the characteristic form for an intercombination transition but, in the absence of a satisfactory theory of Q_{ex} and of complete knowledge of the velocity distribution of the exciting electrons (see Chap. III, § 4.3), no very detailed knowledge of the variation of Q_{ex} with electron energy may be derived.

5.3. *The excitation of stable excited states of H₂*

Comparatively little effort has been devoted to the study of the cross-sections for excitation of stable excited states of H₂. It seems clear that the resonance potential observed at 12.8 eV corresponds to excitation of the $2^1\Pi$ or C state (see Fig. 112). Whiddington's method (Chap. II, § 8.1) for investigating the energy losses of electrons, which have

[†] *Zeits. f. Phys.* **62** (1930), 624.

[‡] *Proc. Roy. Soc. A*, **158** (1937), 729.

suffered very small deviations only, has been applied to this excitation. Roscoe† has used Born's approximation to calculate the differential cross-sections for excitation of the C state as well as the B ($2^1\Sigma$), D ($3^1\Pi$) and 1X ($2^1\Sigma$) states by 400-volt electrons, but the only observations of angular distributions‡ do not extend to electron energies above 150 eV.

Kruthof and Ornstein§ have measured the optical excitation functions of the lines $\lambda = 4,634 \text{ \AA}$ and $4,617 \text{ \AA}$ of the molecule which arise from the $3^1\Sigma$ and $3^3\Pi$ levels respectively. Allowance was made for the variation in the degree of dissociation of the hydrogen with electron energy (see § 5.2, equation (22)). They found the expected shapes characteristic of the corresponding atomic transitions (Chap. II, § 4.41, and Chap. III, § 3.5).

5.4. Ionization of the hydrogen molecule

5.41. Formation of ions with kinetic energy. The first experimental evidence of the formation of ions with kinetic energies of a few electron volts by ionization of hydrogen molecules was noted by Bleakney and Tate|| and, in more detail, by Bleakney,†† in 1930. They used an apparatus of the type described in Chap. II, § 2.2, in which ions produced by a localized electron beam were accelerated to a slit through which they passed into a magnetic analysing chamber. The ion-current peaks observed in the collector after passing through this chamber were quite sharp under certain conditions of electron energy but in others were found to be rather diffuse, indicating a considerable spread in initial velocity of the ions. This method has since been rendered more precise by Hagstrum and Tate,‡‡ whose work will be described in more detail below. It was Lozier§§ who made the first quantitative study of the velocity distributions of the ions, a few months after Bleakney's first experiments.

The apparatus used by Lozier, which is of a type employed in a considerable variety of experiments in other molecular gases, is illustrated in Fig. 119. The principle is a very direct one. An electron beam of homogeneous energy V_e eV is fired through the gas at a pressure of the order 2×10^{-4} mm. Hg, a magnetic field parallel to the beam, of between 100 and 150 gauss, preventing lateral spread. Of the ions produced by the beam, only those moving in a direction perpendicular

† *Phil. Mag.* **31** (1941), 349.

‡ Harnwell, *Phys. Rev.* **35** (1930), 285; Hughes and McMillen, *ibid.* **36** (1930), 1034; Mohr and Nicoll, *Proc. Roy. Soc. A*, **138** (1932), 469.

§ *Physica*, **2** (1935), 611.

†† *Ibid.* **35** (1930), 1180.

‡‡ *Ibid.* **36** (1930), 1285 and 1417.

|| *Phys. Rev.* **35** (1930), 658.

‡‡ *Ibid.* **59** (1941), 354.

to it can move through slots cut in the enclosing metal cylinder. Velocity analysis of these ions may then be carried out by the retarding potential method as they have unidirectional velocities. Referring to Fig. 119,

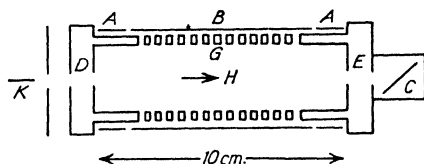


FIG. 119. Lozier's apparatus for measuring the velocity of ions formed by electron impact.

K is the tungsten filament source of the electron beam, which was accelerated through the holes in the diaphragm D by a potential difference of V_e between K and D . After passage through the collision chamber the beam passed through the holes in the diaphragm E and was collected at C . A holding potential of 175 volts was applied between C and E to ensure complete collection. Ions formed in the chamber moved to the walls of the enclosing circular cylinder G in which were cut a number of slots running round the circular boundary of the cylinder. These permitted the passage of ions, moving radially, into the space outside G . They could be collected on the enclosing cylinder B for which the parts A acted as guard rings. A retarding potential V_R could be applied between G and A , so making possible a velocity analysis of the positive ions.

The apparatus was of copper, sealed in a pyrex glass tube, and could be baked out at 400°C . The cylinder was 10 cm. long and the slots in G were 0.5 mm. wide and 3 mm. thick. Electron beam currents of from 5 to 8 microamperes were used. Corrections were applied to V_e for the initial electron velocities and to the observed voltage of the positive ions for the effect of the magnetic field on the positive ion trajectories.

Referring to (17) it will be seen that, if V_i is the minimum electron energy at which ions of energy V_f can be produced in a particular process:

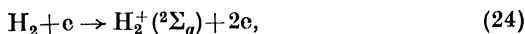
$$V_i = 2V_f + V_0, \quad (23)$$

where V_0 is a constant. For the ionization process with energy 28 eV (see Table I), involving a transition from the ground state to the lowest repulsive state of H_2^+ (see Fig. 113), V_0 is the sum of the dissociation energy $D(\text{H}_2)$ of H_2 in eV and the ionization potential of H, i.e. equals 17.9 eV. In the same way, for a transition in which two protons are produced V_0 is 13.5 eV greater. Lozier was able to observe V_i as a function of V_f for

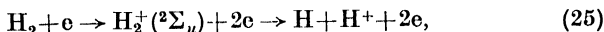
both these transitions—by fixing V_R and hence V_f at any desired value and observing the ion current to B as a function of the electron beam voltage V_e . No ion current was observed until V_e became equal to V_i for the first process, after which it increased smoothly until V_e reached a certain higher value beyond which the slope of the curve changed. This break in slope marked the value of V_i for the second process.

Fig. 120 illustrates the comparison of the relation between V_i and V_f as observed in this way by Lozier and the predicted relation (23) for the two processes. It will be seen that good agreement exists, confirming the theory discussed in § 4.22.

5.42. Effective cross-sections for different ionization processes. The cross-section for ionization of hydrogen by electrons with energies ranging from the threshold to 750 eV has been measured by Tate and Smith† using the apparatus described in Chap. II, § 2.1. In these measurements no attempt was made to distinguish between the different processes of ionization, but a few years earlier Bleakney‡ had given values of the relative probabilities of the most important of these as a function of electron energy. His apparatus was essentially a mass spectrograph similar to that described in § 6.21 of this chapter. With it he detected the slow H_2^+ ions resulting from



the energetic protons from



and also slow protons from



the onset potentials agreeing with the values predicted in Table I. Tate and Hagstrum§ also detected the two groups of protons from the reactions (25) and (26) using their mass spectrograph and the technique

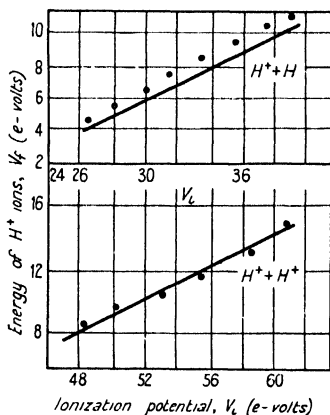


FIG. 120. Appearance potential (V_i) for ions of kinetic energy V_f , produced in the dissociative ionization of H_2 into $H^+ + H$ and $H^+ + H^+$ respectively.
● experimental points;
— predicted curve.

† *Phys. Rev.* **39** (1932), 270. ‡ *Ibid.* **35** (1930), 1180. § *Ibid.* **59** (1941), 354.

described in § 6.21. It has further been shown, however, by these authors that it is very difficult, if not impossible, to obtain information on the relative probabilities of reactions in which ions are formed with very different kinetic energies. It seems probable in most applications that the collecting efficiency is much higher for slow than for fast ions. Little weight can therefore be given to Bleakney's values of the relative probabilities, and the matter was re-examined by Newhall† using an apparatus of the Lozier type except for the mode of velocity analysis and the addition of a means of analysing the ions produced.

Suppose an electron beam is fired along the axis of a metal cylinder enclosing the gas at a low pressure (5×10^{-5} mm. Hg). When the electron current is very small the interior of the cylinder is a field free space, but with a finite current i amperes the space charge leads to a potential excess V_R of the walls over the beam where‡

$$V_R = 1.52 \times 10^4 i (1 + 2 \log R/\rho) / V_0^{\frac{1}{2}}. \quad (27)$$

R is the radius of the cylinder and ρ of the electron beam which possesses a kinetic energy V_0 eV. Under these conditions ions formed with kinetic energy $> V_R$ will reach the walls of the cylinder. A small fraction of these may be allowed to pass out through a slit in the cylinder and after acceleration may be analysed by semicircular focusing in a magnetic field parallel to the electron beam. With this arrangement the collecting efficiency in the receiving electrode of the spectrograph is independent of the initial kinetic energy of the ions. Furthermore, if the ions, on formation, possess only thermal energies the effect of the space charge retarding potential is sufficient to give a marked departure from linearity in the relation between ion and beam currents, for beam currents as low as 2 microamperes.

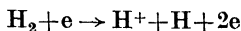
This was observed very clearly by Newhall for the H_2^+ ions, but no departure from linearity was observed for protons for beam currents ranging from a few microamperes to 100 microamperes. For higher beam currents a departure from linearity was found from which the energy distribution of the protons could be derived. It was found to extend over a range of a few eV as expected.

These experiments provide strong evidence that the slow proton group observed by Bleakney and by Hagstrum and Tate arises from a very improbable transition and that the Franck-Condon principle remains a very good guide to the phenomena.

† *Phys. Rev.* **62** (1942), 11.

‡ Smith and Hartman, *J. App. Phys.* **11** (1940), 220.

Using his observed ratios of proton to H_2^+ current in conjunction with Tate and Smith's absolute values for the total ionization cross-section, Newhall obtained the cross-section for the process



illustrated in Fig. 121. He found it to be roughly 1/200 of that for production of H_2^+ . The onset potential agrees quite well with that predicted (28 volts).

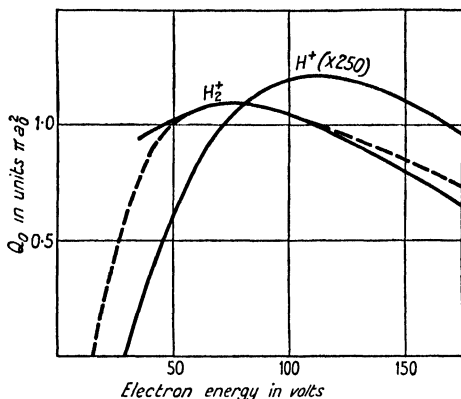
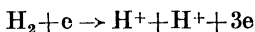


Fig. 121. Observed cross-sections for production of H^+ and H_2^+ in collisions of electrons with H_2 . - - - - Tate and Smith; ——— Newhall.

It remains to allow for the double ionization process



with onset potential 46 volts. So far this has only been detected by Lozier and no estimate of the cross-section is available. Judging by the measured cross-section for double ionization of He it is likely to be comparable with that for the process (26). The fact that it was observed in Lozier's experiments lends support to this.

5.5. Application to design of proton sources

The processes described above for the ionization and dissociation of H_2 by electron impact have an important application to the production of high-energy particles for nuclear investigations. In such sources the aim is to obtain operating conditions under which the ratio of H^+ to H_2^+ ions is as large as possible.

One type of source extensively used is some form of low voltage arc (see Chap. VIII, § 2.1). In such an arc most of the ionization is produced by a beam of electrons of a few hundred electron volts energy from a hot cathode source. In addition some ionization is produced by some of the faster plasma electrons, but since the electron temperature of the arc plasma usually corresponds to an energy of only a few electron volts, this source of ionization is less important.

The cross-section for ionization of H_2 to the stable $^3\Sigma_g$ state of H_2^+ is about 200 times as great as for the $^2\Sigma_u$ state which leads to dissociation into H and H^+ (see § 5.42). Evidently the observed concentrations of H^+ must be produced in multiple processes.

One possible process is the excitation of the $^3\Sigma_u$ state of H_2 followed by dissociation. The atomic hydrogen is then ionized in a second process. Alternatively, protons may be produced by the dissociation of H_2^+ in the transition $^2\Sigma_g \rightarrow ^2\Sigma_u$, or by the direct ionization of H_2^+ into two protons. Since multiple processes are involved, the probability of producing H^+ must remain small compared with that for H_2^+ except at very high ion densities. Also, since the dissociation of H_2 involves an intercombination transition, most of the dissociation is likely to arise from the slow plasma electrons. While the fast electrons will be most important in producing ionizing collisions for the low-voltage arc, for sources of the glow discharge or electrodeless discharge type, where there are no fast electrons, the ionization has to be produced by the plasma electrons.

As an example of the relative importance of the various processes Table II shows the mean estimated chance of ionization and dissociation of an H_2 molecule entering the discharge plasma from a side hole and making a single transit across it. The ionization is supposed to be produced by a beam of electrons of 100 eV energy and a current density of 10 amps/sq. cm. The concentration of plasma electrons is taken to be 10^{12} /c.c. and the electron temperature 4 eV. The discharge is considered to be running in a tube 1 cm. in diameter.

TABLE II

Process	Fraction of molecules undergoing the process in a single transit	
	(a) Due to fast electrons	(b) Due to plasma electrons
(a) Ionization to H_2^+ . . .	30.5×10^{-3}	1.2×10^{-3}
(b) Dissociation to H . . .	..	2.1×10^{-3}
(c) Process (b) followed by ionization of H to form H^+ . .	2.5×10^{-6}	1.4×10^{-7}
(d) Production of H^+ in single process from H_2 . . .	1.5×10^{-4}	..
(e) Process (a) followed by dissociation of H_2^+ to form H^+	1.4×10^{-4}	2.4×10^{-7}

The number of H^+ ions produced by all processes in a single passage across the arc is about 1 per cent. of the number of H_2^+ ions. In the case of the glow discharge or the electrodeless discharge conditions are even less favourable.

Actually much greater proton densities are observed, presumably because atomic hydrogen does not necessarily recombine at the wall but re-evaporates in the atomic form. If equal amounts of atomic and molecular hydrogen re-evaporate the ratio of H^+ to H_2^+ ions formed in a passage across the plasma is about 0.5 in the case of the arc operating under the above conditions. It is evident that the nature of the wall of the discharge in determining whether recombination occurs must play an all-important role in the production of high proton densities.

This is borne out in fact since it is found that in the electrodeless discharge in which all metal walls and electrodes can be eliminated, very

high proton concentrations (up to 80 per cent. of the total ionization) can be obtained.

6. Inelastic collisions of electrons with molecules other than hydrogen

6.1. Introduction

The inelastic collisions of electrons with a great variety of molecules have been studied. The kind of data obtained and the general nature of the experimental technique employed to obtain it can be briefly summarized as follows:

(a) *Dissociation into neutral fragments by electron impact.* Onset potentials for dissociation of some molecules into neutral fragments have been studied by a technique similar to that described above (§ 5.2) for hydrogen.

(b) *Appearance potentials and nature and relative abundance of different ionized products.* The chief method used to obtain this type of data is that of the mass spectrograph, a typical example of which is described in Chap. II, § 2.2. The electron energy range covered is usually from a few to some hundreds of electron volts, and homogeneous electron beams are employed.

(c) *Absolute cross-sections for ionization.* The apparatus used for this purpose is the same as for the corresponding study of the ionization cross-sections of atoms described in Chap. II, § 2.1.

(d) *Relation between electron energy and kinetic energy of ions formed.* Investigations of this type have been carried out with the apparatus of the Lozier type described in § 5.41 above, but the mass spectrograph has also been employed with success in recent experiments. The electron energy range covered is again from a few to some hundreds of electron volts.

(e) *Negative ion formation.* This has been studied both by using homogeneous electron beams as in (c), in which case the work is restricted to electrons with energies greater than a few electron volts, and by use of electron swarms so that mean values of the probability over the electron energy distribution are obtained. The latter method, though giving less definite information, has the advantage that it can be employed to study the behaviour of much slower electrons.

(f) *Optical excitation studies.* These are exactly similar to the corresponding studies for atoms described in Chap. II, § 4.

We shall describe in detail the results of these studies in oxygen, carbon monoxide, and nitric oxide and, more briefly, in nitrogen and the

halogens. This will be followed by a few remarks on some features of interest derived from the study of more complex molecules, but in view of its great volume we must content ourselves by concluding with classified references to the majority of this work.

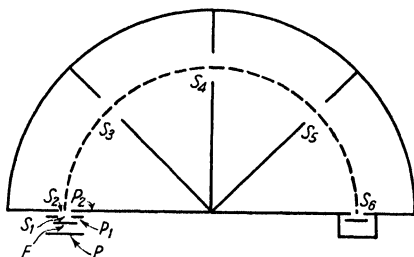


FIG. 122. Diagrammatic representation of mass spectrograph used to study the products of ionization by electron impact.

6.2. *Experimental methods and apparatus*

Many of the experimental techniques already described have been applied to the study of the effects of electron impact on various molecules. There are, however, three further experimental methods, not already described in connexion with studies of electron collisions with atoms or with hydrogen molecules, which have played an important part in the investigation of other molecules. The first of these is the adaptation, by Hagstrum and Tate,[†] of the mass spectrograph to the study of the energy distribution of ions produced by molecular dissociation. The remaining two are concerned with the study of negative ion formation using electron swarms of low mean energy. We shall describe the technique of these methods before discussing the results obtained by their use in conjunction with the methods already discussed.

6.21. *Use of mass spectrograph for investigating ion energy distribution.* Consider the analysis of ions by a mass spectrograph of the usual type. A standard arrangement, actually used by Hagstrum and Tate, is illustrated in Fig. 122. An electron beam F of ribbon shape produces ions in the region between the plates P and P_1 , between which an electric field is maintained in a sense to assist ions of the required sign to the plate P_1 . The accelerating potential is applied between plates P_1 and P_2 so a fraction of ions passing through the slits S_1 and S_2 pass into the analysing chamber. With suitable adjustment of the accelerating potential, the required ions follow a semicircular path, under the action

[†] *Phys. Rev.* **59** (1941), 354.

of the uniform magnetic field perpendicular to the plane of the paper, pass through the defining slits S_3 , S_4 , and S_5 and are collected after passage through the exit slit S_6 . In a typical instrument, that used by Hagstrum and Tate, the slit S_1 was of width 0.037 cm., S_2 0.022 cm., and S_6 was adjustable from 0 to 0.050 cm. The field between plates P and P_1 was about 30 volts per cm. The radius of the semicircular path of the collected ions was 20 cm. and the defining slit of the electron beam, which was placed symmetrically with respect to the plates P and P_1 , had dimensions 0.01×0.5 cm. A pressure of order 10^{-4} mm. of the gas under investigation was maintained between the plates P and P_1 .

The technique developed by Hagstrum and Tate depends on an analysis of the so-called peak shape. As the accelerating potential between P_1 and P_2 is varied, the current of ions, collected after passage through S_6 , rises to a maximum and then falls again. The shape of the variation with accelerating voltage, of the collected current for a particular ion, depends on two factors, one instrumental, the other the initial velocity of the ions formed in the gas by the electrons. If these two can be disentangled a study of peak shapes can yield useful information about the energy distribution of the ions.

For an ion formed with no initial velocity the peak shape is of the form shown in Fig. 123 (a). The shapes which can arise when the ions possess initial velocity are classified by Hagstrum and Tate under three heads, which we shall refer to as types I, II, and III respectively. These arise as follows. The efficiency of collection of ions as a function of their initial energy may be estimated from the trajectories of the ions, derived with neglect of space charge and the magnetic field. In general the efficiency of collection will at first fall off very rapidly as the initial ion energy increases and then decrease somewhat more slowly. Fig. 123 (b) illustrates the efficiency curve estimated by Hagstrum and Tate for their spectrometer. Superposing the efficiency curve on the initial energy distribution function of the ions will give the peak shape. Types I, II, and III arise from three possible forms of the distribution function, illustrated in Fig. 123 (c), (e), (g) respectively. Of these distributions (c) or (e) arises when the potential energy curves of the initial and final state are as illustrated in Fig. 109 (b) and (g) when they are as in Fig. 109 (c). Superposition of these on the efficiency curve of Fig. 124 (a) gives the respective peak shapes I, II, III illustrated in (d), (f), (h). In obtaining these, the instrumental spread associated with the collection of ions with zero initial energy has been allowed for roughly. It will be seen that, with a type III peak, the single maximum and, in one of the

type II, the subsidiary maximum, occurs at about the most probable ion energy. Interpretation of a type I peak is less definite.

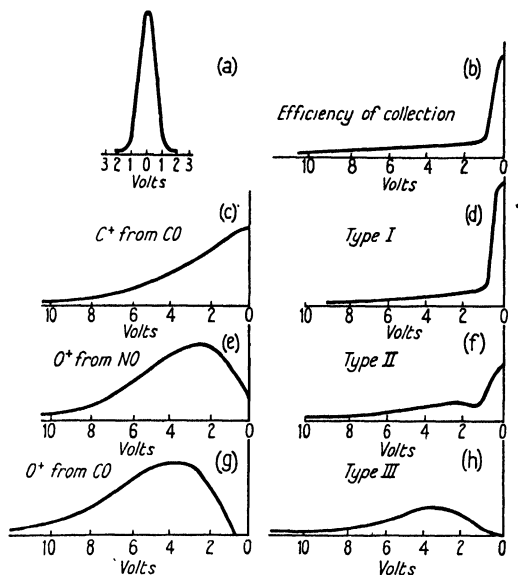


FIG. 123. Dependence of peak shape in a mass spectrograph on the kinetic energy with which ions are formed:

- (a) Symmetrical peak shape produced in a mass spectrograph by an ion formed with no initial energy.
- (b) Estimated collection-efficiency curve for the mass spectrograph of Hagstrum and Tate.
- (c), (e), and (g) Some typical distributions in energy of ions formed by electron impact.
- (d), (f), and (h) show the corresponding observed peak shapes.

The determination of the zero of the ion energy scale is a matter of some difficulty. A study of the effect of variation of the field between the plates P and P_1 is the best way of doing this. The collection of ions with zero initial energy is not likely to be improved by increase of this field. On the other hand, this collection is very sensitive to the application of a small retarding field between the plates.

As will be exemplified below, a study of peak shape on these lines is capable of revealing valuable information on the nature of the reaction involved in ion production. It will be clear, however, that the dependence of collecting efficiency on initial ion energy makes it very difficult to compare the probabilities of the different processes from observations

of the total ion current collected. Any estimates made must include adequate allowance for the efficiency of collection.

6.22. Study of negative ion formation using electron swarms. The principle of these experiments is as follows. Under the influence of an electric field F a stream of electrons drifts through the gas under investigation, at a pressure p . The mean energy of the electron stream which is a function of F/p can be determined from experiments of the type described in Chap. I, § 6, and it can be varied by varying F/p . In general there will be a chance α that an electron of the stream will attach to a gas molecule in drifting unit distance in the direction of the field. The loss dI of electron current in passing a distance dx in this direction, due to this cause, will be given by

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

Integrating this, we have for the ratio of the electron current in the stream at two points x_1, x_2 ,

$$I_2/I_1 = e^{-\alpha(x_2-x_1)}. \quad (28)$$

By observation of this ratio α may be determined. For most applications and interpretations it is necessary to derive from α the mean cross-section $\bar{Q}_a$ for attachment. To do this we note that, in passing a distance δx in the direction of the field, the actual distance traversed by the electron is not δx but $c \delta x/u$, where c is the random and u the drift velocity. Hence

$$\alpha = N\bar{Q}_a c/u, \quad (29)$$

where N is the number of gas molecules/c.c. It follows that provision must be made for determining the ratio c/u by separate experiment, if it is not already available as a function of F/p for the gas concerned from previous work of the type described in Chap. I, §§ 6, 7. It must be remembered also, in interpreting swarm experiments, that, as the cross-section for attachment will in general vary with electron velocity, $\bar{Q}_a$ is a mean over the electron energy distribution. The variation of this mean value with mean electron energy is what is given—a limitation of the type discussed in Chap. I, § 8, in connexion with swarm experiments directed towards the determination of electron-free paths. Despite this limitation, swarm experiments are important in providing data about the formation of negative ions by electrons with much lower energies than can be employed in experiments with homogeneous electron beams.

Two principal methods have been employed for the measurement of $\bar{Q}_a$. One is the direct one employing the electron filter method of Loeb,

Lusk, and Cravath.[†] The other is rather more indirect and is due to Bailey.[‡]

6.221. *The method of the electron filter.* To apply the formula (29) in practice a device must be introduced for measuring the fraction of the beam current which is carried by electrons, at any particular plane per-

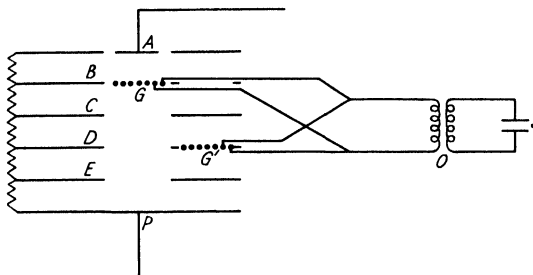


FIG. 124. Apparatus employing the electron filter used by Bradbury to measure attachment coefficients.

pendicular to the field. This may be done by insertion at the plane concerned of an electron filter of the type described in Chap. I, § 7.2. The filter consists of a grid between alternate wires of which a high-frequency alternating electric field may be applied. By suitable adjustment of this field all the electrons in the stream which reach the filter may be swept to one or other grid wire leaving the comparatively heavy negative ions unaffected. The decrease in beam current on passage through the filter may then be taken as a measure of its electron content just before reaching the filter.

The way in which this method was adapted by Bradbury§ in his extensive series of measurements of α is illustrated schematically in Fig. 124. Electrons generated photo-electrically from the plate *A* were allowed to diffuse under the action of an electric field between this plate and the plate *P*. The field was maintained uniform by the guard rings *B*, *C*, *D*, *E*. One half of each of the guard rings *B* and *D* consisted of a grid of fine platinum wires (*G*, *G'* in Fig. 124) which could be slid into position to intercept the electron stream. An alternating potential of frequency 4–15 megacycles/sec. 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., so that the background pressure could be reduced to 10^{-6} mm. Hg. Working pressures ranged from 3 to 90 mm. Hg.

[†] *Phys. Rev.* **33** (1929), 605.

[‡] *Phil. Mag.* **50** (1925), 825.

[§] *Phys. Rev.* **44** (1933), 883.

The measurements made were of the current reaching P , first with one grid in place with and without the alternating field applied, and then with the second grid in place. From these I_2/I_1 and hence α could be determined.

6.222. Bailey's method.[†] The principle of this method, which has been employed for the study of numerous gases and vapours, is illustrated in Fig. 125.

As in the previous method, electrons generated photo-electrically from a plate A drift under the action of a uniform electric field F maintained between the parallel plates A, B, C, D, E , parallel and superposed slits being cut in B, C, D to allow the passage of drift current to the plate E . Some current will be collected on the plates B, C, D due to transverse diffusion, and the measurement of this forms an important part of the method. The separations of the plates B, C and C, D are maintained equal throughout the experiment although both are changed in the course of the observations. These consist of measurements of the currents to the plates C, D, E at two sets of homologous values of plate separation x , gas pressure p , and electric field F . To show how α is obtained we introduce the following symbols:

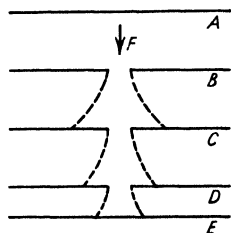


FIG. 125. Illustrating the principle of Bailey's method for measuring attachment coefficients.

S , the ratio of the current passing through a slit to the total current arriving on the plane containing the opening. Suffixes 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 ;

k , the factor by which the mean energy of the random motion of the swarm electrons exceeds that of the gas molecules in temperature equilibrium;

n_0, N_0 , the number of electrons and ions respectively passing through the slit in plate B ;

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

[†] Loc. cit.

Then

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

Elimination of r gives

$$R_e e^{-\alpha x} = \frac{S_1(R - S_2)}{R - S_1} = a_1, \text{ say.} \quad (30)$$

R_e and R are known, from diffusion theory, as functions of F/kx but k , which may be taken as unity for the negative ions, is not known for the electrons. However, since k is a function of F/p , R_e is unaltered if F , p , and x are all increased in the same ratio n . Under these conditions

$$R_e e^{-n\alpha_n x} = a_n.$$

If the attachment probability per collision is independent of the pressure, $\alpha_n = n\alpha$ and

$$\alpha = \frac{1}{x(n^2 - 1)} \log \frac{a_1}{a_n}. \quad (31)$$

This gives α in terms of directly measurable quantities apart from R , which may be calculated reliably from diffusion theory.

In a typical apparatus of this type the electrode plates B , C , D consisted of rings over which silver foil was tightly stretched. The slits cut in the foil were 4 mm. wide and their distance apart was 4 cm. A system of guard rings, 2 cm. apart, maintained a uniform field between the plates. The currents measured were of the order 10^{-12} amps.

Although this method is rather indirect it gives results in reasonable agreement with those obtained by the electron filter method and it has the advantage also that with the same apparatus the mean free path and the mean energy loss per collision may also be determined in the manner described in Chap. I, § 5 (see also § 7 of this chapter).

6.3. Inelastic collisions of electrons with oxygen molecules

6.31. Dissociation without ionization. Dissociation of oxygen molecules by homogeneous electron beams with energy insufficient to produce ionization has been studied by Dalton,[†] by Henry,[‡] and by Glockler and Wilson.[§] In all cases dissociation was observed by a pressure drop in the experimental chamber as, for example, in the corresponding experiments of Glockler, Baxter, and Dalton in hydrogen (§ 5.2). In Glockler and Wilson's experiments a mercury surface and the glass wall of the

[†] *J.A.C.S.* **51** (1929), 2366.

[‡] *Bull. Soc. Chim. Belg.* **40** (1931), 339.

[§] *J.A.C.S.* **54** (1932), 4544.

containing vessel were used to condense any active form of oxygen produced by the electron bombardment. They found a very small pressure change when the electron energy exceeded 3 eV and an enhanced effect at 8 eV.

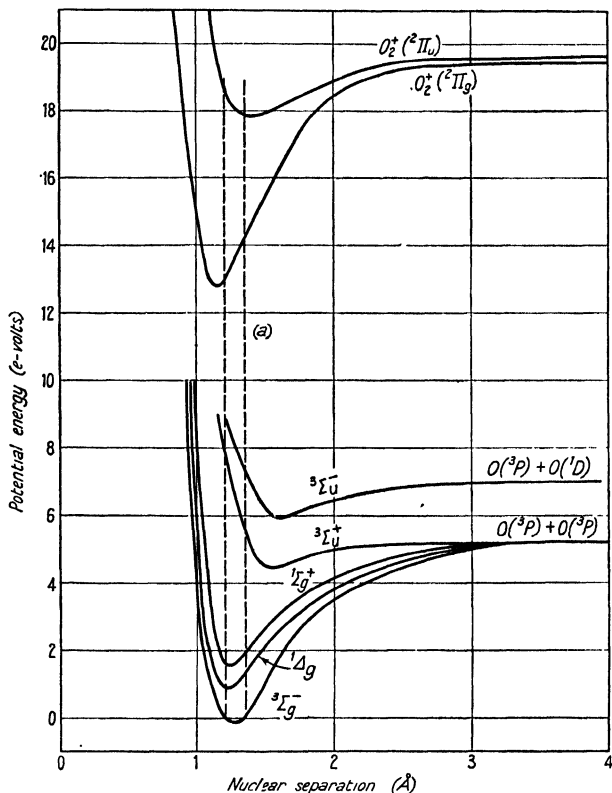
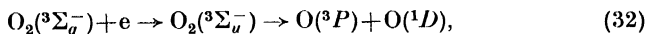


FIG. 126. Potential energy curves for the O_2 molecule.

The interpretation of their results follows from an inspection of the potential energy curves for the lowest states of the molecule, illustrated in Fig. 126. The effect at 8 eV receives the obvious interpretation

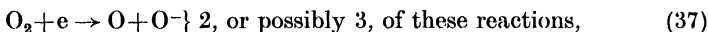


consistent, according to the Franck-Condon principle, with the observed onset potential. No such explanation is available for the weaker effects observed with electrons possessing energy in excess of 3 eV. It is suggested that the fall in this case is due to the action of $^1\Sigma_g^+$ O_2 molecules

which require only 1.62 eV for their excitation. As the $^1\Sigma_g^+$ state is metastable, having a different multiplicity from the ground level, this may well be correct.

6.32. Ionization. The total cross-section for ionization of oxygen has been measured by Tate and Smith† (P.T.) and the results are given in Table IV. The vertical ionization potential is 12.5 ± 0.1 volts.

A detailed series of investigations of the individual ionization phenomena have been carried out using both the retarding potential method of Lozier and the mass spectrograph. The following processes have been observed and studied in some detail:



The first of these is direct ionization involving the transition (a) in the potential energy diagram, Fig. 126.

The appearance potential of (34) is 19.2 ± 0.2 volts. Applying the formula (17) for this case we have

$$\begin{aligned} U_2 - U_1 &= \text{dissociation energy of } \text{O}_2 + \text{ionization energy of O} \\ &= 18.7 \text{ eV.} \end{aligned}$$

It therefore appears that the ion and atom carry away 0.5 eV kinetic energy at least. On the other hand, the mass spectrograph peak shape, observed by Hagstrum and Tate,‡ is of type I (see Fig. 124), indicating that ions with small initial kinetic energy are relatively numerous. It is not easy to see how both these results can be reconciled unless the potential energy curve of the upper state has a subsidiary maximum 0.25 eV above the dissociation limit. A reliable identification of this state cannot be made, but it may be the $^2\Pi$ state (see Fig. 126). The double ionization (35) process has an appearance potential 50.0 ± 0.5 eV, but the process (36) is so weak that no measurements of this potential are available.

The processes leading to negative ion formation are of very considerable interest because they make possible a direct determination of the electron affinity of O and also provide evidence of the existence of an excited state of O^- with very small binding energy, a result not incon-

† *Phys. Rev.* **39** (1932), 270.

‡ *Ibid.* **59** (1941), 354.

sistent with certain interpretations of similar experiments in CO (§ 6.5) and NO (§ 6.6).

Fig. 127 illustrates the efficiency of formation of O^- from O_2 as a function of electron energy, observed by Hagstrum and Tate† with a mass spectrometer set to collect ions of zero initial kinetic energy. It is

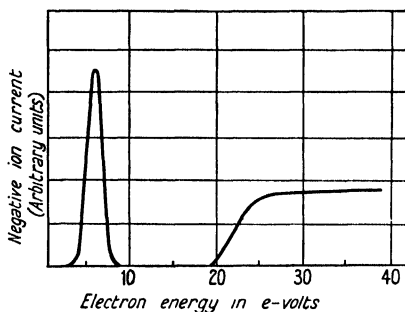


FIG. 127. Efficiency of formation of O^- by electron impact in O_2 observed with a mass spectrometer set to collect ions of zero initial kinetic energy.

clear that more than one process is involved, one with an appearance potential of 3.0 ± 0.4 volts, the other 18.9 volts. Moreover, the first exhibits a variation with electron energy of the form to be expected if electron capture occurs (§ 4.31), the second for one of dissociation into a pair of ions, without electron capture (§ 4.33). Applying the formula (17) to the first we have, since ions with zero kinetic energy are concerned, that

$$U_2 - U_1 = 3.0 \pm 0.4 \text{ eV} \\ = \text{dissociation energy of } O_2 - \text{electron affinity of O.}$$

Taking the dissociation energy of O_2 as 5.09 eV gives the electron affinity of O as 2.09 ± 0.4 eV. Ambiguity could arise in this interpretation if either or both of the products were in excited states. The lowest excited state of O is 2.1 eV above the ground level. If the O atoms produced were in this state the electron affinity of O would come out as 4.1 eV, which is much too large to be probable.‡ Equally, if the O^- ions were excited, the binding energy of the extra electron in the excited state would have to be at least 2.09 eV, which is quite out of the question—any excited state would certainly have a very small binding energy.‡ There would therefore seem to be little doubt of the correctness of the derived electron affinity.

† Ibid.

‡ Massey, *Negative Ions*, Cambridge, 2nd edition (1950), Chap. I.

The electron affinity of 2.2 eV found for O is in agreement with the most recent measurements made by Metlay and Kimball† using an equilibrium method and also with that to be expected on empirical grounds.‡ The first measurements of the electron affinity by the equilibrium method, made by Vier and Mayer,§ gave a higher value of 3.08 eV, but Metlay and Kimball have traced the source of the error and the correctness of the collision value seems to be well established.

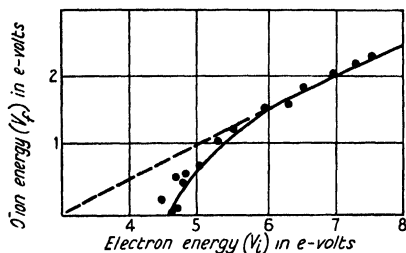


FIG. 128. Appearance potential V_i for O^- ions of energy V_f observed for electron collisions in O_2 .

Additional evidence is derived from Lozier's observations,|| using the retarding potential method, although his results do not entirely agree with those of Hagstrum and Tate. Fig. 128 illustrates the kinetic energy of the negative ions observed by Lozier as a function of the energy of the electron beam. The relation departs from linearity when the ion energy falls below 1.3 eV. If, however, the linear relation is extrapolated to zero ion energy the value of $U_2 - U_1$ found is 2.9 ± 0.2 eV, in good agreement with that obtained by Hagstrum and Tate. The differences observed as regards ion kinetic energy might be due to the upper potential energy curve of the unstable state of O^- being different in the two cases—there are several possible curves which tend in the limit of infinite nuclear separation to normal O and O^- .

Lozier also found a weak group of O^- ions formed by capture of electrons in the energy range 10–18 eV. For this group $U_2 - U_1$ comes out to be 12.0 eV, 9.1 eV higher than for the previously discussed one. This is equal to the excitation energy of the $^5S^0$ state of O, so the process can be interpreted as

$$O_2 + e \rightarrow O(^5S^0) + O^- \quad (39)$$

The process observed by Tate and Hagstrum to have an onset potential of 18.9 ± 0.4 eV is almost certainly to be ascribed to



† *J. Chem. Phys.* **16** (1948), 774.

‡ Batos, *Proc. Roy. Ir. Acad. A*, 151 (1947), 151.

§ *J. Chem. Phys.* **12** (1944), 28.

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

its variation with electron energy being of the type expected for such a reaction. As the spectrometer was set to collect ions of zero initial kinetic energy, $U_2 - U_1$ must be taken as 18.9 eV. The amount by which the combined energy of the ground states of O^+ and O exceeds that of the ground state of O_2 is 18.65 eV. This is equal, within the range of experimental error, to the observed appearance potential. It follows that the

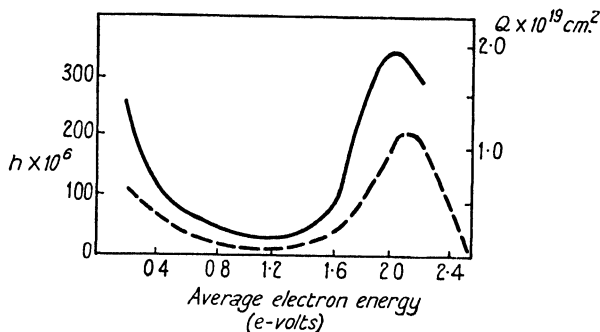


FIG. 129. Observed attachment probability per collision (h) for electrons in O_2 .
 - - - - measured by filter method; — — — measured by diffusion method.

energy of the O^- ion must be very nearly equal to that of the neutral atom. This is of very considerable importance as it suggests the existence of a stable excited state of a negative ion. As it must possess very small binding energy indeed (of the order 0.2 eV or less), there is no contradiction of general theoretical expectations.† Experiments in CO (see § 6.5) and NO (§ 6.6) have provided further but not certain evidence in support of the existence of this stable state. It still remains difficult, however, to provide a detailed theory,‡ and until this is done the reality of the state cannot be regarded as established beyond doubt.

6.33. Swarm experiments. Electron attachment in oxygen has been studied by both the electron filter§ and diffusion methods.|| The results are illustrated in Fig. 129.

The two methods agree in giving much the same variation of the attachment probability per collision, h , with mean electron energy, and differ only in a factor of about two in absolute magnitude. The most distinctive feature is the rapid rise in attachment probability as the

† See Massey, *Negative Ions*, Cambridge (1950), 2nd edition, Chap. I.

‡ Bates and Massey, *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

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

|| Brose, *Phil. Mag.* **50** (1925), 536; Healey and Kirkpatrick, quoted in Healey and Reed, *The Behaviour of Slow Electrons in Gases*, Amalgamated Wireless (A'sia) Ltd., 1941.

mean electron energy decreases below 0.5 eV. It would appear that there are two attachment processes involved, one, which we shall refer to as process *A*, effective at very low electron energies and the other, process *B*, at energies in the neighbourhood of 2.0 eV. The range of mean electron energy covered does not extend far enough for the reactions observed by Lozier and by Hagstrum and Tate to be important, so additional interpretations are required.

6.34. Interpretation of attachment reactions in O_2 in terms of potential energy curves. The location of the low-lying potential energy curves of O_2^- which are likely to be concerned in the various attachment reactions has been discussed by Bates and Massey.[†] It is not possible to come to any precise conclusions, but some general conclusions may be arrived at.

It was first suggested by Bloch and Bradbury[‡] that the very low energy attachment process *A* is of the type in which a vibrationally excited molecular ion O_2^- is first formed (see § 4.31 and Fig. 111 (c)) and is subsequently stabilized by getting rid of its excess energy in a collision. In the swarm experiments the attachment probability appears to be independent of the pressure. This requires a high rate of collision deactivation, involving an effective collision cross-section 1,000 times the gas kinetic value. Whether this is likely is not yet clear.[§] Detailed analysis shows that otherwise the explanation is reasonable, provided the energy excess of the ground state of O_2 above that of the state in which O_2^- is first formed after impact is between 0.17 and 0.07 eV.

The second process, *B*, occurring at mean energies of 1 eV or so, may be explained in a similar way, a transition to a different potential energy level of O_2^- being involved.

The order of the potential energy curves which tend to the ground states of O and O^- for large nuclear separation is fairly definite, but their location relative to the ground (${}^2\Sigma_g^-$) state of O_2 is not easily decided. Bates and Massey^{||} by empirical arguments locate the minimum of the deepest ${}^2\Pi_g$ state of O_2^- as 1 eV below that of the ground state of O_2 . The estimates made by Kazarnovski^{††} (1.0 ± 0.5 eV) and Evans and Uri^{‡‡} (0.75 eV) based on the lattice energies of the polar crystals KO_2 , RbO_2 , and CsO_2 are not inconsistent with this. Fig. 130 represents two possible sets of potential energy curves based on this value. In the first, Fig. 130 (a), process *A* would arise from capture to a highly excited vibrational state of the ground ${}^2\Pi_g$ level of O_2^- , represented by aa' in the diagram, whereas in the second possibility the electron would be captured into a low-lying vibrational level of the ${}^4\Sigma_u^-$ electronic state of O_2^- . The O_2^- state concerned in process *B* might be ${}^2\Delta_u$ or ${}^4\Sigma_u^-$ in the case of Fig. 130 (a), or ${}^2\Delta_u$ or ${}^2\Pi_u$ in the case of Fig. 130 (b). A further possibility for this process might also be that the O^- electronic level is one which tends asymptotically to normal O and the excited state of O^- referred to above. In any case there still remain sufficient states dissociating into normal O and O^- to interpret the results obtained by Hagstrum and Tate and by Lozier. Thus in Fig. 130 (a), capture to ${}^2\Delta_u$ would provide O^- ions of zero kinetic energy and to ${}^2\Pi_u$, ions with minimum energy of the order 1 eV or so.

[†] *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

[‡] *Phys. Rev.* **48** (1935), 689.

[§] See Chap. VII, § 12.

^{||} *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

^{††} *Dokl. Akad. Nauk S.S.S.R.* **59** (1948), 67.

^{‡‡} *Trans. Far. Soc.* **45** (1949), 217.

Although we are a long way from a detailed interpretation of the attachment processes in O_2 , the general features seem fairly well understood. The chief difficulty is the nature of the collision stabilization process which seems so efficient. It is of importance to note that, while the process may be saturated as regards pressure at 3 mm. Hg the attachment probability must fall off directly with the pressure at low pressures to a low finite value of a magnitude determined by the effectiveness of stabilization through radiation of the surplus energy. This limiting value may be 10 or more times smaller than that observed in the swarm experiments.

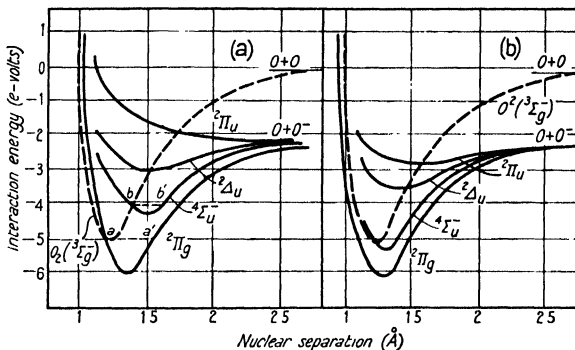


FIG. 130. Two possible sets of potential energy curves for O_2 .

6.4. Electron collisions in nitrogen

The study of the effect of electron impact on nitrogen molecules is of importance not only for the electrochemistry of nitrogen but also because molecular nitrogen is a major constituent of the earth's upper atmosphere. A detailed knowledge of the various cross-sections of the molecule for electron collisions is therefore required for the understanding of the auroral, night sky, and twilight emission effects as well as of the behaviour of the different ionized layers. At present only incomplete data are available and it is not even possible to decide the nature of active nitrogen.

One important difference between oxygen and nitrogen molecules is seen from the failure to observe dissociation of the latter molecule into neutral atoms by electron impact. Experiments similar† to those of Hughes and Skellet described in § 5.2 showed no decrease in pressure until the electron energy exceeded 17.8 volts. As the vertical ionization potential of N_2 is 15.7 volts and the onset potential for the reaction



† Hughes, *Phil. Mag.* **41** (1921), 778 and **48** (1924), 56.

is 22.9 volts (see Table V), it is likely that the observed effects were associated in some way with chemical activity of N_2^+ . It is very desirable that these experiments be repeated with much increased sensitivity as it is of great importance for the theory of the earth's atmosphere to determine whether any process of dissociation into neutral atoms is possible, even with very low probability. Accurate knowledge of the cross-sections for dissociation by electron impact would give indirect information on the possibility of dissociation absorption. The proportion of atomic nitrogen present at various levels in the high atmosphere may well be a decisive feature in certain phenomena.†

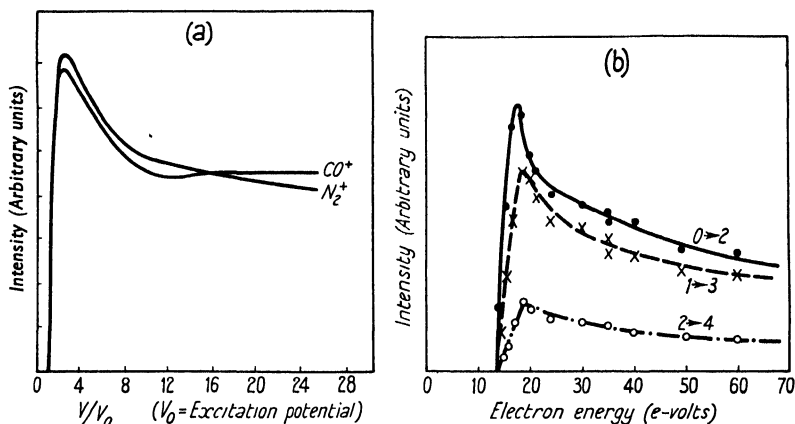
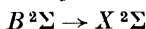
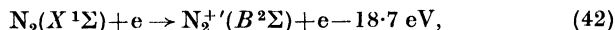


FIG. 131. Observed excitation functions for: (a) the first negative bands of N_2^+ and the comet-tail bands of CO^+ ; (b) the second positive bands of N_2^+ . The changes in vibrational quantum number are shown on the curves.

The optical excitation functions of the second positive bands of N_2^+ and first negative bands of N_2^+ have been measured. The latter bands are a prominent feature of the auroral emission spectrum|| and also occur in the twilight flash.†† They correspond to the transition



of N_2^+ . The impact excitation of the upper level is characteristic of that for an optically allowed transition, viz.



† Bates, *Mon. Not. R. Astr. Soc.* **109** (1949), 215.

‡ Langstroth, *Proc. Roy. Soc. A*, **146** (1934), 166.

§ Ibid.; Bundy, *Phys. Rev.* **52** (1937), 698; Bernard, *Comptes Rendus*, **205** (1937), 793.

|| Bates, Massey, and Pearse, *The Emission Spectra of the Night Sky and Aurora*, 97 (Physical Society, 1948).

†† V. M. Slipher, *Mon. Nat. R. Astr. Soc.* **93** (1933), 657.

as may be seen from the derived variations of the excitation function with electron energy (see Fig. 131). The second positive bands also occur in the auroral spectrum. They correspond to the transition $C^3\Pi-B^3\Sigma$ and the excitation function is of the typical intercombination type.

A number of observations† have been made of the energy losses of electrons in exciting N_2 .

TABLE III

Apparent Cross-section, Q_i , for Ionization of Molecular Gases by Electron Impact

Cross-section in units 10^{-16} cm.²

Gas	CO	NO	O ₂	N ₂	H ₂	C ₂ H ₂
Electron energy eV	(E_i = 14.1 eV)	(E_i = 9.5 eV)	(E_i = 12.5 eV)	(E_i = 15.7 eV)	(E_i = 15.6 eV)	(E_i = 11.6 eV)
10	..	0.03	..	..	..	..
12	..	0.17	..	..	..	..
14	..	0.37	0.06	..	..	0.45
16	0.11	0.54	0.16	..	..	0.85
18	0.26	0.69	0.25	..	0.12	1.48
20	0.41	0.84	0.41	0.20	0.23	1.80
25	0.97	1.25	0.79	0.61	0.46	2.61
30	1.46	1.58	1.18	1.04	0.66	3.31
35	1.78	1.91	1.55	1.40	0.78	3.94
40	2.11	2.15	1.84	1.76	0.88	4.20
50	2.54	2.57	2.18	2.22	0.97	4.60
60	2.77	2.84	2.44	2.52	1.00	4.83
70	2.93	3.02	2.63	2.67	1.01	4.95
80	3.03	3.14	2.76	2.79	1.00	5.00
100	3.07	3.25	2.89	2.87	0.96	4.90
120	3.03	3.25	2.91	2.86	0.90	4.73
140	2.93	3.19	2.87	2.80	0.85	4.53
160	2.82	3.07	2.80	2.72	0.81	4.32
200	2.61	2.85	2.64	2.52	0.73	3.92
250	2.36	2.61	2.42	2.33	0.64	3.45
300	2.15	2.39	2.20	2.12	0.57	3.07
400	1.78	2.02	1.85	1.81	0.46	2.55
500	1.55	1.73	1.61	1.55	0.39	2.21
700	1.22	1.41	1.25	1.22	0.31	1.72

The various ionization processes due to electron impact in nitrogen have been studied using both the retarding potential method of Lozier‡ and the mass spectrograph.§|| †† The total ionization cross-section has

† M. Dufay, and J. Dufay, *Comptes Rendus*, **224** (1947), 1834.

‡ Lozier, *Phys. Rev.* **44** (1933), 575.

§ Vaughan, *ibid.* **38** (1931), 1687.

|| Tate, Smith, and Vaughan, *ibid.* **48** (1935), 525.

†† Hagstrum and Tate, *ibid.* **59** (1941), 354.

been measured by Tate and Smith† and is given in Table III. The appearance potentials for the different ions observed in the several investigations are listed in Table IV.

TABLE IV
Appearance Potentials of Ions produced by Electron Impact in N₂

<i>Ion</i>	<i>Observed appearance potentials in volts</i>
N ₂ ⁺	15.8 ± 0.1, †† 15.7, † 15.65 ± 1. §§ 15.7 ± 0.1 ††
N ⁺	24.5 ± 0.1, †† 24.27 ± 0.1, †† 24.3 ± 0.2 ††
N ₂ ⁺⁺	47 ± 1, †† 49.5 ± 0.5 ††
N ⁺⁺	64 ± 2 ††

The N⁺ ions formed at 24.5 volts were found by Hagstrum and Tate to have zero kinetic energy. They must be formed by a reaction



Since the ionization energy of N is 14.54 eV, application of (17) gives

$$D(\text{N}_2) + E(\text{N}) + E(\text{N}^+) = 9.76 \text{ eV},$$

$E(\text{N})$ and $E(\text{N}^+)$ being the excitation energies of the N and N⁺ produced. If both $E(\text{N})$ and $E(\text{N}^+)$ are zero, $D(\text{N}_2)$ must equal 9.76 eV, a value supported by Gaydon‡ on the basis of spectroscopic and other evidence. On the other hand, if the nitrogen atom is in its lowest excited (²D) state $E(\text{N}) = 2.37 \text{ eV}$, giving $D(\text{N}_2) = 7.38 \text{ eV}$, which agrees with the value advocated by Herzberg§ and by van der Ziel.|| Some evidence in favour of the lower value is afforded by the experiments in NO (§ 6.6).

6.5. *Electron collisions in carbon monoxide*

The retarding potential†† and mass spectrograph methods‡‡ have been applied to a detailed study of the collisions of electrons with CO molecules. The special interest of the work is twofold—it provides evidence concerning the dissociation energy of CO, still a matter of animated controversy, and the stability of the excited state of O⁻.

The reactions which have been studied and which throw light on these matters are as follows:

Process A. $\text{CO} + e \rightarrow \text{C} + \text{O}^-$. The appearance potential as found by both Hagstrum and Tate and by Lozier is 9.5 ± 0.1 volts. Ions of zero initial kinetic energy are formed and the variation of probability with electron energy is of the expected type (§ 4.31).

† *Phys. Rev.* **39** (1932), 270.

‡ *Dissociation Energies* (Chapman and Hall, 1947), Chap. IX.

§ Herzberg and Sponer, *Zeits. f. phys. Chem. B* **26** (1934), 1; Buttenbender and Herzberg, *Ann. der Physik*, **21** (1935), 577.

|| *Physica*, **4** (1937), 373.

†† Hagstrum and Tate, loc. cit.

‡‡ Lozier, loc. cit.

§§ Tate, Smith, and Vaughan, *Phys. Rev.* **48** (1935), 525.

Process B. $\text{CO} + e \rightarrow \text{C}^+ + \text{O}^- + e$. The first appearance potential of C^+ ions at 20.9 volts is found to coincide within experimental error with the second of O^- ions. Moreover, Lozier showed further that the numbers of positive and negative ions formed between 20.9 and 22.8 eV electron energy are equal. The variation of the probability with electron energy is of the expected type (§ 4.33). Little doubt remains that the correct interpretation has been assigned to the process.

Process C. $\text{CO} + e \rightarrow \text{C}^+ + \text{O} + 2e$. This process has an appearance potential of 22.8 ± 0.2 volts and is much more probable than *B*. Ions of zero initial kinetic energy are formed.

Process D. $\text{CO} + e \rightarrow \text{C} + \text{O}^+ + 2e$. Hagstrum and Tate found from the O^+ peak shape, which is of type III (Fig. 123), that the O^+ ions possess a kinetic energy of one or more electron volts. Extrapolation of the appearance potentials observed for ions of 1.5, 2.0, 2.5, and 3.0 eV initial kinetic energy gives 23.5 volts as the appearance potential for ions of zero initial kinetic energy. It must be regarded as an upper limit, likely to be in excess of the true value by 0.4 volts at most.

In connexion with this process it is of interest to note that, in work† previous to that of Hagstrum and Tate, the probability of process *D* was thought to be much smaller than that of *C*. This was based on mass spectrograph observations and did not allow for the decrease in collecting efficiency with initial kinetic energy of the ions concerned. When this is done it appears that the rates of the two processes are comparable.

Let *D* be the dissociation energy of CO, *I*(*X*) the ionization energy, and *E*(*X*) the excitation energy of a particular atom *X*, and *A* the electron affinity of O. Then from the appearance potentials of the four processes we have

$$(A) \quad 9.5 = D + E(\text{C}) - A + E(\text{O}^-),$$

$$(B) \quad 20.9 = D + I(\text{C}) + E(\text{C}^+) - A + E(\text{O}^-),$$

$$(C) \quad 22.8 = D + I(\text{C}) + E(\text{C}^+) + E(\text{O}),$$

$$(D) \quad 23.1 = D + I(\text{O}) + E(\text{C}) + E(\text{O}^+) \text{ (taking the minimum possible value for the appearance potential).}$$

We know that *I*(C) = 11.3 eV, *I*(O) = 13.5 eV, and *A* = 2.2 eV, but the various excitation energies cannot be decided *a priori*. Nevertheless, the possibilities are very limited. They may, of course, be zero in any

† Hogness and Harkness, *Phys. Rev.* **32** (1928), 936; Vaughan, *ibid.* **38** (1931), 1687; Tate, Smith and Vaughan, *ibid.* **48** (1935), 525; Tate and Smith, *ibid.* **39** (1932), 270; Lozier, *ibid.* **46** (1934), 268.

particular case. The lowest values other than zero are as follows: $E(C)$ 1.25 eV (1D), and 2.67 eV (1S); $E(C^+)$ 5.2 eV; $E(O)$ 2.0 eV; $E(O^+)$ 3.3 eV; $E(O^-) \simeq 2.1$ eV.

From process (*D*) it follows that *D* cannot be greater than 9.6 eV. This value is consistent with (*A*) if $E(C)$ is taken as zero and $E(O^-)$ as 2.1 eV, with (*B*) if $E(C^+)$ is taken as zero and $E(O^-)$ as 2.2 eV and with (*C*) if $E(O)$ is taken as 1.9 eV. These excitation energies agree within the experimental error with the true values. Assumption of 9.6 eV as the dissociation energy of CO and of the stability of the excited state of O^- therefore provides a consistent interpretation of the experiments. It is difficult to obtain any other, but it must be remarked that, if the identification or appearance potential of process (*D*) were in error, a higher value of 11.6 eV for $D(CO)$ would be consistent with the first three processes, the excitation energies all being taken as zero. There seems, however, to be no reason to doubt the validity of the measurements for process (*D*). On the other hand, controversy still continues about the dissociation energy of CO.

Gaydon and Penney† have given arguments, based on spectroscopic data, in favour of a value 11.111 eV. This is closer to the higher value 11.6 eV which would be possible if process *D* above were disregarded. As this higher value would imply that the O^- ions produced in processes *A* and *B* are unexcited some doubt is thrown on the evidence from these experiments in favour of the existence of stable excited O^- . However, Hagstrum‡ has recently given a detailed discussion of the evidence concerning the dissociation energy of CO in which he supports the lower value 9.6 eV. The matter must be regarded as still unsettled.

6.6. *Electron collisions in nitric oxide*

The total ionization cross-section has been measured by Tate and Smith§ and is given in Table III.

The following reactions have been studied in this gas using the retarding potential|| and mass spectrograph methods.†† They are of interest in providing further evidence concerning the dissociation energy of N_2 , the electron affinity of O, and the possible existence of the excited state of O^- .

Process A. $NO + e \rightarrow N + O^-$. The variation with electron energy is of the predicted form. Hanson|| obtained by extrapolation the value

† *Proc. Roy. Soc. A*, **183** (1945), 374; Gaydon, *Dissociation Energies* (Chapman and Hall, 1947), Chap. IX.

‡ *Phys. Rev.* **72** (1947), 947.

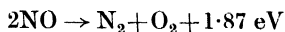
§ *Ibid.* **39** (1932), 270.

|| Hanson, *ibid.* **51** (1937), 86.

†† Tate, Smith, and Vaughan, *ibid.* **48** (1935), 525; Hagstrum and Tate, *ibid.* **59** (1941), 354.

3.2 ± 0.5 volts for the appearance potential for ions of zero kinetic energy.

The dissociation energy of NO can be related to that of N_2 and of O_2 by means of the relation



derived from thermochemical data.† Taking $D(O_2) = 5.084 \text{ eV}$ we find that $D(NO)$ is either 5.29 or 6.49 eV according as $D(N_2)$ is taken to be 7.38 or 9.56 eV (see § 6.4). From the appearance potential of the process A we therefore have, for the electron affinity of O_2 , either 2.09 ± 0.5 or $3.29 \pm 0.5 \text{ eV}$. The former is in agreement with the accepted value (§ 6.3). Hence, either $D(N_2)$ is 7.38 eV or the process A must be disregarded.

Process B. $NO + e \rightarrow N^+ + O^- + e$. The variation with electron energy is as expected. Hagstrum and Tate find the appearance potential to be 20.0 ± 0.3 volts for the negative ions and 19.9 ± 0.2 for the positive, confirming the interpretation of the reaction. In this case we have

$$20 = D(NO) + E(N^+) + E(O^-) - A(O) - I(N).$$

Taking $D(NO) = 5.29 \text{ eV}$, $I(N) = 14.54 \text{ eV}$, $A(O) = 2.2 \text{ eV}$ gives

$$E(N^+) + E(O^-) = 2.37 \pm 0.3.$$

This is consistent with $E(O^-) \simeq 2.2 \text{ eV}$ or with $E(N^+) = 1.9 \text{ eV}$ corresponding to the 1D state. On the other hand, with $D(NO) = 6.49 \text{ eV}$,

$$E(N^+) + E(O^-) = 1.2 \pm 0.3 \text{ eV},$$

which is not consistent with either.

Process C. $NO + e \rightarrow N^+ + O + 2e$. The appearance potential for this process is found to be 21.8 ± 0.2 volts and the peak shape is of type I (Fig. 123), indicating that the ions are formed mainly with very small kinetic energy. We have then

$$21.8 = D(NO) + E(N^+) + E(O) + I(N),$$

giving

$$D(NO) = 7.26 - E(N^+) - E(O).$$

This is compatible with $D(NO) = 5.29 \text{ eV}$ if $E(N^+)$ is taken as 1.9 eV corresponding to the 1D state and $E(O)$ as 0, or if $E(N^+) = 0$ and $I(O) = 1.9 \text{ eV}$ corresponding to the 1D state. It is not compatible with the higher value 6.49 eV for $D(NO)$ unless it be supposed that the ions are formed with $0.7\text{--}0.8 \text{ eV}$ kinetic energy.

Process D. $NO + e \rightarrow N + O^+ + 2e$. The appearance potential is 20.5 ± 0.2 volts and the peak shape is of type II (Fig. 123), indicating that ions with appreciable kinetic energy are formed. These results are

† Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, Reinhold, New York, 1936.

only compatible with $D(\text{NO}) = 5.29$ eV if this kinetic energy is about 1.6 eV, admittedly somewhat larger than might be expected from the peak shape. To that extent they favour the higher value of $D(\text{NO})$ which would be obtained if the ions were formed with 0.4 eV kinetic energy.

6.7. *Summary of conclusions from collision experiments in O_2 , N_2 , CO, and NO*

The electron affinity of O can be regarded as definitely established as close to 2.2 eV. Although it is not completely definite, the evidence from collision experiments strongly favours the values $D(\text{N}_2) = 7.38$ eV, $D(\text{NO}) = 5.29$ eV, and $D(\text{CO}) = 9.76$ eV. In view of the wide variation in the interpretation of other evidence concerning these dissociation energies it is not yet possible to accept these values with assurance. The evidence in favour of the existence of a stable excited state of O^- with nearly zero binding energy is less certain still, but if the above values of $D(\text{NO})$ and $D(\text{CO})$ are accepted it is difficult to interpret certain of the observed processes in NO and CO, as well as in O_2 , without assuming the existence of a stable excited state of this kind. On the other hand, theoretical examination† of the possibilities would make it seem very unlikely that such a state could exist for O^- .

6.8. *Electron collisions in the halogens*

As the atoms of the halogens are the most electronegative of all, the behaviour of electrons in chlorine, bromine, and iodine is of special interest. Hence, in spite of the difficulty of carrying out experiments in such reactive vapours, swarm experiments have been carried out in all three and beam experiments in bromine and iodine. The measurements made, which we shall describe in more detail below, show cross-sections for electron attachment which are very much higher than in other gases, and in addition reveal the existence of stable molecular negative ions I_2^- , Br_2^- . Although the attachment cross-sections are relatively large, the maximum value found, 10^{-17} cm.² for I_2 , is still considerably smaller than the gas kinetic.

The mean attachment cross-section obtained in the usual way from the swarm experiments by multiplying the observed attachment probability per collision h by the mean total collision cross-section derived from the observed mean free path, is subject, in the case of halogens, to considerable error due to the very rapid decrease of mean free path at low electron energies (which is a characteristic of all three

† Bates and Massey, *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

(see Fig. 101(b)). Apart from this the difficulty of making accurate measurements in the halogen vapours reduces the accuracy of the absolute values.

The most extensive investigations have been concerned with iodine. Buchdahl† and Hogness and Harkness‡ have used homogeneous electron beams and Healey§ has used the diffusion method.

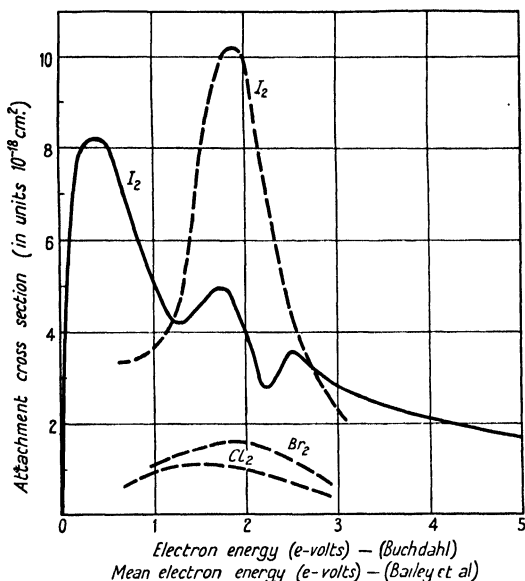


FIG. 132. Observed cross-sections for attachment of electrons to halogen molecules. The full line curve for I_2 was obtained by Buchdahl using homogeneous electrons. The other curves were obtained by Bailey and his co-workers, using the diffusion method.

Their results are illustrated in Fig. 132—the energy scale representing the mean energy in the swarm experiments and the actual energy of the homogeneous electron beam in the measurements of Buchdahl. The maximum found at 2.0 eV mean energy in the former experiments probably corresponds to the two maxima found by Buchdahl at 1.75 and 2.5 eV energy, particularly as the absolute values agree within a factor of 2. There seems, however, to be little trace in the diffusion observations of the low energy maximum found by Buchdahl.

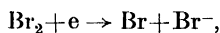
† *J. Chem. Phys.* **9** (1941), 146.

‡ *Phys. Rev.* **32** (1928), 784.

§ *Phil. Mag.* **26** (1938), 940.

In the earlier mass spectrograph experiments of Hogness and Harkness ions I_2^- and I_3^- were observed, undoubtedly formed by some secondary process.

The diffusion method has been applied by Bailey, Makinson, and Somerville† to the study of electron attachment in bromine, while Blewett‡ has obtained some interesting results incidental to an investigation of the isotopic constitution of bromine, using a mass spectrograph. The mean cross-section obtained in the swarm experiments is illustrated in Fig. 132. It will be seen to reach a maximum of 1.6×10^{-18} cm.² Blewett found that there is a sharp maximum in the rates of production of Br_2^- ions by 2.8-volt electrons. He was able to measure the kinetic energy of the ions produced by these electrons and hence to derive the electron affinity. The value found, 3.8 ± 0.2 eV, agrees very well with those derived from the energy of cyclic processes.§ There is no doubt then that the reaction involved is



and it is probable that this also is the one which gives rise to the attachment observed in the diffusion experiments.

Apart from this process Blewett also observed Br^- ions which probably arise from

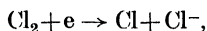


and Br_2^- ions the origin of which is more doubtful. They probably arise from secondary processes such as



which also seems to be operative in iodine.

Chlorine has been investigated by Bradbury|| using the filter method and by Bailey and Healey†† using the diffusion method. The observed attachment cross-sections as functions of the mean electron energy are illustrated in Fig. 132. Although the results are subject to considerable uncertainty, there is reason to believe that the cross-section reaches a maximum at a mean electron energy of about 1.5 eV. It is probable that the process concerned is



as for bromine and iodine, which is certainly possible on energetic grounds—the electron affinity of Cl (3.8 eV) is higher than the dissociation energy (2.8 eV) of Cl_2 .

† *Phil. Mag.* **24** (1937), 177.

‡ *Phys. Rev.* **49** (1936), 900.

§ See Massey, *Negative Ions* (2nd edition, Cambridge, 1950), Chap. I.

|| *J. Chem. Phys.* **2** (1934), 827.

†† *Phil. Mag.* **19** (1935), 725.

6.9. *Electron collisions in other gases and vapours*

The effects of electron impacts in a great number of other gases and vapours have been investigated. For most of this work a mass spectrograph of some type has been employed and the observations made usually consist of the appearance potentials and abundance ratios for different ionic fragments (measured at an electron energy of 100 eV or so). Data of this sort are useful as a means of rapid analysis of such systems as oils, so that a considerable amount of work has been devoted to the study of impact effects in hydrocarbons and other organic compounds. In view of the considerations discussed in § 6.21, too much significance should not be attached to the observed abundance ratios as they undoubtedly include instrumental effects. These are particularly pronounced if the ions concerned possess initial kinetic energy. It seems also that the collecting efficiency of a spectrograph is often very low for negative ions. Otherwise, for those ions whose peak shapes are sharp, indicating very small initial kinetic energy, the abundance ratios are probably at least qualitatively correct.

In a few cases the total cross-section for ionization has been measured over a considerable energy range. These results are included in Table III.

The interpretation of the results becomes more and more difficult as the complexity of the molecule increases. As the initial kinetic energy of the different ions concerned is rarely measured it is usually only possible to obtain rather vague information about such quantities as the ionization potentials of different molecular fragments.

In general the most probable ionization process (allowing for instrumental factors) is one in which a single electron is removed from the molecule but there is a finite probability of any one which is energetically possible. Thus, in Table V the abundance ratios of the ions formed from $C_6H_6^+$ by impact of 72-volt electrons are given. Only ions formed with small initial kinetic energy, as judged from the peak shapes, are included.

TABLE V

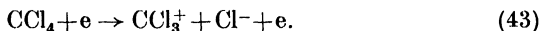
Abundance Ratios of Ions formed, with Small Initial Kinetic Energy, from C_6H_6 by Impact of 72-Volt Electrons

$C_6H_6^+$ 100, $C_6H_5^+$ 15.2, $C_6H_4^+$ 4.6, $C_6H_3^+$ 1.7, $C_6H_2^+$ 4.0, C_6H^+ 1.3, C_6^+ 0.2; C_5H^+ 2.6, $C_5H_2^+$ 0.6, C_5H^+ 0.5, C_4^+ 0.2; $C_4H_4^+$ 13.5, $C_4H_3^+$ 15.7, $C_4H_2^+$ 13.39, C_4H^+ 2.1, C_4^+ 0.3; $C_3H_3^+$ 0.6, $C_3H_2^+$ 3.6, C_3H^+ 2.5, C_3^+ 0.3; $C_2H_4^+$ 0.2, $C_2H_3^+$ 1.3, $C_2H_2^+$ 1.1, C_2H^+ 0.14, C_2^+ 0.03; CH_3^+ 0.01, CH_2^+ 0.02, CH^+ 0.03, C^+ 0.05; H_2^+ 0.15, H^+ 0.2; $C_6H_6^{++}$ 1.8, $C_6H_5^{++}$ 0.18, $C_6H_4^{++}$ 0.42, C_6H^{++} 0.015.

Exceptions to the rule concerning the most probable process occur in certain molecules which include chlorine atoms. Thus Baker and

† Hustrulid, Kusch, and Tuto, *Phys. Rev.* **54** (1938), 1037.

Tate† found that, in CCl_4 , CCl_3^+ ions were by far the most abundant, the intensity of CCl_4^+ ions being only 2×10^{-4} times as large. They produced evidence, from a study of the abundance of Cl^- , that the most probable primary process in this case is



A similar but not so pronounced effect was observed by Vought‡ for SiCl_4 . With his spectrograph the abundance ratio of SiCl_4^+ to SiCl_3^+ was as 56:100 but, owing to the poor collecting power of his instrument for negative ions, he was unable to establish with certainty that the process concerned is similar to (43). Kusch, Hüstrulid, and Tate§ have found also that, for the three chlorides PCl_3 , AsCl_3 , SbCl_3 the ions XCl_2^+ are more abundant than XCl_3^+ in the ratio 1.82, 1.66, 1.71 for the respective cases. Although no observations were made of the negative ions it is again probable that for these cases also the most probable primary reaction is of the type (43).

A summary of the molecules which have been investigated is given in Appendix II which includes the relevant references to the original papers.

6.91. Metastable ions. It is rather surprising that such a bewildering variety of stable ions may be produced as are actually observed to arise from benzene. One might expect that some initial products of electron impact might well be unstable and dissociate spontaneously a short time after impact. Evidence of the formation of such metastable ions has been given by Hipple and Condon.|| This was discovered in the following way.

In the course of study of the ions formed from normal butane (C_4H_{10}) using a sector-type mass spectrograph employing a 90° deflexion, three diffuse peaks were observed near masses 30, 32, and 39. The last appeared as a 'hump' on the side of the main peak and was attributed to C_3H_7^+ ions formed with initial kinetic energy. In obtaining these results the potentials were applied in the usual way (Fig. 133(a)), so that the ions reached the collector plate with the full energy to which they had been accelerated before passing into the analyser chamber. If, on the other hand, the collector plate was maintained at the same potential as the first slit of the spectrograph (Fig. 133(b)), then the ions reached the collector with a few volts energy only. It was found that, when the spectrograph was connected in this way, the diffuse peaks disappeared, showing that the ions producing them had lost energy after passing out of the ion gun. This would be so if the ions concerned were produced by the break-up of a larger ion into smaller fragments after acceleration from the ion gun.

Let m_0 be the mass of the metastable ion, m_1 that of the smaller ion fragment produced by its break-up. If the break-up involves no release of internal kinetic energy and occurs before entering the magnetic field, the ion fragment will be focused as if it possessed a mass m^* where

$$m^* = m_1^2/m_0. \quad (44)$$

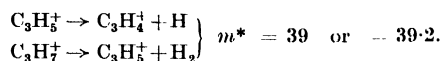
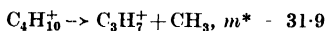
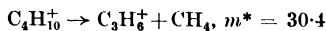
† *Phys. Rev.* **53** (1938), 683.

§ *Ibid.* **52** (1937), 840.

|| *Ibid.* **68** (1945), 54; also Hipple, *ibid.* **71** (1947), 594.

‡ *Ibid.* **71** (1947), 93.

The diffuse peaks, obtained with butane, can be explained in this way as arising from



or

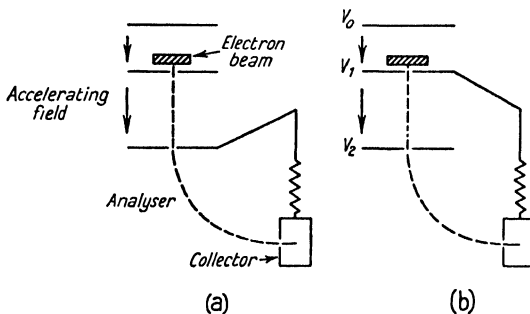


FIG. 133. Schematic diagram showing electrical connexions in mass spectrograph to demonstrate the presence of metastable ions. (a) ions reach collector with full energy of accelerating field; (b) ions reach collector with only a few eV energy.

Evidence in favour of this explanation was obtained by studying the variation of peak height with the potential drawing ions from the beam to the first slit of the ion gun† (the potential $V_1 - V_0$ in Fig. 133 (b)). The faster the metastable ions are drawn out the less the chance that they should suffer dissociation before reaching the analysing chamber, so that the relative intensity of the diffuse peaks should increase with increase of $V_1 - V_0$. This was observed quite definitely for all three. From the magnitude of this effect Hipple‡ was able to estimate the half-lifetime of the metastable ions as of order 10^{-6} sec.

Similar effects have been observed with a number of other hydrocarbons. The formation of metastable ions also seems to explain a number of other features of the mass spectra of hydrocarbons such as the variation of abundance ratios from one instrument to another and with the initial temperature of the vapour concerned.

The conditions in which the effect was found were especially favourable inasmuch as the ions after leaving the gun traversed a considerable path before entering the magnetic field. The fact that similar peaks were observed with instruments employing semicircular focusing in which their path was relatively much shorter was raised as an argument against Hipple and Condon's suggestion. It has been shown, however, by Hipple‡ that the position of the peak due to a dissociation fragment is still given approximately by the relation (44) even when the dissociation takes place after appreciable travel through the analyser. Using the estimated half-lifetime he was able to show that the expected peaks would be much as observed even in a 180° instrument of the standard type.

† Hipple, Fox, and Condon, *ibid.* 69 (1946), 347.

‡ *Ibid.* 71 (1947), 594.

In view of these results it is clear that care must be taken, when dealing with complex molecules, to distinguish between diffuse peaks due to ions with initial kinetic energy and to dissociation of metastable ions.

7. Excitation of molecular vibration and rotation by electron impact

In view of the large mass ratio of nuclei to electrons it is to be expected that, on impact between an electron and a molecule, there will only be a very small chance that any of the kinetic energy of the electron will be transferred to excite molecular vibration or rotation. The fact that the Franck-Condon principle provides a good description of electronic transitions in a molecule, due to electron impact, supports this viewpoint. On the other hand, there is a variety of evidence to show that electrons which are so slow as to be unable to excite any electronic transitions do, nevertheless, lose energy in passing through a molecular gas at a rate faster than would be the case if the collisions were elastic only (i.e. if the fractional loss per impact were, on the average, equal to $2m/M$, where m is the mass of an electron and M that of the molecule). The subject has recently become important for the interpretation of certain phenomena involving the interaction of radio waves.

7.1. *The interaction of radio waves*

The first observations of interaction between radio waves from two different stations were made in 1933 in Holland† and England. Thus it was found that, in reception from various medium-wave transmitters located in western Europe, modulation of the long-wave transmitter at Luxemburg (252 kc.) could also be traced. This interference was especially marked at night, indicating that the interaction occurred in the ionosphere, a result confirmed by later work. Since these initial observations extensive investigations of the effect have been carried out.

The theoretical explanation of the phenomenon was first given by Bailey and Martyn‡ in 1934 and is now well established. According to this, absorption of the interfering waves increases the mean energy of the electrons in the ionosphere. This in turn leads to an increase in the collision frequency of the electrons. As the absorption of a wave in a region of the ionosphere is determined by the collision frequency of the electrons in that region, the absorption of the 'wanted' wave is changed by the presence of the interfering wave. This modification takes the form of an impressed modulation of the wanted wave characteristic of that in the interfering wave.

The detailed theory is complicated by the effect of the earth's magnetic field. We shall content ourselves here with merely outlining the relation of the cross modulation to the electron collision frequency and the average energy loss experienced by an electron per collision with an atmospheric molecule, neglecting the earth's magnetic field.

† Telligen, *Nature*, **131** (1933), 840.

‡ *Phil. Mag.* **18** (1934), 369; Bailey, *ibid.* **23** (1937), 929 and **26** (1938), 425; Huxley, Foster, and Newton, *Proc. Phys. Soc.* **61** (1948), 134; Ratchliffe and Shaw, *Proc. Roy. Soc. A*, **193** (1948), 311.

Let W be the work per second done on an electron by the interfering wave. Part of the energy gained in this way by an electron will be lost in collisions with gas molecules, only the remainder leading to an increase in electron energy. If $\Delta\epsilon$ is the average excess energy at time t of an electron above that of the mean energy of the gas molecules, due to the interfering waves, then the average loss of energy per collision of an electron may be written $G \Delta\epsilon$ (see Chap. I, § 5.3).† We have then

$$W = \frac{d(\Delta\epsilon)}{dt} + \nu G \Delta\epsilon. \quad (45)$$

Also as the mean velocity v of an electron is related to the collision frequency by the relation $v = \nu l$, where l is the mean free path, we have

$$\Delta\epsilon = m l^2 \nu \Delta\nu,$$

where $\Delta\nu$ is the increase of ν due to the interfering wave. Hence

$$\frac{d}{dt}(\Delta\nu) + \nu G \Delta\nu = W/m l^2 \nu. \quad (46)$$

We now consider the calculation of W . If the absorption coefficient of the interfering wave is κ_i , measured along the direction x of propagation, the magnitude of the electric vector may be written

$$E = E_0 e^{-\kappa_i x}. \quad (47)$$

The energy absorbed per second in a slab of the ionosphere of thickness δx and unit cross-section will therefore be

$$- \frac{d}{dx} \left(\frac{K E^2}{4\pi} \right) \delta x,$$

where K is the dielectric constant of the region within the slab. In view of (47) this may be written

$$K \kappa_i E_0^2 \delta x / 2\pi. \quad (48)$$

As the slab contains $n_e \delta x$ electrons, n_e being the electron concentration,

$$W = \frac{K \kappa_i}{2\pi n_e} E_0^2.$$

Since the absorption coefficient κ_i is given by‡

$$K \kappa_i = \frac{2\pi n_e \epsilon^2}{mc} \left\{ \frac{\nu}{p^2} + \frac{\nu}{\nu^2} \right\}, \quad (49)$$

where p is the frequency of the interfering wave, we have

$$W = \frac{\epsilon^2}{mc} E_0^2 \frac{\nu}{p^2 + \nu^2}.$$

For sinusoidal modulation of the interfering wave with frequency $n/2\pi$,

$$E = E_1(1 + M \sin nt),$$

$$\text{so} \quad W = \frac{\epsilon^2}{mc} E_1^2 \frac{\nu}{p^2 + \nu^2} \{1 + 2M \sin nt + \frac{1}{2} M^2 (1 - \cos 2nt)\}. \quad (50)$$

Hence if we ignore the term in M^2 the modulation contributes an amount

$$W_n = M E_1^2 \nu f(p, \nu) \sin nt. \quad (51)$$

This gives, on substitution in (46),

$$\Delta\nu = \Delta\nu_0 \sin(nt - \phi), \quad (52)$$

† The relation between G and λ is discussed in § 7.3.

‡ Booker, *Proc. Roy. Soc. A*, **150** (1935), 267.

$$\text{where} \quad \Delta\nu_0 = ME_1^2 f(p, \nu) / m l^2 \nu G \{1 + (n/G\nu)^2\}^{\frac{1}{2}}, \quad (53)$$

$$\text{and} \quad \tan \phi = n/G\nu. \quad (54)$$

It remains to determine the effect of this oscillation of $\Delta\nu$ on the wanted wave. According to (49), the absorption coefficient of the wanted wave is proportional to the collision frequency ν provided $p \gg \nu$, as it is for the cases of interest. The amplitude of the electric vector of the wanted wave after passage through the interacting region will therefore be given by

$$E_w = E_w^0 e^{-\alpha\nu}, \quad (55)$$

where α is a constant independent of ν . Since, with the interfering wave present,

$$\nu = \nu_0 + \Delta\nu_0 \sin(nt - \phi),$$

$$\text{we have} \quad E_w = E_w^0 e^{-\alpha\nu_0 \{1 - M_i \sin(nt - \phi)\}}, \quad (56)$$

where

$$M_i = \alpha \Delta\nu_0 \\ = \frac{\alpha M (E_w^0)^2 f(p, \nu)}{m l^2 \nu G \{1 + (n/G\nu)^2\}^{\frac{1}{2}}}. \quad (57)$$

The wanted wave is thus modulated with the modulation frequency of the interfering wave, the coefficient of modulation M_i being as given in (56). It depends on the modulation frequency n of the interfering wave through the factor

$$\{1 + (n/G\nu)^2\}^{\frac{1}{2}}.$$

Observations of M_i at different values of n thus enable $G\nu$ to be determined.

7.2. The observed results on energy losses by very slow electrons

The only direct experiments which have been made are those of Harries† in nitrogen and Ramien‡ in hydrogen using the Hertz method (see Chap. II, § 5.2, and § 5.2 of this chapter). In the latter experiments an energy loss was found which could be interpreted as due to excitation of one vibrational quantum (0.54 eV) with a chance per collision decreasing from 0.03 for 3.5-volt electrons to 0.02 for 7-volt electrons. Harries found a similar but less probable effect in nitrogen, the chance per collision for 5.2-volt electrons being 1/79.

Information, of a less definite character, may also be obtained from swarm experiments. It was shown in Chap. I, § 5.2, that if electrons are allowed to diffuse through a gas at pressure p under the influence of a uniform electric field of strength F and the drift and random velocities u and c are both measured, then the mean free path l for momentum transfer and the mean fractional energy loss λ per collision may both be determined for electrons of mean energy determined by F/p . For present purposes the formulae (29) and (30) of Chap. I, § 5.3, may be used to give approximately

$$\lambda = 2u^2/c^2.$$

† *Zeits. f. Phys.* **42** (1927), 26; Harries and Hertz, *ibid.* **46** (1927), 177.

‡ *Ibid.* **70** (1931), 353.

A more precise treatment would require detailed knowledge of the nature of the impacts giving rise to the energy loss and is only likely to introduce a numerical factor of order unity in this expression.†

Methods of measuring the drift and random velocities of a diffusing swarm have been described in Chap. I, §§ 6 and 7, and these may be applied to determine λ for a number of molecular gases for electrons of quite low mean energies.

Results that have been obtained are given in Table VI.‡ They have been derived from measurements of the random velocity by Townsend's method (Chap. I, § 6) and of the drift velocity by the method of Townsend and Bailey (Chap. I, § 7.1). Drift velocities have also been measured by Bradbury and Nielsen's method (Chap. I, § 7.2) for a number of the gases investigated. These agree well with those obtained with the other method and separate values are not given in the table.

TABLE VI
Average Fractional Energy Loss λ due to Collisions with Gas Molecules of Electrons of Different Mean Energy $\bar{\epsilon}$

Gas	Air		H ₂	N ₂	O ₂	CO	NO	HCl	N ₂ O	CO ₂	NH ₃
$2m/M \times 10^4$	0.372		5.45	0.387	0.341	0.387	0.363	0.298	0.247	0.247	0.641
$\bar{\epsilon}$ (eV)	$\lambda \times 10^4$										
	(i)	(ii)									
0.1			25			45		250	600	360	285
0.2	13	26	29	7	65	70	110	600	1,500	580	420
0.4	13	26	31	6	55	89	390	450	1,300	650	370
0.6	13	26	36	6	33	70	450	350	1,100	630	330
0.8	13	26	42	6.5	24	54	380	290	1,000	600	305
1.0	14	28	47	8.8	20	62	320		900	575	280
1.2	15	30	51	12.8	15	75	275		880	560	255
1.4	16	43	56	22.5	24	110	275	..	860	550	240
1.6	17	83	62	48	32	150	280	..	800	540	220
1.8	19	150	71	90	70	195	320	..	740	535	215
2.0	20	220	80	162	105	250	..	..	690	535	230
2.5	28	335	100	294	240	360	..	..	600	515	..
3.0	40	415	130	389	355	470	..	..	540	..	..
4.0	62	580	255	500		..	..	..	..	..	..
5.0	86	725	440	580		..	..	..	..	..	..
6.0		870									

The values given in this table are those quoted in Healey and Reed, *The Behaviour of Slow Electrons in Gases*, except in the case of column (i) for air. The values in this column are those of Huxley and Zaazou, and they differ markedly from the values of Townsend and Bailey given in column (ii). The differences in λ arise from very considerable differences in the measured relation between ϵ and F/p .

It will be seen that in all molecular gases λ is considerably greater than the value $2m/M$ expected if only elastic collisions occur. Little has been done to analyse these data further as there is little theoretical guidance available from which to proceed. Massey§ has calculated the probability

† With a velocity distribution of the form (12) of Chap. I the factor is 1.27 and with a Maxwellian distribution it is 1.178.

‡ Following Townsend, *Motion of Electrons in Gases*, p. 17, the relation $\lambda = 2.46u^2/c^2$ has been used to obtain this table.

§ *Trans. Far. Soc.* **31** (1935), 556. See also Wu, *Phys. Rev.* **71** (1947), 111.

of exciting a vibrational quantum of H_2 by applying the usual collision theory. He finds that it is necessary to allow for the variation with nuclear separation of the screening effect of one atom on the field of the other in order to obtain agreement with Ramien's observations. This is equivalent to supposing that the electron acts not purely dynamically but by changing the relative energy of the atoms due to its Coulomb field, a possibility first pointed out by Franck.[†] It has also been pointed out by Massey[‡] that the excitation of rotational motion in molecules possessing a dipole moment is likely to be quite efficient. The small mass of the electron is partly compensated by the great range at which it can interact with the molecule, so the effective couple it can exert is not necessarily small. Bennett and Thomas[§] have made a rough analysis of the observed value of λ for hydrogen in which they show that the efficiency of rotational excitation must be quite high even in this molecule which possesses no dipole moment. Care must be taken, in interpreting the results, that the effects are not due to electronic excitations involving comparatively small energy losses. Thus for O_2 the first excited electronic level lies only about 1 eV above the ground level. Energy loss due to excitation of this level by the higher energy electrons in the swarm would clearly give rise to a value of λ considerably in excess of $2m/M$ for mean energies much less than 1.62 eV. As inadequate knowledge is available of the cross-sections for the excitation of these low-lying electronic levels it is not possible to decide to what extent they contribute to the observed values of λ . Much more remains to be done before the interpretation is on a satisfactory basis. It seems improbable, however, that all the observations can be explained in terms of losses in excitation of electronic levels by the faster electrons. This is particularly true for hydrogen, as in this case there is no low-lying excited electronic level.

7.3. Application to radio wave interaction

The results for air are of special interest in view of their application to radio interaction effects. The values given have been obtained by Huxley and Zaazou|| with the apparatus described in Chap. I, §§ 6 and 7.1. Extrapolating these results to zero mean energy gives the value of λ to be used in the interpretation of the radio data (see § 7.1).

It must be noted that G is equal to λ only when the electron energy is considerably in excess of that of the gas molecules. When it is only slightly in excess

$$\lambda = G(1 - 4\epsilon_0/3\bar{\epsilon}),$$

[†] Franck and Jordan, *Anregung von Quantensprungen durch Stösse* (1926), p. 255.

[‡] *Proc. Camb. Phil. Soc.* **28** (1932), 99.

[§] *Phys. Rev.* **62** (1942), 41.

|| *Proc. Roy. Soc. A*, **196** (1949), 402.

where ϵ_0 is the mean energy of the molecules. It is found to be 1.3×10^{-3} .† (For contrast the value given on the assumption of an average fractional loss $2m/M$ would be only 3.4×10^{-5} .) Since the diffusion cross-section may also be obtained from the measurements as described in Chap. I, § 5, the collision frequency and hence $G\nu$ may be obtained as a function of air pressure. The values of $G\nu$ derived in this way are found to agree with those derived from observations of radio interaction if the pressure in the region of interaction is between 5×10^{-3} and 7×10^{-3} mm. Hg.‡ From data secured by rocket observations§ this places the height of the region between 82 and 85 km., considerably below the E' region of the ionosphere.

† Huxley and Zaazou, loc. cit. But see footnote to Table VI.

‡ Huxley, *Proc. Roy. Soc. A*, **196** (1949), 427.

§ Best, Havens, and La Gow, *Phys. Rev.* **71** (1947), 915.

REFLECTION AND SECONDARY EMISSION FROM SURFACES DUE TO ELECTRON BOMBARDMENT

1. Introduction

WHEN a beam of electrons is allowed to fall on a metal surface, some of the electrons are scattered, elastically or inelastically, and may have their directions deflected through angles greater than 90° , in which case they will appear to be 'reflected'. If such electrons have been scattered elastically they will emerge from the surface with an energy practically equal to that of the incident electrons, while if they have suffered inelastic scattering they will emerge with energy somewhat less than that of the primary electrons. It is found, however, that another group of electrons emerges from the metal. These electrons possess low energies, no more than a few tens of volts. Most of them have an energy of 2 or 3 eV only, and this energy is practically independent of the energy of the incident electrons. The electrons in this group are actually ejected from the metal as a result of the bombardment of the incident electrons. They are called secondary electrons, and under some circumstances their number may exceed the number of primary electrons incident on the surface.

Fig. 134 illustrates a typical energy distribution obtained by Rudberg† for electrons emerging from a target of silver as a result of bombardment by primary electrons of 150 eV energy.

In this figure four main regions in the energy distribution of the scattered electrons may be distinguished. *A* consists of the electrons which have undergone large angle scattering and appear as 'reflected' electrons. *B* consists of a small portion of the distribution, representing electrons which have undergone single inelastic scattering and show a fine structure determined by the distribution of the energy bands for the electrons in the metal. The low-energy group *D* represents true secondary emission of electrons from the metal. The intermediate group *C* is rather difficult to specify. It is composed partly of the high-energy tail of the secondary electron distribution. In the main, however, it arises from the primary electrons that have lost energy in multiple scattering—the so-

† *Phys. Rev.* **50** (1936), 138.

called 'back-diffused' electrons. It is clear that the separation of regions *C* and *D* will be very difficult. Ordinarily it is not attempted.†

Secondary electron emission seems to have been observed first by Austin and Starke‡ and a very extensive literature is now available.§

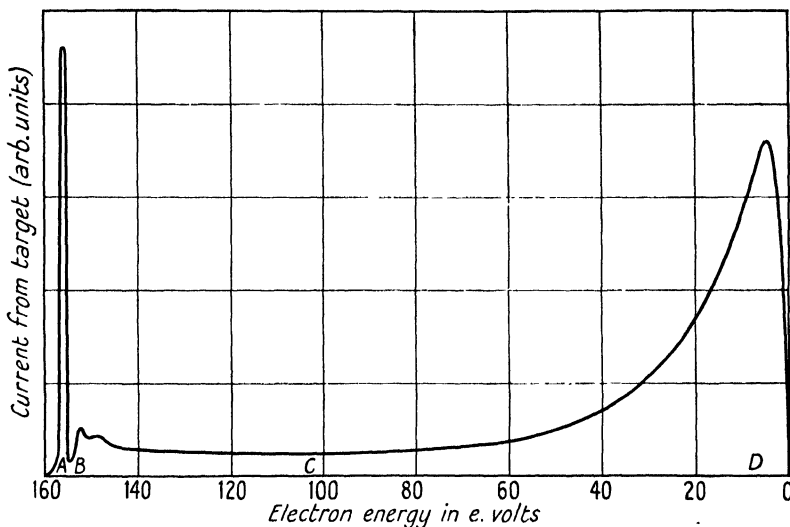


FIG. 134. Energy distribution of electrons emerging from a target of silver following bombardment by primary electrons of energy 150 eV.

The subject has achieved great practical importance, particularly as a result of the application of the phenomena in the electron multiplier tubes of television. Such tubes have recently been used also for the counting of single ionizing particles.

The topics to be studied in connexion with the reflection and secondary emission of electrons from surfaces include the number of emergent electrons of the different types compared with the number incident, and its dependence on the energy of the primary electrons, the angles

† Rudberg's measurements refer to electrons emerging from the surface of the target at an angle of 45° to the normal. The beam is also incident at 45° to the normal and the incident and emergent electrons are at right angles. This arrangement will tend to increase the importance of the 'back-diffused' electrons. But they seem always to be present.

‡ *Ann. der Physik*, **9** (1902), 271.

§ Two excellent reviews of the subject of secondary electron emission have been published in recent years, viz. Bruining's *Die Sekundär-Elektronen-Emission fester Körper* (Berlin, Springer, 1942) and an article by McKay in *Advances in Electronics* (Academic Press Inc., New York, 1948), p. 66. These works carry extensive lists of references.

of incidence and emission, the nature of the emitting material, and the condition of its surface. Strictly speaking, the phenomena of electron diffraction are also involved, but in view of the extensive literature which already exists on this important subject† we shall somewhat arbitrarily exclude it from the scope of this book.

We deal first with the case of slow primary electrons (of energy less than 1,000 eV) and discuss in turn the secondary emission and elastic and inelastic scattering. We return later to a brief discussion of effects produced by the impact of faster beams of electrons with surfaces.

1.1. *The coefficient δ of secondary electron emission*

The coefficient of secondary electron emission is defined as the ratio of the number of secondary electrons emitted from a surface to the number of primary electrons incident.

In order to distinguish true secondary electrons from reflected, inelastically scattered, or back-diffused electrons it would be necessary to carry out an analysis of the energy of the emitted electrons. The slow electrons would then be interpreted as being true secondaries, while the faster groups would be interpreted as scattered primaries. However, such a separation has been made in comparatively few experiments. Accordingly, in the rest of this chapter the so-called 'coefficient of secondary electron emission' measures the ratio of the total electron current issuing from the target to the total primary current incident. For the understanding of the physical processes occurring it is very desirable that more data should be obtained in which the various effects are separated out. The fraction of the apparent secondary current that arises from the elastic scattering (or 'reflection') of the primary electrons decreases with increase of primary electron energy. At a primary electron energy of 100 eV it is of the order of 0.1, so that above this energy the measurements of the coefficient of secondary emission include few reflected electrons.‡ Measurements carried out at lower energies, however, may contain comparable numbers of electrons of each type.

For primaries of a few electron volts energy there are no secondary electrons, but about 20 per cent. of the incident electrons may be reflected with their full energy. True secondary electrons begin to appear at primary energies of 10–20 eV. The coefficient of secondary

† See, for example, G. P. Thomson and Cochran, *Theory and Practice of Electron Diffraction*, Macmillan, London (1939).

‡ The difficulty of separating the 'back-diffused' electrons from the secondary electrons still remains, however. Normally at low primary energies (less than 1,000 eV say) no attempt is made to do so. They are all included as secondary electrons.

electron emission δ increases rapidly with increase of primary electron energy E_p^0 , reaches a rather flat maximum at a primary electron energy of some hundreds of electron volts, and then falls off slowly with further increase of E_p^0 . The form of the relationship between δ and E_p^0 is reminiscent of the curves showing the variation of the ionization cross-section of atoms by electron impact as a function of electron energy (see Chap. 11, Fig. 17; Chap. III, Fig. 80).

The quantity δ , as we shall see, depends to some extent on the angle the incident electron beam makes with the surface. In this chapter, unless otherwise stated, the values of δ refer to normal incidence.

2. Experimental methods of studying secondary electron emission

2.1. Measurement of δ

The measurement of the secondary electron emission coefficient, δ , from a metal surface is simple in principle. A beam of electrons of known energy is directed on to the metal surface and the emitted secondary electrons observed. A typical arrangement is shown in Fig. 135, which illustrates the apparatus used by Farnsworth.[†]

Electrons ejected from the indirectly heated oxide-coated cathode K are accelerated through holes 3 mm. in diameter in electrodes A , B , C . They are collected by the Faraday cylinder, F , which is made 15 cm. long in order to prevent the escape of secondaries. This measures the true primary current passing through the hole D , 1 cm. in diameter. A target T is then moved magnetically into the path of the beam between D and F and the current to it measured. Let i_F , i_T be respectively the current to the Faraday cage F and to the target T . Then the total number of electrons reflected or emitted from the target T is $i_F - i_T$.

By magnetic means the target T can be moved into the side tube G and outgassed by eddy-current heating, or alternatively an evaporated film may be deposited on it by heating a metal disk in another side tube.

2.11. Measurement of δ for a metal wire. Most of the measurements of secondary electron emission have been made by means of a method

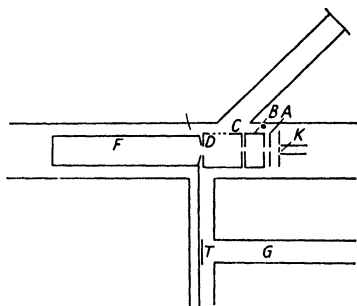


FIG. 135. Illustrating Farnsworth's apparatus for measuring δ .

[†] *Phys. Rev.* **25** (1925), 41.

similar in principle to that of Farnsworth. For some special purposes, however, it is more convenient to use different arrangements. For example, when a study is being made of the effect of surface contaminations on the secondary electron emission it is convenient to have some means of thoroughly cleaning the specimen by heating it to a high temperature. For such applications an ingenious method of measurement has been developed by Treloar.[†] His arrangement (Fig. 136 (a))

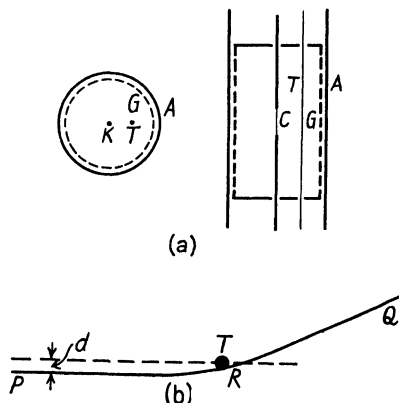


FIG. 136. Treloar's apparatus for measuring δ for a metal surface. (a) electrode arrangement; (b) illustrating a typical electron trajectory in the apparatus.

consists of a cylindrical nickel anode A , 40 mm. long and 25 mm. diameter. Concentric with the anode is a grid G , of diameter 22 mm., consisting of 0.11-mm. nickel wire, spaced 2.1 mm. apart. A cathode K of 0.105-mm. tungsten wire, 12 mm. long, is placed along the axis of the system. The cathode and grid are maintained at the same potential. The material under investigation is in the form of a fine wire, T , which can thus be easily outgassed. The field due to the potential V_A on the anode penetrates into the space between K and G . If the potential, V_T , of T is greater than that of the surrounding space, secondary electrons emitted from T cannot escape. On the other hand, no secondary electrons can leave the anode on account of the potential difference between A and G . If, however, the anode potential is raised to a sufficiently high value the potential of the space around T exceeds that of T itself, so that secondary electrons are now able to leave T and pass to the anode.

[†] *Proc. Phys. Soc.* **48** (1936), 488.

Thus by varying the potential of A over a wide enough range it is possible either to prevent secondaries from leaving T or to collect them to the anode A .

Consider the electron path PRQ (Fig. 136(b)) which just grazes the wire T (radius a). Let d be the impact parameter corresponding to this electron and let v, v' be its velocity at P, R , respectively so that

$$mvd = mv'a \quad \text{and} \quad d = v'a/v.$$

If l is the length of the cathode and j the current density at T , the current striking T is $i = 2jdl = 2jal(V_T/cV_A)^{\frac{1}{2}}$, where V_T, V_A are respectively the potentials of the target and the anode and c is a constant. The experiment consisted in the measurement of the net target current i_T as a function of $(V_T/V_A)^{\frac{1}{2}}$ for a series of values of V_T . If there were no secondary emission the relation between these quantities would be linear.

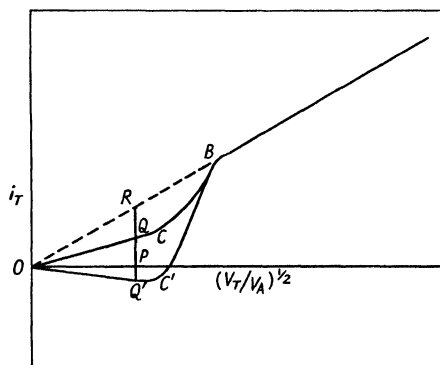


FIG. 137. Current to the wire in Trelour's experiment plotted against $(V_T/V_A)^{\frac{1}{2}}$ for constant V_T . Curve OCB is obtained for $\delta = 1$; $OC'B$ for $\delta < 1$.

Fig. 137 shows a typical curve obtained for constant V_T . For small values of V_A (i.e. large $(V_T/V_A)^{\frac{1}{2}}$), the secondary electrons cannot escape from T so that the current to T is a true measure of the actual primary current reaching it. As $(V_T/V_A)^{\frac{1}{2}}$ decreases a point B is reached at which secondary electrons from T pass to A . When this occurs, the curve falls below the line OB until a point C is reached at which all the secondary electrons are collected to A . When V_A is further increased, i_T lies on another straight line, OC . The line OB represents the primary current to T for different values of V_A . The difference between the curves OC and OB represents the secondary emission current from T . The secondary electron emission coefficient is then given by $\delta = QR/PR$.

2.12. Thermionic valve methods of measuring δ . The triode valve has been used by many workers for the determination of the secondary electron emission coefficient. Thus consider a triode with cylindrical grid and anode and axial cathode. The material being investigated is placed on the inside of the anode surface. Let V_A , V_G be the potential differences between the cathode and the anode and grid respectively, and suppose V_G is greater than V_A so that secondary electrons pass from the anode to the grid. Let i_c be the total cathode current and f the fraction of this current which goes to the grid so that the current to the anode is $(1-f)i_c$. If δ is the secondary emission coefficient of the anode, the secondary emission current from the anode is

$$i_s = \delta(1-f)i_c. \quad (1)$$

The total anode current is accordingly

$$i_A = (1-f)i_c + i_s. \quad (2)$$

On the other hand, the grid current is

$$i_G = fi_c + i_s. \quad (3)$$

From equations (1), (2), and (3) we obtain then

$$\delta = 1 - \frac{i_A}{(1-f)(i_G + i_A)}. \quad (4)$$

The difficulty in this method of measurement lies in the uncertainty in the determination of the factor f . Hyatt and Smith† did this by introducing caesium vapour into the triode so that caesium ions were produced by surface ionization at the hot tungsten filament. These ions do not produce secondary electrons when their energy is below 100 eV, so that, by reversing the potentials to the grid and anode while maintaining them below 100 volts, Hyatt and Smith were able to measure f for different values of the ratio V_A/V_G , quite independently of secondary emission effects. Assuming (in the absence of space-charge effects) the electron optics to be independent of whether electrons or ions are being used, the value of f so determined can be substituted in (4), and δ can be calculated.

Some investigators‡ have attempted to deduce f by measuring the ratio of currents to the grid and anode for very small values of V_A , but maintaining V_G/V_A constant. However, when such small plate voltages are employed, although the true secondary emission is small, the fraction of electrons undergoing elastic reflection may be considerable (up to 20 per cent. of those incident) so giving rise to a considerable error. Correction is also needed for contact potential differences.

† *Phys. Rev.* **32** (1928), 929.

‡ Vide, for example, van der Pol, *Physica*, **3** (1923), 253.

Myers† measured the true primary current to the anode by measuring its rise in temperature by means of a thermocouple and calculating the heat dissipation. However, he had to assume the average energy of emission of the secondaries was negligible compared with the primary electron energy—an assumption that is only justifiable provided the primary electron energy is large (say greater than 100 volts).

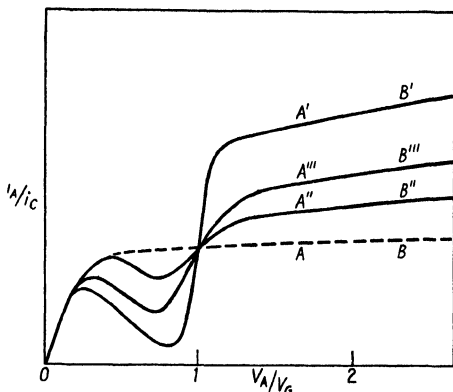


FIG. 138. Illustrating the determination of δ from triode characteristics. The curves show i_A/i_C plotted against V_A/V_G for different values of V_G .

De Lussanet‡ investigated the ratio of the anode current i_A to the total cathode current i_C for a triode (or tetrode) as a function of the ratio V_A/V_G , for a series of different values of V_G . A series of curves similar to those of Fig. 138 were obtained, each curve corresponding to constant V_G . When $V_A/V_G > 1$ the current to the anode includes, in addition to the current direct from the cathode, a portion due to secondary emission from the grid. For $V_A/V_G < 1$ the current to the anode is less than that directly from the cathode by the amount of secondary emission from the anode to the grid. If the curve OAB , which would be obtained for i_A/i_C as a function of V_A/V_G in the absence of secondary emission, could be found, the family of curves of Fig. 138 could be used to determine δ both for the anode and the grid for a wide range of incident electron voltages. For example, for a given value of $V_A/V_G (> 1)$, let α'_A be the value of i_A/i_C actually observed while α_A is the value that would be observed if there were no secondary emission, then

$$\delta(\text{grid}) = (\alpha'_A - \alpha_A)/(1 - \alpha_A), \quad (5)$$

† *Proc. Phys. Soc.* **49** (1937), 264.

‡ *Hochfrequenztechn.* **41** (1933), 195.

provided the ratio V_A/V_G is so high that all the secondaries from the grid reach the anode.

For the same value of V_A/V_G let α_A'' be the value of i_A/i_C observed for a different value of V_G and α_B , α_B' , α_B'' the quantities corresponding to α_A , α_A' , α_A'' for a different value of V_A/V_G . Then, since $\delta(\text{grid})$ for any curve of Fig. 138 is constant,

$$\frac{\alpha_A' - \alpha_A}{\alpha_A'' - \alpha_A} = \frac{\alpha_B' - \alpha_B}{\alpha_B'' - \alpha_B}. \quad (6)$$

If one point of the curve OAB is known it is possible from equation (6) to determine the whole curve. In general no point is known to begin with. De Lussanet chose a number of arbitrary starting-points and thus obtained a family of possible curves OAB , for which equation (6) held. These curves converged as V_A/V_G decreased towards unity. The same procedure was then applied in the region $V_A/V_G < 1$ giving a family of possible curves OAB , converging as V_A/V_G increased towards unity. The final curve OAB chosen was one of the family for the case $V_A/V_G > 1$ which fitted smoothly to one for $V_A/V_G < 1$.

The work of de Lussanet is probably the most thorough to be carried out in which δ is measured by means of a thermionic valve. Nevertheless, it suffers from the disadvantage that it is very difficult to ensure that all the anode-grid secondary electrons are collected.

Treloar† has used a pentode to obtain valve characteristics independent of secondary emission effects. The presence of the suppressor grid at the cathode potential, between the screened grid and the anode of the pentode, eliminates secondary electron currents. If now a tetrode is constructed of the same cathode, control grid, and screened grid construction as for the pentode, but with its plate in the same position as the suppressor grid of the pentode, and with a plate potential equal to the effective potential in the plane of the suppressor grid, then the difference in the characteristics of the two tubes should be due entirely to secondary emission in the tetrode. Comparison of anode and grid currents under the same conditions in the two tubes enables δ to be determined.

2.13. Measurement of δ for insulating materials. The methods described above cannot be used conveniently to measure δ for insulating materials, since the surface of the target will charge up. If δ is less than unity the surface will charge negatively until its potential is equal to that of the electron gun. If δ is greater than unity it will charge positively until its potential is so close to that of the collector that the space-charge

† *Wireless Engineer*, 15 (1938), 535.

limited current of electrons from the target is just equal to the incident current.

If thermal decomposition does not occur, the insulator may be heated so that it becomes a semi-conductor of resistance small compared with that of the measuring circuit. The methods applicable to conductors may then be used. This method has been applied, for instance, to determine δ for phosphorus.[†]

If the incident current is kept very small, the charging up of the insulating surface may take an appreciable time and, if some method can be found of measuring the potential of the surface at any instant, δ can be calculated from the rate of increase of this potential and the effective capacity of the insulator. The potential of the surface has been determined[‡] by passing an electron beam parallel to the surface and a few millimetres away from it and observing its deflexion on a fluorescent screen, or more directly by measuring the potential of wire probes embedded in the insulator near the surface.[§]

In a method used by Salow^{||} the specimen T is placed at the centre of the tube shown in Fig. 139 and surrounded by a collector C . A square-topped pulsating potential V_1 (frequency 50 kc.) produces an electron current i_1 from the gun G_1 while a steady potential V_2 produces the current i_2 from the gun G_2 . V_2 and the maximum of V_1 are chosen so that $\delta < 1$ for i_2 and $\delta > 1$ for i_1 .

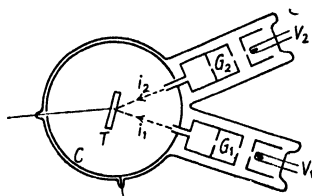


FIG. 139. Illustrating Salow's two-beam method for determining δ for non-conducting materials.

From time t_0 to t_1 the steady current i_2 is flowing and the potential V_T of T tends to drop towards V_2 . At time t_1 the current i_1 begins to flow, and V_T tends to rise to that of the collector. At time t_2 the current i_1 is interrupted and the steady current i_2 alone flows to T . V_T then tends to fall again towards V_2 . The displacement current i_3 , arising from the fluctuations of V_T , is shown in Fig. 140. It can be measured by an oscilloscope.

The potential V_T of T at time t is given by

$$CV_T = (\delta - 1) \int_0^t i_1(t) dt - \alpha i_2 t,$$

[†] Nelson, *J. App. Phys.* **9** (1938), 592; Martin and Headrick, *ibid.* **10** (1939), 116. See also von Frerichs and Krautz, *Phys. Zeits.* **40** (1939), 229; Mueller, *J. App. Phys.* **16** (1945), 453.

[‡] Scherer, *Arch. Elektrotech.* **34** (1940), 143; Piore and Morton, *J. App. Phys.* **11** (1940), 153.

[§] Nottingham, *ibid.* **8** (1937), 762.

^{||} *Zeits. f. techn. Phys.* **21** (1940), 8.

where C is the effective capacity of the plate P and α a constant. Thus i_3 is given by

$$i_3 = CdV_T/dt = (\delta - 1)i_1(t) - \alpha i_2.$$

From the oscillograph trace the contribution to i_3 from the current i_1 can be measured, and thence, knowing i_1 , the value of δ corresponding to electrons of energy V_1 can be determined.

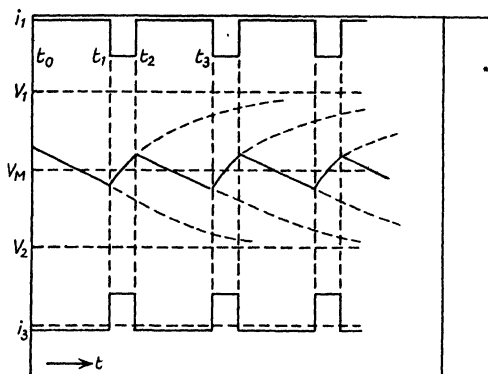


FIG. 140. Illustrating the fluctuation of the potential of the specimen about the mean value V_m in Salow's method of determining δ .

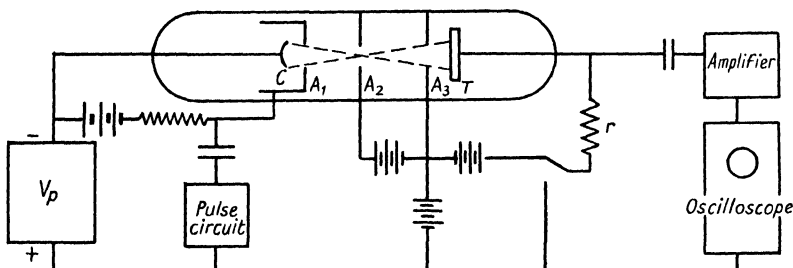


FIG. 141. Johnson's arrangement for determining δ for insulators.

Heimann and Geyer† have also used a pulse method for the measurement of δ , but the most elegant use of the pulse method has been due to Johnson,‡ using an apparatus whose principle is clear from Fig. 141. The insulator T is placed on the anode of the five-electrode tube and is connected to earth through the resistance r . Owing to the small but finite conductivity of the target it is at earth potential when no current

† *Elektrotech. Nachr.* **17** (1940), 1.

‡ *Phys. Rev.* **73** (1948), 1058.

flows in the tube. Normally current is prevented from leaving the cathode C by the retarding potential applied to the electrode A_1 . A square-topped positive pulse of duration 1 microsecond is applied to A_1 as a result of which a current pulse passes to T . Then, just as in Salow's method, the anode current of the tube while the pulse lasts is equal to $(1-\delta)i(t)$, where i is the incident current. The anode current pulse is observed by a single-sweep oscilloscope, synchronized with the application of the pulse to A_1 . If the potential of T increases appreciably during the pulse length of 1 microsecond, this can be observed immediately because the pulse on the oscilloscope will not be square-topped. In Johnson's work the recurrence frequency was made small enough to enable the target face to reach earth potential after each pulse.

The primary current could be determined either by measuring the total current to A_2 and A_3 when the target T was allowed to charge up, or by measuring the total current from the cathode. This latter method could only be used if the focusing were so good that all the cathode current reached the target—a condition satisfied in Johnson's work.

2.2. *Measurement of the energy distribution of the emitted electrons*

Although the ratio of the secondary to the primary current can be measured as described above, it is not possible by these methods to measure the energy distribution of the emitted electrons. This has been done either by retarding potential measurements or by magnetic deflexion methods employing techniques similar to those described in connexion with the measurement of inelastic scattering of electrons in Chap. II (§ 8).

The apparatus used by Bruining and de Boer,† shown in Fig. 142, is typical of the arrangements used when employing the retarding potential method. Electrons accelerated from a filament F , collimated by passage along the canal G , impinge on the target T which carries the material under investigation. The electron current emitted by the target is collected by the spherical collecting electrode S . Retarding potentials between S and T enable an analysis of the energy of the ejected electrons to be made.

Two methods of magnetic analysis of the secondaries have been employed. Fig. 143 illustrates the apparatus used

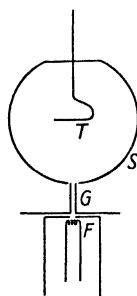


FIG. 142. Illustrating the apparatus used by Bruining and de Boer for determining the energy distribution of emitted secondary electrons by a retardation method.

† *Physica*, 5 (1938), 17.

by Rudberg,[†] employing the conventional transverse magnetic field. Electrons from the gun G strike the target T at an angle of incidence of 45° . A cylindrical shield S surrounds T and collects the bulk of the secondaries so that the total current to S and T gives a measure of the

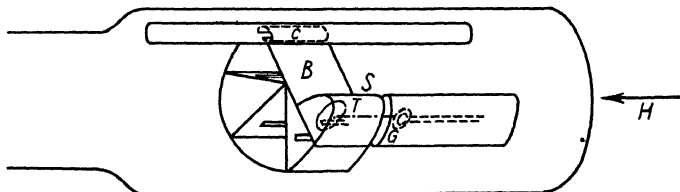


FIG. 143. Illustrating apparatus used by Rudberg for measuring the energy distribution of secondary electrons employing a transverse magnetic field.

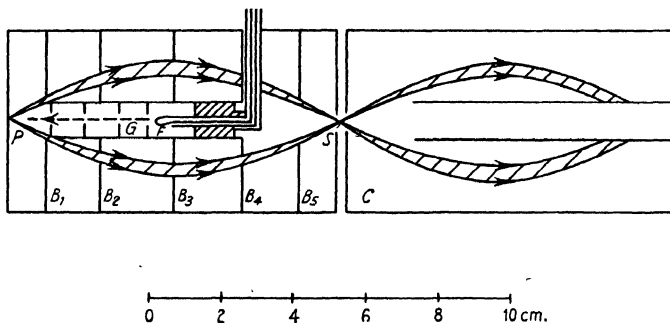


FIG. 144. Illustrating apparatus used by Kollath for measuring the energy distribution of secondary electrons employing a longitudinal magnetic field.

primary current. Some secondaries emitted at right angles to the primary beam pass through a slit and enter the deflexion box B . A magnetic field parallel to the axis of the system forms a velocity spectrum and focuses a definite velocity range into the collector C . In the usual procedure T , S , and B were maintained at the same potential, so that the velocity spectrum observed represented the true velocity distribution of the secondaries. Since the bulk of these electrons have low energies the radius of curvature is rather small.

A different method of studying the energy distribution of the ejected electrons has been used by Kollath.[‡] He used a longitudinal magnetic field to analyse the electron energies, his apparatus being shown in Fig. 144. Electrons emitted from the hot filament F are accelerated along the magnetic field by means of the gun G and impinge on the plate P .

[†] *Phys. Rev.* **50** (1936), 138.

[‡] *Ann. der Physik*, **39** (1941), 19.

Secondary electrons ejected from P in a range of solid angle between the two cones defined by the arrow lines in Fig. 144 are brought to a focus again at S . The motion of the secondary electrons is not, of course, confined to the plane of the diagram, but owing to the component of their motion perpendicular to the magnetic field they will tend to spiral around the direction of the field. At S the rays enter the collecting chamber and are measured. Baffle plates B_1, B_2, B_3, B_4, B_5 serve to define the beam and prevent scattered electrons from passing into C . If l is the length SP (about 9 cm. in Kollath's apparatus) and H the magnetic field, electrons of momentum p will be brought to a focus at S , where $l = (2\pi p/\epsilon H)\cos\alpha$, α being the angle the initial direction of the secondary electrons makes with the direction of the field.

Kollath's method provides much higher intensities than the method of the transverse magnetic field since, owing to the cylindrical symmetry, electrons in the whole solid angle defined by two coaxial cones can be collected. The primary electrons, moving along the lines of force of the field, are practically uninfluenced by the change in the magnetic field. It is much more difficult to ensure this in the method of the transverse magnetic field. Furthermore, since the analyser is a tube 2 in. in diameter it can be readily sealed in hard glass and thoroughly baked.

3. The theory of secondary electron emission

Three processes are important in the consideration of the production of secondary electrons. In the first place the primaries enter the target material and are rapidly slowed down. The maximum depth d_p to which the primaries penetrate is determined by their incident energy.

Secondly, in passing through the target the primaries suffer inelastic collisions with the electrons of the target as a result of which these latter (secondary) electrons receive energy sufficient to enable them to leave it if they are moving in the right direction.

Thirdly, the secondaries are themselves rapidly slowed down in passing through the target. Only if they are formed at a depth less than a certain maximum, d_s , can they escape. Since, as we shall see, the energy of the true secondaries is very insensitive to the primary energy, d_s is practically constant for all primary energies.

Provided the primary electrons are so slow that $d_p < d_s$, one would expect the true secondary electron coefficient to be an increasing function of the primary electron energy, while if $d_p > d_s$, δ should increase or decrease with primary electron energy according as the cross-section for inelastic collisions of primary electrons with the target electrons is increasing or decreasing with energy.

In analogy with inelastic collisions of electrons with atoms one might expect this cross-section eventually to decrease with increase of primary energy. From these general considerations then one would expect δ to increase to a maximum $\delta_{\max}$, at a certain primary voltage V_p . We shall see later (§ 4.1) that this behaviour is just what is observed.

3.1. The allowed energies and wave functions of electrons in a crystal

Before discussing the theory of secondary emission it is necessary to summarize certain of the main features of the allowed levels in a crystal.

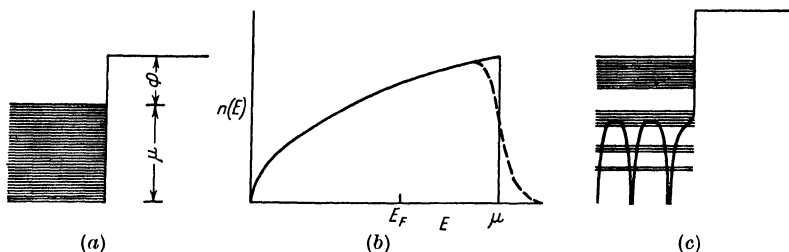


FIG. 145. Illustrating the energy levels of an electron in a crystal:
 (a) Ignoring the periodic field of the crystal lattice.
 (b) Fermi distribution of energies in case (a). ——— absolute zero; - - - - - at a high temperature.
 (c) Energy levels allowing for the periodic field of the crystal lattice.

An electron in a crystal can be regarded as moving in a potential well which is uniform throughout the volume of the crystal except for modulations due to the periodic field of the lattice ions. If this modulation were ignored any energy value above that of the bottom of the well would be permitted. At the absolute zero of temperature the crystal electrons would occupy the lowest possible set of energy levels consistent with the Pauli principle. As a result all levels up to a height μ eV above the bottom of the well would be occupied. μ , the so-called maximum 'Fermi' energy, is given by

$$\mu = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{\frac{2}{3}}, \quad (7)$$

where N is the total number of electrons and V the volume of the crystal.

To remove an electron from the crystal an energy at least as great as ϕ eV must be communicated to it. This is known as the work function of the crystal. At a temperature T some electrons will occupy excited states above the maximum Fermi energy, but for our present purposes these may be ignored. This simple model is illustrated in Fig. 145(a), and in Table I the values of μ and ϕ for a number of metals are given.

To this approximation the electron wave functions throughout the body of the crystal may be represented by plane waves.

$$V^{-1}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (8)$$

where $\mathbf{k}\hbar$ is the momentum of the electron related to its energy E by

$$k^2 = 2mE/\hbar^2.$$

The effect of the crystal field is to restrict the allowed energy values, for negative energies, to a discrete series of bands as shown in Fig. 145 (c). These bands correspond to the different energy levels of the individual crystal atoms which have been broadened by the mutual perturbation. Thus the lowest band is a $1s$ band, the next a $2s$ band, and so on. The number of energy levels in a band arising from an s atomic level is equal to $2N$, from a p level $6N$, from a d level, $10N$, and so on. The deeper the atomic level the less the broadening, and the electrons belonging to the inner shells of the atoms can be regarded as remaining localized. The outer energy levels are broadened into wide bands which may overlap. Thus Fig. 156 illustrates the level density distribution for copper showing the overlap of d and s bands. As for the simple model, the electrons at absolute zero will occupy the lowest possible set of energy levels. If the crystal is a metallic conductor this distribution will still leave unoccupied levels in the uppermost partially filled band. Except in levels near the top and bottom of a band the electrons behave nearly as if free. The appropriate wave function can be written

$$V^{-1}u_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (9)$$

where $u_{\mathbf{k}}(r)$ has the periodicity of the lattice. For a simple cubic lattice $u_{\mathbf{k}}(r)$ may be expanded as a triple Fourier series in the form

$$u_{\mathbf{k}} = \sum_{\mathbf{m}} a_{\mathbf{m}}(k) \exp\{2\pi i \mathbf{m} \cdot \mathbf{r}/a\}, \quad (10)$$

where a is the lattice spacing and $\mathbf{m}$ is a vector each of whose components is an integer, positive or negative. To correspond to a single electron $\sum a_{\mathbf{m}} a_{\mathbf{m}}^* = 1$. For metals the $a_{\mathbf{m}}$ are very small except for $\mathbf{m} = 0$, so that the energy and momentum of an electron represented by the wave function (9) can be taken as $\hbar^2 k^2/2m$ and $\mathbf{k}\hbar$, respectively, without serious error.

3.2. The Fröhlich-Wooldridge theory† of secondary emission

When a primary electron enters a metal it comes into interaction with the nearly free metallic electrons. Owing to this interaction it can transfer energy to them which, if great enough, will enable them to leave

† *Phys. Rev.* **56** (1939), 562. See also Fröhlich, *Ann. der Physik*, **13** (1932), 229.

the metal. If the metallic electrons were entirely free, the requirements of the conservation of momentum would prevent any backward emission. To account for this emission allowance must be made for the effect of the lattice field on the metal electrons. This enables the lattice to take up momentum so that an electron can be projected in a backward direction. This means that, in developing a theory of secondary emission, we must use a wave function for the metal electrons of the form (9) with $u_k \neq 1$.

The first step in developing a theory of secondary emission is to calculate the rate at which a primary electron, possessing an energy $k^2\hbar^2/2m$ and momentum $\mathbf{k}\hbar$ within the metal, undergoes inelastic collisions with a metal electron. The rate of production of secondary electrons by such a primary will depend on the orientation of the crystal axes with respect to the direction of the incident momentum. An actual metal is composed of a great number of crystallites of random orientation so that the probability must be averaged over all orientations of the axes. It is necessary to determine the fraction of secondary electrons produced within the metal which escape through its surface. This can only be done empirically and is a weak spot in the theory. Finally a curve is obtained giving the variation of the secondary emission coefficient δ with energy of the incident primary. Absolute values of δ can only be estimated roughly.

We shall now give a sketch of Wooldridge's theory in terms of which it is convenient to correlate much of the experimental data.

For present purposes we are concerned only with collisions in which the energy transferred is sufficient to enable the metal electron to leave the metal. It is not necessary to allow for the detailed structure of the allowed energy bands as this is largely lost in the continuous spectrum of emitted electrons. When, however, it is necessary to develop a theory of inelastic collisions of electrons with a metal in which electrons are excited from one band to another, the details must be taken into account (see § 6.1). In this section we use the simple model of Fig. 145 (a) except that the crystal modulation is included in the wave functions of the metal electrons.

Using the wave functions (9) for the metal electrons and following Born's approximation (Chap. III, § 3.1), the number of inelastic collisions taking place per second in which the wave vector of the metal electron changes from $\boldsymbol{\kappa}$ to $\boldsymbol{\kappa}'$ and of the primary electron from $\mathbf{k}$ to $\mathbf{k}'$ will be given by $NQ\hbar/m$, in which the effective cross-section Q is given by

$$Q = \frac{4\pi^2 m^2 \epsilon^4}{V^2 \hbar^4} \frac{k'}{k} \sum |U(\mathbf{k}, \boldsymbol{\kappa}; \mathbf{k}', \boldsymbol{\kappa}')|^2, \quad (11)$$

where

$$U(\mathbf{k}, \kappa; \mathbf{k}', \kappa') = \iint \frac{u_{\mathbf{k}}(\mathbf{r}) u_{\kappa'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|^2} \exp i[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} + (\kappa - \kappa') \cdot \mathbf{r}] d\tau d\tau'$$

and, from the conservation of energy,

$$k^2 + \kappa^2 = k'^2 + \kappa'^2. \quad (12)$$

The summation is to be carried out over all directions of the vectors $\mathbf{k}'$ and κ' for which the cross-section is finite.

Since†

$$\int \frac{\exp\{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}\}}{|\mathbf{r} - \mathbf{r}'|^2} d\tau' = \frac{4\pi}{|\mathbf{k} - \mathbf{k}'|^2} \exp\{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}\},$$

we have, on substituting the Fourier expansions (10) for $u_{\mathbf{k}}, u_{\kappa'}$,

$$U(\mathbf{k}, \kappa; \mathbf{k}', \kappa') = \frac{4\pi}{|\mathbf{k} - \mathbf{k}'|^2} \sum_{\mathbf{m}, \mathbf{n}} \int a_{\mathbf{m}}(\kappa) a_{\mathbf{n}}^*(\kappa') \exp\{i(\mathbf{k} - \mathbf{k}' + \kappa - \kappa' + \alpha \rho_{\mathbf{mn}}) \cdot \mathbf{r}\} d\tau, \quad (13)$$

where

$$\rho_{\mathbf{mn}} = \mathbf{m} - \mathbf{n}, \quad \alpha = 2\pi/a,$$

in terms of the notation used in (10).

This may be rewritten

$$U(\mathbf{k}, \kappa; \mathbf{k}', \kappa') = \frac{4\pi}{|\mathbf{k} - \mathbf{k}'|^2} \sum_{\mathbf{p}} \left(\sum_{\mathbf{m}} a_{\mathbf{p}+\mathbf{m}}(\kappa) a_{\mathbf{m}}^*(\kappa') \int \exp\{i(\mathbf{k} - \mathbf{k}' + \kappa - \kappa' + \alpha \mathbf{p}) \cdot \mathbf{r}\} d\tau \right).$$

We may then consider separately the contributions from different values of $\mathbf{p}$.

The integral only exists if

$$|\mathbf{k} - \mathbf{k}' + \kappa - \kappa' + \alpha \mathbf{p}| = 0, \quad (14)$$

when it has the value V . If $\mathbf{p} = 0$ (14) is the same momentum condition as that which would be valid if the metal electron were free. For true secondary emission, which takes place in the backward direction, we must take $\mathbf{p} \neq 0$. The only important terms will then be those for which $|\mathbf{p}| = 1$, as the coefficients $a_{\mathbf{m}}$ are very small for higher values of $|\mathbf{p}|$. Let us consider the consequences of the energy and momentum relations for a particular value of $\mathbf{p}$.

With the conditions (12) and (14) simultaneously satisfied we have

$$|\mathbf{k} - \mathbf{k}' + \kappa + \alpha \mathbf{p}|^2 = k^2 + \kappa^2 - k'^2,$$

$$\text{so that} \quad k'^2 - 2\mathbf{k}' \cdot \mathbf{C} + C^2 = \frac{1}{4}(k^2 + \kappa^2 - \alpha^2 \rho^2 - 2\alpha \kappa \cdot \mathbf{p} - 2\mathbf{k} \cdot (\kappa + \alpha \mathbf{p})), \quad (15)$$

where

$$\mathbf{C} = \frac{1}{2}(\mathbf{k} + \kappa + \alpha \mathbf{p}).$$

This shows that, corresponding to each value of the angle χ between $\mathbf{k}'$ and the fixed vector $\mathbf{C}$, there are only two values of k' . The situation may be illustrated by means of a vector diagram such as Fig. 146.

In this diagram $\vec{AB}$ is the vector $2\mathbf{C} = \mathbf{k} + \kappa + \alpha \mathbf{p}$. If $\vec{AP}$ represents the vector $\mathbf{k}'$ then, according to (14), $\vec{PB}$ represents κ' . OP^2 is equal to $k'^2 - 2\mathbf{k}' \cdot \mathbf{C} + C^2$, which because of (15), is determined by the initial vectors $\mathbf{k}$, κ , and $\mathbf{p}$ only. It follows that, if the final energy $k'^2 \hbar^2 / 2m$ of the primary electron is varied, the momentum condition in the final state is represented by a vector $\vec{OP}$ of constant

† Bethe, *Ann. der Physik*, 5 (1930), 325.

length, i.e. the representative point lies on a sphere of radius OP with centre O .

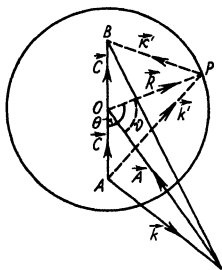


FIG. 146.

The probability of a collision to a final state with a particular value of $\mathbf{k}'$ is thus determined by the angle θ

between the corresponding vector $\vec{OP}$ and a fixed direction such as OA . This suggests a convenient way of summing the secondary electron production over all final states.

In the expression (11) for the cross-section, with $|U|^2$ given by

$$\frac{16\pi^2 V^2}{|\mathbf{k}-\mathbf{k}'|^4} \left| \sum_{\mathbf{m}} a_{\mathbf{p}+\mathbf{m}}(\kappa) a_{\mathbf{m}}^*(\kappa') \right|^2 \quad (16)$$

with the conditions (12) and (14), the only factor which will vary rapidly with the angle θ is $|\mathbf{k}-\mathbf{k}'|^4$. The

vector $\vec{OP}$ is given by

$$\begin{aligned} \vec{OP} &= \mathbf{R} = -\mathbf{C} + \mathbf{k}', \\ |\mathbf{k}-\mathbf{k}'| &= |\mathbf{A}-\mathbf{R}|, \end{aligned} \quad (17)$$

so we have

where

$$\begin{aligned} \mathbf{A} &= \mathbf{k} - \mathbf{C} \\ &= \frac{1}{2}(\mathbf{k} - \kappa - \alpha\mathbf{p}). \end{aligned} \quad (18)$$

As the vector $\vec{OP}$ rotates, $|\mathbf{k}-\mathbf{k}'|$ will vary from a minimum value $A \sim R$ to a maximum $A+R$, so that $(|\mathbf{k}-\mathbf{k}'|)^{-4}$ will have a sharp maximum when $\mathbf{R}$ is parallel to $\mathbf{A}$. To sum over all possible final states (for a given $\mathbf{p}$) we need only integrate $(|\mathbf{A}-\mathbf{R}|)^{-4}$ over all orientations of the vector $\mathbf{R}$, including the appropriate weighting factor for the density of states for a given $\mathbf{R}$, and substituting in the slowly varying factors the values of $\mathbf{k}$ and $\mathbf{k}'$ corresponding to $|\mathbf{k}-\mathbf{k}'| = A \sim R$. We find then that

$$\begin{aligned} Q &= \frac{128\pi^5 m^2 \epsilon^4}{h^4} \left(\frac{2R}{k} \right) \left| \sum a_{\mathbf{p}+\mathbf{m}}(\kappa) a_{\mathbf{m}}^*(\kappa') \right|^2 \int_0^\pi \frac{\sin\vartheta d\vartheta}{(A^2 - 2AR\cos\vartheta + R^2)^2} \\ &= \frac{256\pi^5 m^2 \epsilon^4}{h^4} \left(\frac{2R}{k} \right) \left| \sum a_{\mathbf{p}+\mathbf{m}}(\kappa) a_{\mathbf{m}}^*(\kappa') \right|^2 / (A^2 - R^2)^2. \end{aligned}$$

Since

$$\begin{aligned} R^2 &= k'^2 - 2\mathbf{k}' \cdot \mathbf{C} + C^2 \\ &= \frac{1}{4}[k^2 + \kappa^2 - \alpha^2 \rho^2 - 2\alpha\kappa \cdot \mathbf{p} - 2\mathbf{k} \cdot (\kappa + \alpha\mathbf{p})], \end{aligned}$$

and

$$\begin{aligned} A^2 &= \frac{1}{4}[k^2 + \kappa^2 + \alpha^2 \rho^2 - 2\mathbf{k} \cdot (\alpha\mathbf{p} + \kappa) + 2\alpha\kappa \cdot \mathbf{p}], \\ (A^2 - R^2)^2 &= \frac{1}{4}\{\alpha\mathbf{p} \cdot (\alpha\mathbf{p} + 2\kappa)\}^2. \end{aligned}$$

If we are dealing with high-energy primary electrons for which $k \gg \kappa$ and $\alpha\rho$, then

$$\begin{aligned} A - R &= \frac{1}{2}\{\alpha\mathbf{p} \cdot (\alpha\mathbf{p} + 2\kappa)\} / (A + R), \\ &\simeq \frac{1}{2}\alpha\mathbf{p} \cdot (\alpha\mathbf{p} + 2\kappa) / k, \end{aligned}$$

and is very small compared with k , i.e. compared with either A or R . Hence the probability has a sharp maximum when

$$\mathbf{k} \simeq \mathbf{k}', \quad (19)$$

or

$$\mathbf{k}' \simeq \kappa + \alpha\mathbf{p}. \quad (20)$$

We therefore have finally, for the particular value of ρ ,

$$Q \simeq \frac{64\pi m^2 \epsilon^4}{\hbar^4} \frac{(2R/k)}{\{\alpha \rho \cdot (\alpha \rho + 2\kappa)\}^2} \left| \sum a_{\rho+m}(\kappa) a_m^*(\kappa + \alpha \rho) \right|^2, \quad (21)$$

where

$$2R/k \simeq \{1 - (\alpha \rho/k)^2 - 2\alpha \kappa \cdot \rho/k^2\}^{\frac{1}{2}}. \quad (22)$$

To complete the discussion of this aspect it is necessary to sum over all values of ρ . As pointed out earlier, the coefficients a_m diminish rapidly with increasing m . For metals $|a_{000}|^2$ may be taken as $\simeq 1$ and all coefficients for which $|m| > 1$ may be neglected. This gives

$$\begin{aligned} \left| \sum a_{\rho+m}(\kappa) a_m^*(\kappa + \alpha \rho) \right|^2 &\simeq |a_{\rho}(\kappa) a_{000}^*(\kappa + \alpha \rho) + a_{000}(\kappa) a_{\rho}^*(\kappa + \alpha \rho)|^2 \\ &\simeq |a_{\rho}(\kappa) + a_{\rho}^*(\kappa - \alpha \rho)|^2 \\ &= |b_{\rho}(\kappa)|^2, \text{ say.} \end{aligned} \quad (23)$$

The only vectors ρ which we need include are those with components

$$\pm 1, 0, 0; \quad 0, \pm 1, 0; \quad 0, 0, \pm 1.$$

We now have the following picture of the primary collision process.

Since $\kappa' \simeq \kappa + \alpha \rho$, the mean energy $\overline{\kappa'^2} \hbar^2/2m$ of a secondary electron will be given by

$$(\overline{\kappa'^2} + \alpha^2) \hbar^2/2m = E_F + E_0, \quad (24)$$

where E_F is the mean energy $\frac{3}{8}\mu$ of a metal electron and $E_0 = \alpha^2 \hbar^2/2m = \hbar^2/2ma^2$. As may be seen by reference to Table I, E_0 is always considerably greater than E_F and it follows therefore that the vector $\kappa' \simeq \alpha \rho$, i.e. the directions of motion of the secondary electrons just after their production are concentrated about the directions of the cubic axes of the crystallite in which they are formed.

So far we have taken no account of any possible effect of the Pauli principle in limiting the allowed transitions. After an inelastic collision in which a secondary electron is produced the primary must still possess an energy in excess of the maximum Fermi energy in the metal. There is no vacant state of smaller energy into which it may drop in the collision. According to (24) the mean energy of a secondary is about $\hbar^2/2ma^2$ which is considerably greater than the maximum Fermi energy. A primary electron must thus have energy, within the metal, a little greater than $\hbar^2/2ma^2$ in order that it can produce secondaries to an appreciable extent. Referring to Table I it will be seen that, for a metal such as silver, the primary energy within the metal must exceed 28 eV.

We now proceed to the next stage of the calculation, that of averaging the emission over all orientations of the crystallites so that the vector ρ is randomly oriented. The fraction of all the crystallites which have one of their six directions for $|\rho| = 1$, making an angle θ with the normal to the target surface within a solid angle $d\omega$, is $6 d\omega/4\pi$. Hence using (21), (22), and (23), and ignoring κ in comparison with $\alpha \rho$, the number dn of secondaries emitted per second at an angle to the target surface within a solid angle $d\omega$ by a volume element $d\tau$ of the metal will be given by

$$\begin{aligned} dn &= 6j_p Q \sigma d\tau d\omega/4\pi \\ &= 96m^2 j_p \epsilon^4 |b|^2 F_1(k, \theta) \sigma d\tau d\omega/\hbar^4 \alpha^4, \end{aligned} \quad (25)$$

where, for normal incidence,

$$F_1(k, \theta) = [1 - (\alpha \rho/k)^2 - 2(\alpha \rho/k) \cos \theta]^{\frac{1}{2}}. \quad (26)$$

j_p is the number of primary electrons/cm.²/sec. and σ is the number of electrons/c.c. within the metal.

We must now allow for the chance that a secondary electron, once produced,

may not be moving with suitable energy and momentum to enable it to escape from the metal. If a secondary is produced within a volume element $d\tau$ very close to the target surface it will escape provided the energy of its motion normal to the surface exceeds $\mu + \phi$, μ being the maximum Fermi energy and ϕ the work function.

Since $E_0 + E_F$ is the mean energy of a secondary just after production, this requires that $\theta < \theta_m$, where

$$(E_0 + E_F)\cos^2\theta_m = \mu + \phi, \quad (27)$$

so that the fraction f which can escape is given by

$$f = \frac{\int_0^{\theta_m} F_1 d\theta}{\int_0^\pi F_1 d\theta}. \quad (28)$$

Allowance must now be made for the production of secondaries at a depth x below the surface. Wooldridge assumed that, in this case, the chance that a secondary, produced under conditions satisfying $\theta < \theta_m$ at this depth, will escape is given by

$$f(x)e^{-\gamma x}, \quad (29)$$

where $f(x)$ is given by (28) but with the value of the primary momentum $\mathbf{k}h$, that which the primary would possess after penetrating to a depth x . Evidence in support of the exponential factor is produced by the experiments of Becker† on the penetration of electrons through thin metal films.

We now have for the secondary emission coefficient, integrating over all directions of emission,

$$\delta = \frac{384\pi m^2 \epsilon^4}{\alpha^4 h^4} \sigma |b|^2 \int_0^l f(x)e^{-\gamma x} dx. \quad (30)$$

l is the distance the primary electrons, which enter the target with given energy E_p (just within the metal), travel before they are too slow to produce secondaries, that is to say, before their energy approaches E_0 .

For high bombarding voltages, writing $F_1 = 1$,

$$f(x) \sim \frac{1}{2} [1 - \{(\mu + \phi)/E_0\}^{\frac{1}{2}}] \quad (31)$$

and

$$\delta_\infty = \frac{192\pi m^2 \epsilon^4}{\alpha^4 h^4} \frac{\sigma |b|^2}{\gamma} [1 - \{(\mu + \phi)/E_0\}^{\frac{1}{2}}]. \quad (32)$$

This may be used to obtain a rough quantitative check of the theory. Taking for silver $\mu + \phi = 10$ eV, $\alpha = 3 \times 10^{-8}$ cm.; $E_0 = 25$ eV, $\gamma = 2 \times 10^6$ cm.⁻¹, and $\sigma = 1/a^3$ gives

$$\delta_\infty \simeq 80 |b|^2. \quad (33)$$

According to observation $\delta_\infty \simeq 1.5$, so $|b|^2 \simeq 0.02$, which is quite consistent with estimated values. Thus $|b|^2$ may be as high as $4|a_1|^2$, where $|a_1|^2$ is of order 10^{-2} .

To calculate δ/δ_∞ it is necessary to determine both l and the energy $E(x)$ for a primary electron with given energy E_p when just within the metal. This may be done if it is supposed that the primary electron loses energy solely by producing secondaries. In traversing a distance dx normal to the surface the energy loss will be

$$-dE \simeq E_0 \frac{dn}{dx} dx, \quad (34)$$

where dn is the number of secondaries produced in this distance. From (25) and (26)

$$\begin{aligned} \frac{dn}{dx} &= \frac{384\pi m^2 \epsilon^4}{h^4 \alpha^4} |b|^2 \sigma \\ &= 2\gamma \delta_\infty [1 - \{(\mu + \phi)/E_0\}^{\frac{1}{2}}] \end{aligned} \quad (35)$$

† *Ann. der Physik*, **2** (1929), 249.

from (32). Hence $E(x) = E_p - Ax$, (36)

where $A = E_0 \frac{dn}{dx}$

and $l = (E_p - E_0)/E_0 \frac{dn}{dx}$.

Using these results $f(x)$ and δ may be evaluated in terms of E_p , μ , and E_0 . The value of δ so obtained increases to a maximum at an energy of a few hundred electron volts and then decreases very slowly with further increase of electron energy.

To compare the theoretical variation of δ with primary energy E_p with that observed, allowance must be made for the fact that the theory is unreliable for very large E_p . Under such conditions the assumption that the primary electrons lose energy mainly in producing slow secondaries becomes very doubtful. The following procedure was therefore adopted. By trial and error a value of δ_∞ was chosen to give agreement between the magnitudes of the observed and calculated values of $\delta_{\max}$, the maximum value of δ , which occurs at a primary energy for which the theory should be valid.

The foregoing theory has been worked out on the assumption of a simple cubic lattice structure, for the metal. It may be extended to apply to face-centred or body-centred cubic lattices or close-packed hexagonal lattices by replacing a by $0.9v^{1/3}$, where v is the atomic volume.

3.3. *Kadyshevich's theory of secondary emission*

According to Wooldridge's theory collisions between the primaries and effectively free electrons cannot be important in producing secondary electrons because secondaries produced in such collisions could not leave the surface of the target. An alternative theory, however, has been put forward by Kadyshevich† according to which the secondary electrons are produced in collision processes with effectively 'free' electrons. The secondary electrons thus produced undergo multiple elastic collisions so that a certain fraction are eventually able to leave the surface.

The idea of this theory is as follows. A relatively fast primary electron encounters an effectively free electron in the metal and communicates momentum to it in a direction normal to the primary direction of motion. If the primary direction is normal to the metal surface the secondary electron produced in this way will never be moving in a direction to enable it to leave the surface no matter how energetic it may be. The secondary may, however, suffer an elastic collision with a lattice ion so that, while retaining its energy, it is now moving in a

† *J. Phys. U.S.S.R.* **2** (1940), 115; **4** (1941), 341; **9** (1945), 431.

direction such that the energy of its motion normal to the surface is sufficient to take it out of the metal on the side of primary incidence.

The detailed working out of a theory on these lines is very complicated. It is first necessary to work out the chance per cm. path that a primary moving with given speed V at a depth z within the metal, in a direction making an angle α with the normal, will communicate sufficient energy to a secondary so that, if it continued to move freely, it would leave the front face of the metal. This chance vanishes when $\alpha = 0$. It will be independent of z unless account is taken of the chance that a primary will suffer a collision before reaching the depth z and that a secondary, once produced, will be prevented from reaching the surface by collision. If Λ_1 and Λ_2 are the mean free paths of the primary and secondary for all types of collision within the metal, the chance that the primary will reach the depth z without suffering a collision will be $e^{-z/\Lambda_1 \cos \alpha}$, and a similar expression will give the chance that the secondary will leave the metal without undergoing a collision which would prevent it from passing out of the surface. The free paths Λ_1 and Λ_2 may be written in the form

$$\frac{1}{\Lambda_1} = \frac{1}{\lambda_1} + \frac{1}{l_1}, \quad \frac{1}{\Lambda_2} = \frac{1}{\lambda_2} + \frac{1}{l_2}, \quad (37)$$

where λ_1, λ_2 represent the mean free paths for inelastic collisions with the metal electrons and l_1, l_2 for elastic collisions with the lattice ions. Whereas the former reduce the secondary emission by reducing the energy of primary and secondary, the latter can give rise to a finite chance that, even if $\alpha = 0$, true secondary emission will occur. To allow for this, calculation must now be made of the chance that a secondary produced at a given depth z will when at a depth z_0 suffer one or more elastic collisions which deviate it finally without loss of energy into a direction which enables it to leave the front surface of the metal.

Calculations on these lines have been carried out approximately by Kadyshovich. He finds that, for normal incidence of the primaries, its secondary emission coefficient due to the sequence of processes described is given by

$$\delta = \frac{0.13\pi\Lambda_1\Lambda_2^2}{l_2 E_p (\Lambda_1 + 0.56\Lambda_2)}. \quad (38)$$

As a rough approximation Λ_2 can be taken as independent of energy for the slow secondaries and Λ_1 proportional to E_p^2 , as would be characteristic of Rutherford scattering. This leads to a variation of δ with E_p of the form

$$\delta = \frac{2\delta_{\max}(E_p/E_p^{\max})}{1 + (E_p/E_p^{\max})^2}, \quad (39)$$

where the maximum value $\delta_{\max}$ occurs at an energy $E_p^{\max}$. At this energy $\Lambda_1 = 0.56\Lambda_2$.

The absolute magnitude of δ is determined largely by the ratio λ_2/l_2 of the free paths for elastic and inelastic scattering. Making the reasonable assumption that these are of the same order of magnitude (cf. Chap. III, § 3.8), $\delta_{\max}$ comes out to be of the correct order, unity.

In comparing Kadyshovich's theory with experiment it has to be remembered that it will probably fail at high energies because secondary effects involving the interaction of fast electrons with the atoms of the lattice (excitation, ionization, etc.) have been neglected. Also it will be unreliable at low energies because the assumption that Λ_1 is proportional to E_p^2 will no longer be true.

The most satisfactory theory of secondary emission would probably be a synthesis of the two theories outlined in the previous sections. There is no doubt that the failure to take adequate account of the interaction of the metal electrons with the crystal lattice is a serious weakness of Kadyshovich's theory. On the other hand, the importance of elastic collisions of the secondary electrons with the lattice prior to leaving the metal has not been adequately considered by Wooldridge. This probably accounts for the much better agreement between calculation and observation on the energy distribution of the ejected secondaries obtained by Kadyshovich (§ 5).

4. Discussion of experimental results for the measurement of δ and comparison with theory

4.1. Variation of δ with primary electron energy

The primary electron energy E_p^0 is normally measured outside the metal. It is to be distinguished from E_p , the energy when just within the metal, which is used in the theory of § 3.2. They are related by

$$E_p = E_p^0 + \mu + \phi. \quad (40)$$

Fig. 147 shows the comparison of the variation of δ with E_p^0 as calculated from the theories of § 3.2 and § 3.3 and as observed by Warnecke† for silver and copper. The comparison with Wooldridge's theory is seen to be very satisfactory. The comparison with Kadyshovich's theory is not so satisfactory in these cases, but the theory departs from the observed results at high and low primary energies in the manner expected from consideration of the assumptions involved. As explained above, the theoretical curve is normalized to give the observed value of

† *J. Phys. Rad.* 7 (1936), 270.

$\delta_{\max}$. This is the only arbitrary factor in the comparison. It has been pointed out that both theories give an estimate of the absolute value of $\delta_{\max}$ which is not far wrong in this case.

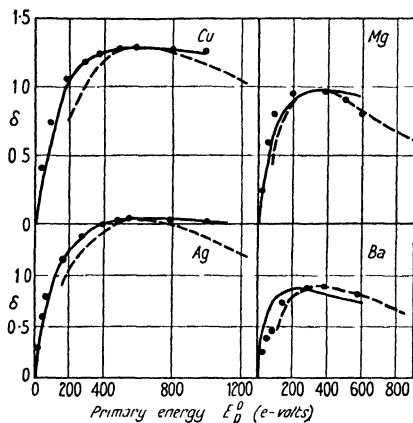


FIG. 147. Variation of δ with primary energy E_p^0 for Cu, Ag, Mg, Ba. • experimental points; — — — calculated variation using Wooldridge's theory; - - - - calculated on Kadyshovich theory. In each case the scale is adjusted to give agreement between observed and calculated values of $\delta_{\max}$.

Fig. 147 also shows the comparison of the theory with the experimental results of Bruining and de Boer† for Mg and Ba. The agreement with Wooldridge's theory is not so good in these cases and is least satisfactory for metals with a large atomic volume. For such elements the assumption that collisions with free electrons can be ignored is unlikely to be valid. Kadyshovich's theory, which considers only collisions with free electrons, agrees much better with the observations in these cases although there are discrepancies which still remain at low energies. It should of course be borne in mind in all these comparisons of the theory that the measured values of δ include the elastically reflected electrons. Part of the discrepancy at small values of E_p^0 could be due to this, but it cannot account for the discrepancy at larger values of E_p^0 .

When Wooldridge's theory is applied to BaO and Cs₂O using, in the absence of more exact information, values of μ and ϕ appropriate to the pure metal, the theory agrees very well with experiment. This is illustrated in Fig. 148, which shows the comparison for a BaO surface. This agreement was not altogether expected since the theory is really only

† *Physica*, 5 (1938), 17.

applicable to cases where the electrons are nearly free—probably a good approximation in the case of a metal, but less good in the case of a non-metal.

The form of variation predicted by Kadyshevich's theory is also sketched in Fig. 148. The agreement is very poor at high energies. Since he considered the electrons of the solid to be entirely free it is not surprising that his theory breaks down in this case.

The curves of Fig. 147 are typical of those obtained for secondary electron emission from metals. A rapid rise at low energies is followed by a flat maximum and then a slow drop in δ . Table I shows $\delta_{\max}$, the

TABLE I

$\delta_{\max}$, $E_{\max}^0$, ϕ , μ , a , and Mean Energy of Secondary Electrons (calculated on Wooldridge's theory)

Element	$\delta_{\max}$	$E_{\max}^0$ (eV)	ϕ (eV)	μ (eV)	$a^\dagger$ (10^{-8} cm.)	Mean secondary energy (calculated) ($\frac{1}{2} h^2/2ma^2$) (eV)	References
Li . . .	0.57	100	2.28	4.7	2.77	23.8	3
Be . . .	0.4–0.55	220–300	3.16	13.5	2.00	45.9	3, 6
C (smooth)	1.01	300	4	..	..	..	2
C (rough)	0.48	500	4	..	..	..	2
Mg . . .	0.95	290	2.42	9.0	2.84	22.8	3
Al . . .	0.98	300	2.26	16	2.54	28.4	3
Ca . . .	0.74	150–300	2.24	..	3.43	15.5	1, 8
Ti . . .	0.90	285	..	..	2.56	28.0	3
Fe . . .	1.3	400	4.77	..	2.27	35.8	9
Ni . . .	1.28–1.35	500	5.0	..	2.19	38.5	9, 10
Cu . . .	1.27	550	4.4	7.1	2.27	35.8	10
Rb . . .	0.85	400	2.18	1.8	4.44	9.2	1
Zr . . .	1.10	400	..	..	2.80	23.5	3
Cb . . .	1.20	350	..	5.4	2.58	27.7	10
Mo . . .	1.25–1.30	450	4.15	6.0	2.45	30.7	5, 9, 10
Ag . . .	1.48	800	4.74	5.5	2.56	28.2	10
Cs . . .	0.70–0.90	450	1.81	1.5	4.89	7.6	3, 8
Ba . . .	0.90	400	2.11	3.6	3.98	11.6	3
Ta . . .	1.30	700	4.12	..	2.57	27.9	10
W . . .	1.27–1.42	400–700	4.54	..	2.47	30.1	4, 7, 9, 10
Pt . . .	1.79	750	6.27	6.2	2.42	31.4	5
Au . . .	1.2–1.45	400–1,000	4.9	5.6	2.51	29.0	5, 9, 10

† In each case a is taken as the cube root of the atomic volume.

References:

1. Afanasjowa and Timofeev, *Techn. Phys. U.S.S.R.* **4** (1937), 953.
2. Bruining, *Diss.*, Leiden (1938).
3. Bruining and de Boer, *Physica*, **5** (1938), 17.
4. Coomes, *Phys. Rev.* **55** (1939), 519.
5. Copeland, *J. Frank. Inst.* **215** (1933), 435, 593.
6. Kollath, *Ann. der Physik*, **33** (1938), 285.
7. Kreft, *Phys. Rev.* **31** (1928), 199.
8. Mahl, *Jb. A.E.G. Forschung*, **6** (1939), 33.
9. Potry, *Phys. Rev.* **26** (1925), 346; *ibid.* **28** (1926), 362.
10. Warnecke, *J. Phys. Rad.* **7** (1936), 270.

maximum value of δ , $E_{\max}^0$ the primary electron energy at which this maximum occurs, ϕ the work function of the surface, μ the maximum Fermi energy, a the lattice distance, and $\hbar^2/2ma^2$, the mean energy of the secondary electrons calculated from Wooldridge's theory, for a number of elements.

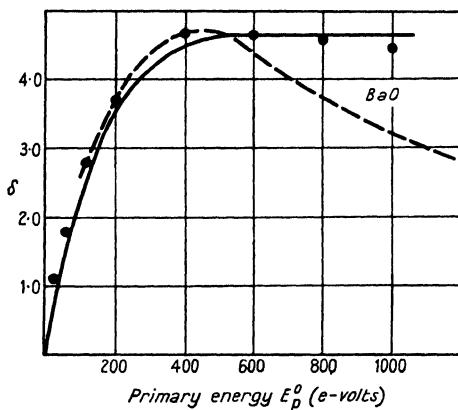


FIG. 148. Variation of δ with primary energy E_p^0 for BaO.
 • experimental points; ——— calculated variation using Wooldridge's theory; ---- calculated on Kadyshovich theory.

4.2. Dependence of $\delta_{\max}$ on work function ϕ

One would expect from the theory (as is discussed below) that $\delta_{\max}$ would be greatest for metals with low work functions. The tendency from Table I appears to be just the opposite. For example, caesium with a work function of 1.81 eV has $\delta_{\max} = 0.7\text{--}0.9$, while platinum, with a work function of 6.27 eV, has $\delta_{\max} \simeq 1.8$. On the other hand, beryllium, with a work function of 3.16 eV shows a maximum value of δ of from 0.40 to 0.55. Evidently factors other than the work function play a more important role in determining the secondary electron emission coefficient.†

The effect of the work function on δ has been studied directly by placing a monatomic layer of some electro-positive metal on a surface.‡

† The relative magnitudes of δ for different elements may be changed at low voltages. For instance, Table I shows $\delta_{\max}$ for Ag to be much greater than for Ba. However, Bruining (*Physica*, 5 (1938), 913) has shown that below a primary energy of about 30 eV the relative magnitudes of δ are reversed.

‡ Sixtus, *Ann. der Physik*, 3 (1929), 1017; Treloar, *Nature*, 137 (1936), 579; Afanasjowa and Timofeew, *Tech. Phys. U.S.S.R.* 4 (1937), 953; de Boer and Bruining, *Physica*, 6 (1939), 941; McKay, *Phys. Rev.* 61 (1942), 708; Bronstein, *Tech. Phys. U.S.S.R.* 13 (1943), 176.

It is well known that the work function of such a surface at first decreases with the fraction of the surface covered by the monatomic layer, passes through a minimum, and then increases again to the value characteristic of the material being deposited. The secondary emission measurements have shown that δ changes in a manner analogous to that of the work function, as the surface becomes covered with the monatomic layer. It has been found in fact that, provided the impurity is small, a linear relation exists between $\log \delta_{\max}$ and the work function ϕ , and that this relation is substantially independent of the nature of the contaminant. In the case of tungsten, measurements have been carried out with surface layers of thorium,[†] barium,[‡] and sodium.[§] For the quantity $-d(\log \delta_{\max})/d\phi$ values of 0.11, 0.12, and 0.13 eV were obtained from the data given in the three sets of measurements. The measurements of McKay indicate that, after the work function has fallen from a value of 4.54 eV for a clean tungsten surface to 2.6 eV for a surface contaminated with sodium, the increase in $\log \delta_{\max}$ is faster than linear for further decrease in ϕ .

Wooldridge^{||} has estimated the value of $d(\log \delta_{\max})/d\phi$ to be expected for tungsten on the basis of his theory. To do this it is necessary to make a reasonable assumption as to the way in which the absorption of secondaries in the metal varies with the energy. On the basis of such an assumption Wooldridge predicted a value of $-d(\log \delta_{\max})/d\phi$ of 0.11 eV for tungsten, in surprisingly good agreement with the experimental data.

It is not difficult to see that although one would expect an increase of $\delta_{\max}$ with decrease of ϕ , the effect should be much smaller than for thermionic emission. For secondary emission the electron energy is large in comparison with the change in work function effected by the surface layer, whereas for thermionic emission the reverse is true. For example, Sixtus^{||} pointed out that, if one could suppose the secondary electrons to have a Maxwellian distribution of mean energy 10 eV, a change of work function of 2 eV would cause an increase of secondary electron emission by a factor $e^{0.2} = 1.21$. On the other hand, for thermionic emission, where the electron temperature is of the order of 0.2 eV, the thermionic emission would increase by a factor of $e^{10} = 2.2 \times 10^4$.

4.3. *Effect of surface conditions on δ*

Much of the earlier work on the determination of δ had little meaning because the surface of the target was not sufficiently clean. Large

[†] Sixtus, loc. cit.; Treloar, loc. cit.

[§] McKay, loc. cit.

[‡] Treloar, loc. cit.

^{||} Loc. cit.

errors are liable for surfaces which oxidize readily, if the oxide coating is so thick that an appreciable fraction of the secondaries originate within it. In the case of monatomic layers the effect on δ is small and due only to the work-function change which, as has been seen in § 4.2, does not produce a very large effect.

Real differences have been observed between secondary emission coefficients for smooth and amorphous surfaces of the same material,[†] but this effect appears to arise simply from the greater absorption experienced by the secondary electrons in leaving the roughened surface.

4.4. Effect of crystal structure on δ

Differences have been observed between the value of δ for single crystals and polycrystalline copper and nickel,[‡] although the magnitude of the effect is not very certain. A convincing demonstration that the effect is real has been given by Knoll and Theile,[§] who used the ejected secondaries to give an electron-optical picture of a silver-steel surface. The picture so obtained revealed clearly the polycrystalline structure of the surface, owing apparently to differences in δ for the different crystalline faces.

A small change of δ (up to 10 per cent.) has been observed at melting for lead, tin, antimony, and bismuth.^{||} Similar measurements at the Curie point^{††} have led to conflicting results, but it appears that the change here, if real, is very minute.

An accurate investigation of the effect of change of structure on δ has been made by Wooldridge^{‡‡} for iron, nickel, and cobalt. He measured the energy of the incident electrons for which δ is exactly equal to unity. Since, in these circumstances, no net current flows to the target, a very accurate null method could be employed to detect the target current so that small changes in δ could be followed readily. If the slope of the $\delta-E_p^0$ curve near $\delta = 1$ is known, the variation of δ at constant energy can then be obtained.

Using this method Wooldridge observed abrupt changes of 1–2 per cent. in δ to accompany the α - γ transition of iron while the hexagonal to face-centred transformation of cobalt was accompanied by a change

[†] Bruining and de Boer, *Physica*, **5** (1938), 17.

[‡] Rao, *Proc. Roy. Soc. A*, **128** (1930), 41, 57; Bekow, *Phys. Zeits.* **42** (1941), 144.

[§] *Zeits. f. Phys.* **113** (1939), 260.

^{||} Schwietzke, *Diss.* Berlin (1937) (quoted by Bruining, *Die Sekundär-Elektronen-Emission fester Körper*); Morozov, *J. exp. theor. phys. U.S.S.R.* **11** (1941), 410.

^{††} Tartakowsky and Kudrjawzewa, *Zeits. f. Phys.* **75** (1932), 137; Hayakawa, *Sci. Rep. Tokoku Univ.* **22** (1933), 934; Treloar and Landon, *Proc. Phys. Soc.* **50** (1938), 625.

^{‡‡} *Phys. Rev.* **58** (1940), 316.

in δ of 0.4 per cent. The magnetic transformation in nickel altered δ by less than 0.3 per cent.

A similar method was used by Wooldridge and Hartman† to study the effect of the order-disorder transformation in the alloy Cu_3Au . They concluded that δ for an ordered specimen of Cu_3Au differs from that of the same specimen in a disordered state by not more than 1–2 per cent.

4.5. *Effect of temperature on δ*

On the basis of Wooldridge's theory of secondary emission the rate of production of secondaries in the solid would be expected to increase roughly as the cube of the lattice constant, a , i.e. it should be of the same order as the volume coefficient of expansion. Treloar and Landon‡ and Wooldridge§ have found that for Fe, Ni, and Co the temperature coefficient of secondary emission, if it exists at all, is very small. This is taken to mean that the increase of production of secondaries in the metal is largely offset by a comparable increase in their absorption before leaving it. This would be the case if the secondaries lose their energy by the same kind of transitions of the metal electrons as those in which they are themselves produced by the primaries.

4.6. *Effect on δ of angle of incidence of the primaries*

As the angle of incidence of the primary electron beam is increased an increasing fraction of the primary electrons will produce secondaries sufficiently close to the surface of the metal to enable them to leave without absorption. Thus δ should increase with increase of angle of emission. This has been observed in a number of experiments.|| Bruining and de Boer†† have also shown that the increase of δ with angle of incidence is greatest at high primary energies, as is seen from Fig. 149 for nickel carbide. This is just what would be expected since the mean depth of production of the secondaries increases with energy (see § 3).

4.7. *Depth of origin of the secondaries*

From the way in which δ varies with angle Bruining and de Boer†† estimated by an elementary calculation that the mean depth of production of secondary electrons in lithium by primary electrons of 500 eV energy is about 30 Å.

† Ibid. 381.

‡ *Proc. Phys. Soc.* **50** (1938), 625.

§ *Phys. Rev.* **58** (1940), 316.

|| Farnsworth, *ibid.* **25** (1925), 41; Bruining, *Physica*, **3** (1936), 1046; Lukjanov and Bernatovitch, *J. exp. theor. phys. U.S.S.R.*, **7** (1936), 856; Muller, *Zeits. f. Phys.* **104** (1937), 475; Bruining and de Boer, *Physica*, **5** (1938), 901; Lukjanov, *Phys. Zeits. Sowjetunion*, **13** (1938), 123.

†† Loc. cit.

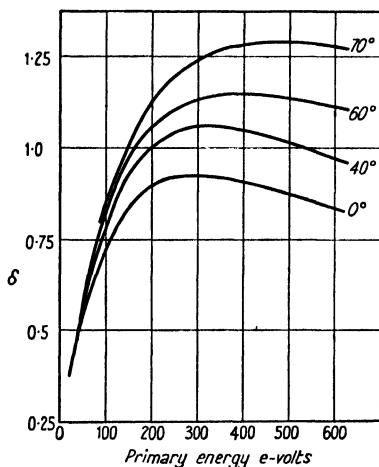


FIG. 149. Variation of δ with primary energy E_p^0 for different angles of incidence on a polished target of nickel carbide. The numbers on the curves represent the angles of incidence.

Attempts have also been made to estimate the depth of origin directly using a 'layer' technique. In this a layer of a material in which it is desired to measure the depth of production of the secondaries is placed on a target. When the layer is very thin (a few atoms thick) the observed value of δ is practically that due to the underlying metal, apart from the effect of the altered work function due to the presence of the film. For a thick layer δ is characteristic of the material of the layer. The depth of production can then be estimated by finding the minimum thickness of layer required to give a value of δ characteristic of the layer material. In this way Copeland† has estimated from observations of a Pt layer on Al that, for primaries of energy 500 eV, the mean depth of production of the secondaries corresponds to about 15 atomic layers, while for 2,000 eV primaries the corresponding mean depth is about 100 layers.‡

4.8. Angular distribution of the secondaries

Although there is little recent work on the angular distribution of the secondaries leaving the target, the earlier work showed the intensity in a given direction to be roughly proportional to the cosine of the angle ψ

† *Phys. Rev.* **58** (1940), 604.

‡ An error may arise in this method if the work function has a large influence on δ since the work function for a layer a few atoms thick is not the same as for the solid material. See, for example, Kadyshevich, *J. Phys. U.S.S.R.* **9** (1945), 436.

between that direction and the normal to the surface over a large range of angle, but at large angles it decreases more rapidly than this with increase of ψ .† Kadyshovich's theory gives for the variation of the secondary emission coefficient with ψ the form

$$\delta(\psi) = \frac{k \cos^3 \psi}{1 + (0.73 \Lambda_2 / \Lambda_1) \cos \psi}.$$

This varies too rapidly with ψ at large angles. However, no account has been taken of the refraction of the electron waves in passing through the surface. Allowance for this should tend to make the variation of $\delta(\psi)$ less rapid at large angles.

4.9. Time required to liberate secondary electrons

An estimate of the time required for the liberation of secondary electrons has been obtained in an ingenious way by Wang‡ and by Greenblatt and Miller.§ They replaced the reflector plate of a reflex klystron by a secondary emitting surface and were able to obtain satisfactory operation at a frequency up to 4,000 megacycles/sec. They concluded that this could not have been possible unless the time required for emission of the secondaries was less than 5×10^{-11} sec.

4.10. Secondary electron emission from non-metallic surfaces

Secondary electron emission coefficients much greater than those observed for metals have been obtained for metallic compounds. The measurement of δ in such cases is much less accurate because the coefficient depends to some extent on the previous history of the specimen.

Table II, an extension of a similar table in McKay's article, shows $\delta_{\max}$ and $E_{\max}$ for some such compounds. In this table two other constants are given, viz. E_1 and E_{11} . These are the lower and upper primary energies for which δ is unity. It is clear from § 2.13 that these quantities play an important role in the measurement of δ for insulators.

It is seen from Table II that compounds of electropositive metals have a high secondary electron coefficient. It was pointed out earlier in §§ 4.1 and 4.2 that Wooldridge's theory predicted a large value of δ for materials with a large lattice constant, a small Fermi energy, and a small work function. Electropositive metals satisfy these conditions, but δ was found to be small for them. This was attributed to the fact that the binding of the valence electrons to the metal lattice field must

† See, for example, Farnsworth, *Phys. Rev.* **25** (1925), 41.

‡ Ibid. **68** (1945), 284.

§ Ibid. **72** (1947), 160.

TABLE II
 $\delta_{\max}$, $E_{\max}$, E_1 , and E_{11} for Various Insulators

Material	Reference	$\delta_{\max}$	$E_{\max}$ (eV)	E_1 (eV)	E_{11} (eV)
ALKALI HALIDES					
<i>LiF</i> . . .	3	5.6	..	..	..
<i>NaF</i> . . .	3	5.7	..	..	..
<i>NaCl</i> . . .	3	6.8	..	..	..
<i>NaCl</i> . . .	4, 7	6.0	600	20	1,400
<i>KCl</i> . . .	3	7.5	..	..	..
<i>RbCl</i> . . .	3	5.8	..	..	..
<i>CsCl</i> . . .	3	6.5	..	..	..
<i>NaBr</i> . . .	3	6.2	..	..	..
<i>NaI</i> . . .	3	5.5	..	..	..
<i>KI</i> . . .	3	5.5	..	..	..
<i>CaF₂</i> . . .	3	3.2	..	..	..
<i>BaF₂</i> . . .	3	4.5	..	..	..
ALKALINE EARTHS					
<i>BeO</i> . . .	5	3.4	2,000	..	..
<i>MgO</i> . . .	5	2.4	1,500	..	..
<i>MgO</i> . . .	2	4.0	400	..	..
<i>CaO</i> . . .	5	2.2	500	..	..
<i>SrO</i> . . .	5	2.6	500	..	..
<i>BaO</i> . . .	5	2.3	1,600	..	..
<i>BaO</i> . . .	2	4.8	400	..	..
Oxide cathode (<i>BaO</i> , <i>SrO</i>)	13	8.0	1,500	60	3,500
Oxide cathode (<i>BaO</i> , <i>SrO</i>)	8	5-12	1,400	40	..
PHOSPHORS					
Willemite . .	12	..	..	..	3,000-7,000
„ . . .	9	..	..	..	5,000-10,000
„ . . .	11	..	..	..	20,000
Zinc sulphides	9	..	..	..	6,000-9,000
Calcium tungstate .	9	..	..	..	3,000-5,000
GLASSES					
Pyrex . . .	10, 14	2.3	400	< 40	2,400
Nonex . . .	9, 11	..	340	..	3,000-5,000
Soda . . .	6	2.1	300	..	900
Cover . . .	14	1.9	330	< 60	1,700
Ground . . .	14	3.1	420	..	3,800
Quartz . . .	14	2.1-2.9	400-440	30-50	2,300
MISCELLANEOUS					
<i>MoS₂</i> . . .	3	1.10	..	..	..
<i>MoO₂</i> . . .	1	1.09-1.33	..	..	..
<i>WS₂</i> . . .	3	0.96-1.04	..	..	..
<i>Ag₂O</i> . . .	1	0.90-1.18	..	..	..
<i>Cu₂O</i> . . .	3	1.19-1.25	..	..	..
<i>Al₂O₃</i> . . .	2, 6, 7, 14	1.5-4.8	350-1,300	20	1,200-1,700
<i>Mica</i> . . .	6, 7, 14, 15	2.4	300-380	20-30	1,000-3,500

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1. Afanasjew and Timofeew, *Phys. Zeits. Sowjetunion*, **10** (1936), 831.
2. Bruining and de Boer, *Physica*, **5** (1938), 17.
3. *Ibid.* **6** (1939), 834.
4. Vudynski, *J. Tech. Phys. U.S.S.R.* **9** (1939), 271.
5. Geyer, *Ann. der Physik*, **42** (1942), 241.
6. Heimann and Geyer, *Elektrotech. Nachr.* **17** (1940), 1.
7. Hintenberger, *Zeits. f. Phys.* **114** (1939), 98.
8. Johnson, *Phys. Rev.* **73** (1948), 1058.
9. Martin and Headrich, *J. App. Phys.* **10** (1939), 116.
10. Mueller, *ibid.* **16** (1945), 453.
11. Nelson, *ibid.* **9** (1938), 592.
12. Nottingham, *ibid.* **8** (1937), 762.
13. Pomerantz, *J. Franklin. Inst.* **241** (1946), 415; *ibid.* **242** (1946), 41.
14. Salow, *Zeits. f. tech. Phys.* **21** (1940), 8.
15. Scherer, *Arch. Elektrotech.* **34** (1940), 143.

be very weak because of the large atomic volume. This meant that collisions between the primaries and effectively free electrons in which no momentum is transferred to the lattice must be very important and δ correspondingly decreased. For the compounds of these metals, however, the lattice spacing is large and the mean Fermi energy low, but the lattice field is much stronger so that collisions with electrons which are effectively free are much less probable. Thus they would be expected to be very good emitters.

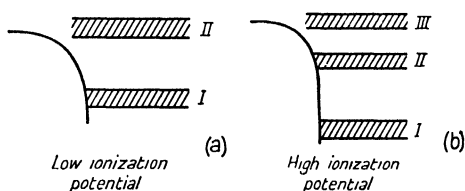


FIG. 150. Energy-level diagrams for two compounds: (a) low ionization potential; (b) high ionization potential.

In Table II the compounds italicized have low ionization potentials. The compounds in bold-face type have high ionization potentials. The big difference in secondary emission coefficients in the two cases has been explained by Bruining and de Boer,[†] in terms of the positions of the highest occupied electron bands.

Fig. 150 shows energy-level diagrams for two compounds, one (a) with a low ionization potential, and another (b) with a high ionization potential. In case (a) all the levels of band I are occupied. The unoccupied band, II, is such that its energy is above that required for emission. Electrons raised from band I to II cannot return to I because all its levels are

[†] *Physica*, **6** (1939), 834.

occupied. Since they have sufficient energy to leave the metal they will do so. In case (b), however, electrons ejected from band I to the lowest unoccupied band II still have insufficient energy to permit their leaving the metal. Before they can do so they must be excited to band III. But not all electrons excited into band III will leave the metal because some will return to band II which is practically unoccupied. Thus one would expect the secondary electron yield in case (b) to be much smaller than in case (a). As an example, consider the case of KBr. Fleischman† has shown that the longest wave-length of light absorbed by pure KBr is capable of freeing photo-electrons from the compound. This implies that the position of the bands in this metal is similar to those of Fig. 150 (a) so that a high value of δ would be expected. From Table II it is seen that $\delta_{\max}$ for the alkali halides is about 6. On the other hand, for Cu_2O , Fleischman showed that, while the work function is 5.4 eV, the highest energy of the absorption band corresponds to an energy of 2 eV, which is not nearly sufficient to allow ejection of photo-electrons. Evidently then, the position of the energy bands in this compound is similar to that of Fig. 150 (b) so that a small value of δ would be predicted. It is seen from Table II that $\delta_{\max}$ in this case is about 1.2.

4.11. *Very large apparent values of δ for non-metallic surface layers—the Malter effect*

Very complicated effects occur in some cases of non-conducting surface layers and give rise to apparently very high values of δ . For example, in the so-called Malter effect, or thin film emission, apparent values of δ up to 1,000 have been obtained.‡

This effect has been observed as a result of the electron bombardment of a complex target consisting of an aluminium plate with a thin layer of oxide on the surface, this being covered in turn with a thin layer of Cs_2O . As the Cs_2O layer has a value of δ greater than 1, more electrons are emitted than are incident and the layer becomes positively charged. This positive charge produces a very intense electrostatic field across the aluminium oxide layer which is sufficiently large to cause field emission from the aluminium plate. Estimates have been made by Mahl§ of the magnitude of the potential drop giving rise to this field emission and he has found that for an aluminium oxide layer of 2,000 Å thickness

† *Zeits. f. Phys.* **84** (1933), 717.

‡ Malter, *Phys. Rev.* **49** (1936), 478; *ibid.* **50** (1936), 48; Mahl, *Zeits. f. tech. Phys.* **18** (1937), 559; *ibid.* **19** (1938), 313; Koller and Johnson, *Phys. Rev.* **52** (1937), 519; Mühlenpfordt, *Zeits. f. Phys.* **108** (1938), 698; Wolff, *Ann. der Physik*, **39** (1941), 591.

§ Loc. cit.

the potential drop may be from 10 to 40 volts, giving rise to an electric field of the order of 10^6 volts/cm.—i.e. sufficiently high for field emission to occur. The importance of field-emission processes has also been shown by Wolff,[†] who coated a metal surface with a thin layer of quartz and measured the emission from a very thin film of platinum on the quartz. The value of δ he obtained depended markedly on the presence of a field tending to extract electrons from the metal.

The very high value of δ observed in the case of the Malter effect decreases very rapidly with time of bombardment (δ may decrease by a factor of 10 in the first minute of the electron bombardment).

The value of δ for a layer of an insulating material depends critically on the thickness of the material. Thus Geyer[‡] has found that for NaCl on Ni, $\delta_{\max}$ increases from about 1.4 for the pure metal to about 10 for a layer 30 atoms thick, and then decreases again to about 1 for a layer 1,000 atoms thick. He showed further that this high value of $\delta_{\max}$ in the intermediate layer was associated with field-emission effects.

Other evidence[§] points to the influence of the resistance of the layer on the observed value of δ . All the factors concerned in determining δ for insulating layers on metals are not well understood and their further consideration is outside the scope of this work.

The practical problem of the development of suitable multiplier tubes for television has emphasized the need for the development of a material with a large and constant value of δ . The most useful surface developed seems to be a composite Ag—Cs₂O, Ag—Cs surface. On a block of silver a thin composite layer of silver and Cs₂O is formed with an adsorbed layer of Cs at the surface. Such a surface has a high and stable value of δ . Zworykin, Morton, and Malter^{||} report for it a maximum value of δ of 8.4 for a primary electron energy of 500 eV.

5. Energy distribution of the ejected secondaries

Owing to the lack of precise knowledge of the absorption of the secondaries in the metal and of its variation with energy, comparison of the energy distribution of the ejected secondaries with theory is difficult. Neglecting the effects of absorption and scattering of the secondaries in the metal, Wooldridge's theory would predict a maximum in the observed distribution at an energy of about $E_0 + E_j - \mu - \phi$. This is considerably greater than the energy of the experimentally determined maximum. For instance, for silver it would point to a maximum

[†] Loc. cit.

[‡] *Ann. der Physik*, **41** (1942), 117.

[§] Bruining and de Boer, *Physica*, **6** (1939), 823.

^{||} *P.I.R.E.* **24** (1936), 351.

yield of secondaries at an energy of 21 eV, whereas the experimentally observed maximum occurs at 5.4 eV† or even lower.‡ The theory, however, predicts that the secondary electron energy should be small, that it should have a spread in energy of about the magnitude observed, and that the secondary energies should vary very little with incident primary energy, all of which agree with observation.

On the other hand, the assumption that all the electrons initially have an energy equal to the mean Fermi energy, E_F , and that as a result of the impact they gain the mean energy E_0 , naturally makes Wooldridge's theory incapable of predicting in detail the distribution in energy of the ejected electrons.

Kadyshevich's theory is more successful than that of Wooldridge in predicting the form of the energy distribution of the secondary electrons. For normal incidence of the primary electrons his theory gives the following expression for the number of secondary electrons with energy lying between E_s and $E_s + dE_s$:

$$\Phi(E_s) dE_s = (D\mu^{\frac{1}{2}}\lambda_2\Lambda_1/l_2 E_p^0)(\phi + E_0)^{-\frac{1}{2}}[1 - (\lambda_2/(\lambda_2 + l))^{15}] \times \\ \times \left[(\chi - 1) - \frac{\Lambda_1}{\Lambda_2} \log \left\{ \frac{(\Lambda_1/\Lambda_2) + \chi}{(\Lambda_1/\Lambda_2) + 1} \right\} \right] E_s^{\frac{1}{2}} dE_s, \quad (41)$$

where D is a constant and $\chi = \{(\mu + \phi)/(\mu + \phi + E_s)\}^{\frac{1}{2}}$.

The position of the maximum of the velocity distribution predicted by expression (41) is markedly dependent on the work function ϕ . Fig. 151(a) shows the function plotted for a number of cases.

It is seen that the maximum in the distribution changes from 3 eV to 6 eV in passing from $\phi = 1$ eV to $\phi = 4$ eV. The form of the distribution is not very sensitive to change of μ_0 , so these curves should give a good idea of the kind of distribution to be expected for metals with different work functions.

Curves I and II of Fig. 151(a) were calculated for $\Lambda_1/\Lambda_2 = 0.56$, a condition which we have seen (§ 3.3) should apply under conditions where δ is a maximum. Curve III shows the case of a metal with the same work function as for curve II but with $\Lambda_1/\Lambda_2 = 1$. There is very little change in the distribution, showing that one would not expect it to be very sensitive to the energy of the primary electrons, just as observed.

A detailed experimental study of the energy distribution of the secondary electrons has been carried out by Kollath§ for Mo, Ta, Be

† Rudberg, *Proc. Roy. Soc. A*, **127** (1930), 111.

‡ Langenwalter, *Ann. der Physik*, **24** (1935), 273.

§ Ibid. **39** (1941), 59.

using the method of the longitudinal magnetic field described in § 2.2. His results are shown in Fig. 151(b).

Table III, compiled from a similar one in Kollath's paper, summarizes the results of measurements of the energy distribution of secondary electrons due to primaries with energy up to 1,000 eV.

TABLE III
Most Probable Energy of Emission of Secondary Electrons

<i>Material</i>	<i>Primary energy (eV)</i>	<i>Most probable secondary energy (eV)</i>	<i>Method</i>
Be	0-30	1.8	L.M.F. ⁽¹⁾
C (lamp black)	24-1,075	2	R.F. ⁽²⁾
C (graphite)	100-1,000	5.15	T.M.F. ⁽³⁾
Al	36, 176	5-6	T.M.F. ⁽⁴⁾
Cu	150	3.3	T.M.F. ⁽⁵⁾
Cu	100-1,000	5.15	T.M.F. ⁽³⁾
Cb	0-150	4.5	T.M.F. ⁽⁶⁾
Mo	0-150	3	T.M.F. ⁽⁷⁾
Mo	7.5-1,000	4	T.M.F. ⁽⁸⁾
Mo	0-30	2.1	L.M.F. ⁽¹⁾
Pd	0-100	2	R.F. ⁽⁹⁾
Ag	150	5.4	T.M.F. ⁽⁵⁾
Ag	0-100	2.3	R.F. ⁽⁹⁾
Ta	0-30	1.5	L.M.F. ⁽¹⁾
Pt	100-1,000	5.15	T.M.F. ⁽³⁾
Pt	0-100	2.3	R.F. ⁽⁹⁾
Au	150	5.4	T.M.F. ⁽⁵⁾
Cs (photolayer)	50 300	1.3	R.F. ⁽¹⁰⁾

R.F., retarding field method; T.M.F., transverse magnetic field method; L.M.F., longitudinal magnetic field method.

References

1. *Ann. der Physik*, **39** (1941), 59.
2. Becker, *ibid.* **78** (1925), 228.
3. Sharman, *Proc. Cambridge Phil. Soc.* **23** (1927), 523, 922.
4. Brinsmade, *Phys. Rev.* **30** (1927), 494.
5. Rudberg, *ibid.* **50** (1936), 138.
6. Harworth, *Phys. Rev.* **50** (1936), 216.
7. *Ibid.* **48** (1935), 88.
8. Soller, *ibid.* **36** (1930), 1212.
9. Langenwalter, *Ann. der Physik*, **24** (1935), 273.
10. Pjatnitsky, *Phys. Ber.* **20** (1939), 437.

A feature of Table III is the extraordinary discrepancy between the results of different observers. All agree that the most probable secondary energy is very low, but its actual value appears to be very dependent on surface conditions. To illustrate the importance of surface conditions

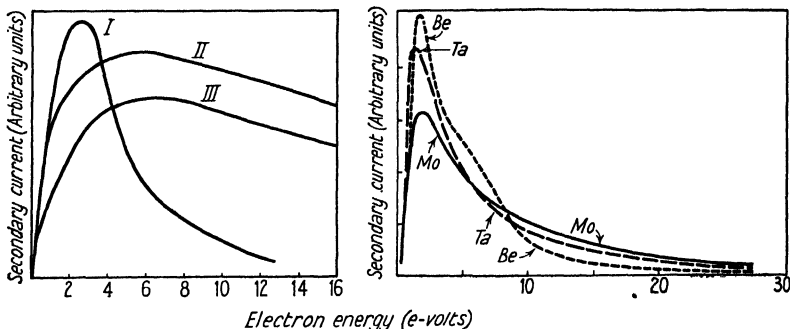


FIG. 151. (a) Energy distribution of secondary electrons in a number of cases calculated by Kadyshovich. Curve I: $\mu = 5$ eV, $\phi = 1$ eV, $\Lambda_1/\Lambda_2 = 0.56$. Curve II: $\mu = 5$ eV, $\phi = 4$ eV, $\Lambda_1/\Lambda_2 = 0.56$. Curve III: $\mu = 5$ eV, $\phi = 4$ eV, $\Lambda_1/\Lambda_2 = 1.0$. (b) Observed energy distribution of secondary electrons emitted from Be, Ta, Mo by primary electrons of energy 30 eV.

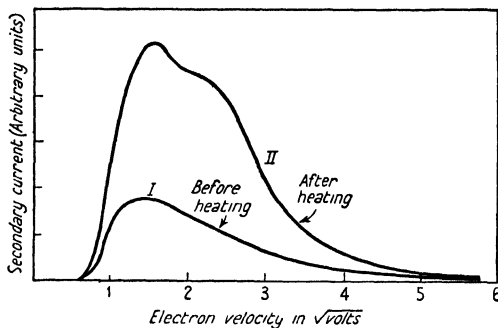


FIG. 152. Observed velocity distribution of secondary electrons emitted from a thin beryllium film. Curve I refers to a freshly deposited film, curve II to a film after it has been heated to a red heat for 10 minutes.

on the energy distribution of the secondaries, Fig. 152 shows curves obtained by Kollath† for the energy distribution of secondary electrons from an evaporated layer of beryllium on a molybdenum plate, taken immediately after evaporation (curve I), and also after being maintained at a red heat for 10 minutes (curve II). The effect of the heat treatment in this case is to change quite markedly both δ and the energy distribution of the secondaries.

A systematic investigation of the effect of surface conditions on the energy distribution has been made by Bronstein.‡ By depositing thin

† Loc. cit.

‡ *J. Tech. Phys. U.S.S.R.* **13** (1943), 176.

layers of silver on a nickel base he found that at the beginning of the evaporation, as the work function decreased, there was a continuous shift of $E_s^{\max}$, the most probable energy of the secondaries, towards smaller values. This shift continued until for a thickness of 0.8 to 0.9 of an atomic layer the work function reached a minimum. For further increase of the thickness the work function increased again and at the same time $E_s^{\max}$ moved out to higher values until a thickness of 1.5 atomic layers was reached and the surface had a work function characteristic of solid silver. This kind of behaviour can be interpreted very readily in terms of Kadyshevich's theory (see Fig. 151 (a)).

The variation of $E_s^{\max}$ with the angle of emergence of the secondaries has been investigated by Krishnan and Frumin.† They found $E_s^{\max}$ to increase with increase of this angle.

6. Reflection of electrons from surfaces

Little work has been done on the measurement of the elastic reflection coefficient, r , of electrons from surfaces as distinct from the secondary emission coefficient. As has been noted earlier (§ 1.1), most measurements of δ have included reflected electrons, but this is not serious for primary energies in excess of 100 eV.

For very slow electrons Gimpel and Richardson‡ have made a careful examination of the reflection coefficients from copper. They found that the energy distribution in the incident and reflected electron beams was identical and that r had a value of 0.24 in the range of primary energy from 0.35 eV up to a few eV with a slight minimum at 0.85 eV.

Farnsworth§ gives the values of r shown in Table IV for electrons of primary energy from 5 to 10 eV.

TABLE IV
Reflection Coefficients r of Slow Electrons

<i>Element</i>	<i>r</i>
Mg	0.40
Al	0.57
Ni	0.16
Pd	0.36
Ag	0.40
W	0.32
Pt	0.30
Au	0.39

† Ibid. **11** (1941), 317.

‡ *Proc. Roy. Soc. A*, **182** (1943), 17.

§ *Phys. Rev.* **20** (1922), 358; *ibid.* **25** (1925), 41.

Bruining† measured r in the energy range 2.5 to 25 eV for Ba, Ag, and BaO. The values he obtains for Ag are little more than one-third of those given by Farnsworth, indicating once again the great importance of clean surfaces. Since the slow electrons concerned in this work will penetrate very few atomic layers, the values of r obtained refer mainly to the surface layers and not to the bulk of the material. Bruining found a decrease of r with energy in all three cases. For BaO r becomes very large for very slow electrons.

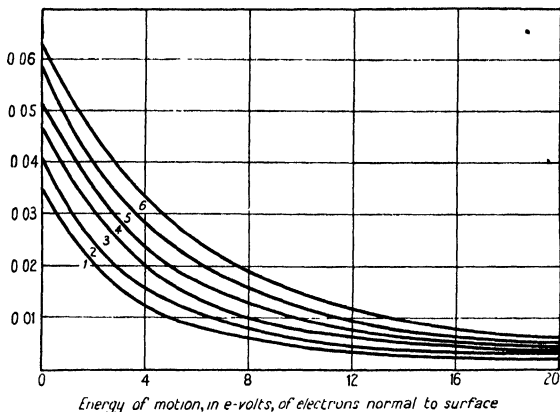


FIG. 153. Calculated reflection coefficients r for electrons at a metal surface. Curves 1–6 refer to depth ($V_0 = \mu + \phi$) of the metal 'well' of 10, 12, 14, 16, 18, 20 eV respectively.

Calculations of r have been carried out for metals by MacColl.‡ Using Nordheim's image force hypothesis he wrote for the potential energy of the field in which the primary electron moves

$$\left. \begin{aligned} V(x, y, z) &= -V_0 = -\epsilon^2/4x_0 \quad \text{for } x \leq x_0 \text{ (inside the metal)} \\ &= -\epsilon^2/4x \quad \text{for } x \geq x_0 \text{ (outside the metal)} \end{aligned} \right\}. \quad (42)$$

The problem simply consists then of solving the wave equation for motion of the electrons in this field, and thus obtaining the reflection coefficient as the square of the ratio of the amplitudes of incident and reflected electron waves.

For low-energy electrons the theory gives

$$r = \hbar^2 V_0^4 / 8\epsilon^4 m, \quad (43)$$

while for large values of E_x , the energy of the primary due to its motion normal to the surface,

$$r \sim \hbar^2 V_0^4 / 8\epsilon^4 m E_x^3. \quad (44)$$

† *Physica*, **5** (1938), 913.

‡ *Phys. Rev.* **56** (1939), 699.

Fig. 153 shows the results obtained by MacColl for V_0 in the range 10–20 eV. (From Table I it is seen that $V_0 = \phi + \mu$ is 10.2 eV for silver, 5.7 eV for barium.) The curves are in qualitative agreement with those observed by Bruining, but the decrease with increasing electron energy is more rapid and the values of r smaller than those observed.

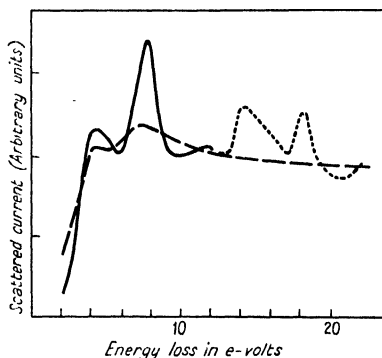


FIG. 154. Energy distribution of electrons with 200 eV incident energy scattered inelastically from a copper surface. ——— calculated distribution; - - - - - observed distribution.

7. Inelastic scattering of electrons from solids

There remain to be discussed those electrons which emerge from the surface with an energy which, while not equal to that of the primary electrons, is far too great for them to be considered as secondary electrons. The energy distribution of these electrons, which have been scattered inelastically from the solid, have been shown, by a number of investigators,[†] to exhibit a structure of maxima and minima characteristic of the solid surface under bombardment. The phenomenon has been studied in some detail for polycrystalline targets of Cu, Ag, and Au by Rudberg,[‡] and for scattering from a single crystal of silver by Turnbull and Farnsworth.[§]

Fig. 154 shows the curve obtained by Rudberg[‡] for the energy distribution near the maximum in the case of copper. The curve shown refers to a primary energy of 200 eV but is typical of that obtained generally. There is a deep valley near the reflection peak which indicates

[†] Brown and Whiddington, *Nature*, **119** (1927), 427; Whiddington, *Proc. Leeds Phil. Lit. Soc.* **1** (1928), 242; Rudberg, *Proc. Roy. Soc. A*, **127** (1930), 111; Haworth, *Phys. Rev.* **37** (1931), 93; *ibid.* **42** (1932), 906; *ibid.* **48** (1935), 88.

[‡] *Ibid.* **50** (1936), 138.

[§] *Ibid.* **54** (1938), 509.

the absence of inelastic collisions with small energy losses. This is followed by two main maxima. All three metals studied by Rudberg showed two maxima below 10 eV, the most pronounced one being that for silver at 3.9 eV.

In order to obtain some idea of the depth at which the inelastic scattering occurs, films of Ca, CaO, Ba, and BaO of known thickness were deposited on the silver. The results indicated that the inelastic scattering structure was determined by the first few atomic layers near the surface. In fact Rudberg has suggested that a study of the energy distribution of electrons scattered inelastically from a surface would provide a very sensitive method of studying the condition of the surface. He showed that a deposit of 5×10^{14} atoms/cm.² of Ca or CaO on silver—less than a monatomic layer—was readily detected by this method.

The results obtained by Turnbull and Farnsworth† for a single crystal of silver were similar to those of Rudberg for polycrystalline silver. They obtained two peaks corresponding to energy losses of approximately 3.9 eV and 7.3 eV respectively. Unlike polycrystalline silver, however, the relative intensities of the two peaks depended on both primary voltage and target angle in the neighbourhood of the diffraction beams.

A detailed calculation of the distribution of energy loss for electrons scattered by metallic copper has been carried out by Rudberg and Slater.‡ Their theory follows essentially the same lines as the Wooldridge theory of secondary emission, using metal wave functions of the type (9) and Born's approximation to calculate the collision cross-sections. On the other hand, the transitions concerned are from levels in the uppermost partly occupied band (see § 3.1) to unoccupied levels above in which the electron is still bound in the metal. The chance of a given energy loss depends markedly on the energy distribution of the states in both the initial and final bands and the theory is directed particularly towards predicting this effect. As only primary electrons which are scattered out of the metal before penetrating far are concerned, the question of energy loss within the metal does not arise nor is one concerned with the ultimate fate of the excited metal electrons. For these reasons Rudberg and Slater took into account the detailed level distribution within the initial and final bands and were able to predict the probability distribution of energy loss, whereas Wooldridge was only concerned to predict the mean energy of secondary electrons. Nevertheless, to simplify the calculation, they assumed that the direction of

† *Phys. Rev.* **54** (1938), 509.

‡ *Ibid.* **50** (1936), 150.

motion of the primary electron was oriented at random. This is probably justified because of the random orientation of the metal crystallites and in any case may well occur as a result of collisions with the lattice ions in the surface layers.

Corresponding to each energy level within a particular band there is a wave vector κ , the wave function for the level having the form

$$\psi_a(\kappa, \mathbf{r}) = u_{a\kappa}(\mathbf{r})e^{i\kappa \cdot \mathbf{r}},$$

as in (9), the suffix a distinguishing the particular band. With the assumption of a random direction of incidence of the primary the probability of an excitation from a level (a, κ) to (b, κ') , involving an energy loss ϵ small compared with the incident energy, is given by a formula exactly similar to the corresponding one for excitation of an optically allowed level of an atom by an electron (Chap. III, § 3.2), viz.

$$p(a, \kappa; b, \kappa') \propto |\mathbf{r}(a, \kappa; b, \kappa')|^2 \log(2k/\epsilon), \quad (45)$$

where $k\hbar$ is the momentum of the incident electron and

$$\mathbf{r}(a, \kappa; b, \kappa') = \int_{V_0} \psi_a^*(\kappa, \mathbf{r}) \mathbf{r} \psi_b(\kappa', \mathbf{r}) d\tau, \quad (46)$$

where V_0 is the volume of the metal. Apart from the logarithmic factor, which varies very slowly with ϵ for large k , the probability is practically the same as that for optical absorption between the two levels.

To evaluate $\mathbf{r}(a, \kappa; b, \kappa')$ for a given κ' it may be assumed that $\kappa \simeq \kappa'$ as there is a sharp maximum for small momentum changes of the incident electron. The integral may be transferred to one over a lattice cell with the function normalized to unity through the volume of a cell. This has the advantage that the initial function ψ_a becomes practically a d -wave function for a free copper atom. This is because the a -band is a d -band in which there is little broadening by the perturbations of neighbouring atoms. On the other hand, the wave function ψ_b for the upper level corresponds to the opposite approximation of nearly free electrons and may be represented by a plane wave except for the necessity that

$$\int \psi_a^* \psi_b d\tau = 0$$

taken over a lattice cell. This was adjusted by omitting the part of the plane wave corresponding to d electrons in the cell, i.e. to electrons with angular momentum $6\frac{1}{2}\hbar$ about the centre of the cell. With these approximations Slater and Rudberg obtained $|\mathbf{r}|^2$ as a function of the energy $\kappa'^2\hbar^2/2m$ of the upper state as illustrated in Fig. 155.

To complete the calculation it is only necessary to use the energy-level distribution in the upper and lower bands and the assignment of the κ and κ' values to the different levels in each, taking account of the fact that a transition can only occur to a (b, κ') level from a level in the a -band with $\kappa \simeq \kappa'$. The energy loss involved in a transition to a particular (b, κ') level is thus fixed and the weight to assign to this loss is proportional to the value of $|\mathbf{r}|^2$ and the density of initial states around κ .

Using the level distribution illustrated in Fig. 156 and $|\mathbf{r}|^2$ from (46), Slater and Rudberg obtained the probability distribution of energy loss which is compared with the observed in Fig. 154. Fair agreement is obtained. Both curves show a very small number of electrons suffering

small energy loss. This arises from the low-level density at the top of the occupied band *a* (see Fig. 156). The maxima at 4.3 and 7 eV are due respectively to the peaks *A* and *B* in the level distribution. However,

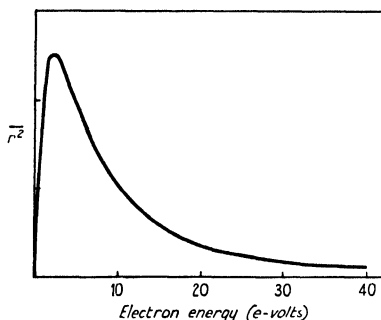


FIG. 155. Mean square $\overline{\mu^2}$ of the dipole moment associated with transitions to upper states of different energy.

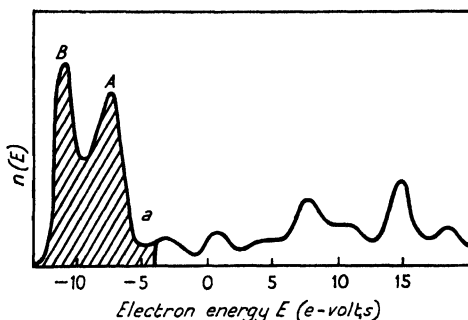


FIG. 156. Energy-level distribution for metallic copper. $n(E)$ is the number of electrons with energy between E and $E+dE$. The shaded region indicates the occupied levels of the *a*-band.

the theory predicts further maxima at 14 and 18 eV which are not observed. These partly arise from the detailed character of the upper band and are hardly likely to be given correctly by the crude plane-wave approximation used for the upper state wave function. A further factor which could tend to smooth out any peaks at the higher energy losses is the possibility of multiple scattering.

7.1. Fine structure in the observed $\delta-E_p^0$ curve at low primary energies

Another effect arising partly from inelastic scattering is the fine structure which has been observed in the curve representing the variation

of δ with primary electron energy E_p^0 when this energy is low. Rao† and Richardson‡ found a close correlation between the δ - E_p^0 curve and the X-ray excitation curve for the same metal. The reflected and secondary electrons were not distinguished in these measurements.

The correlation between electron emission and the optical properties of a solid were studied in some detail by Hilsch.§ He used deposited layers of the alkali halides as target. In each case he found a marked fine structure in the δ - E_p^0 curve at low energies. Thus Fig. 157 shows

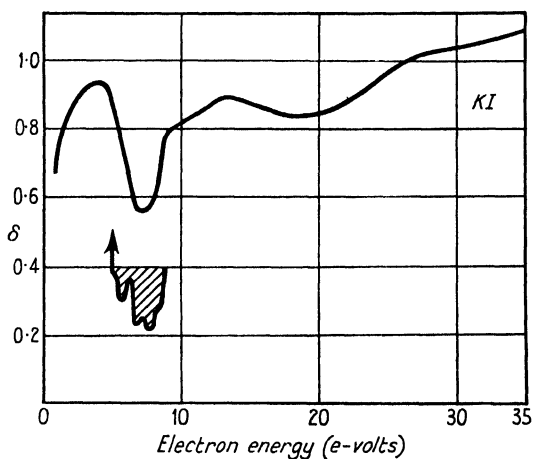


FIG. 157. Observed variation of δ with primary energy for KI at low primary energies. The small inset shaded diagram shows the optical absorption spectrum of KI in which the intensity of radiation transmitted through a layer of KI is plotted against quantum energy in eV. The low-energy limit of the absorption band practically coincides with a maximum in the curve for δ .

a typical curve for a potassium iodide layer. The figure also shows the position (on a voltage scale) of an absorption band for KI. It is seen that the lower limit of the absorption band coincides almost exactly with the maximum of the δ - E_p^0 curve at 5 eV. This result can be understood on the basis of inelastic scattering. Electrons of energy less than 5 eV possess insufficient energy to effect a transition from the uppermost levels of the fully occupied energy band of the compound to the lowest (unoccupied) levels of the band above it. Above 5 eV incident energy this transition can be produced. Electrons which lose energy in this way will no longer possess sufficient energy to escape again from the

† *Proc. Roy. Soc. A*, **128** (1930), 57.

‡ *Ibid.* 63.

§ *Zeits. f. Phys.* **77** (1932), 427.

metal as reflected electrons. Thus δ , or more correctly r , decreases with increase of E_p^0 in this region.

The results obtained by Hilsch† are summarized in Table V, which shows a comparison of the electron energy corresponding to the maximum in his $\delta-E_p^0$ curves with the lower energy limit of the optical absorption band. The correlation is seen to be very striking.

TABLE V

Correlation between Fine Structure in the $\delta-E_p^0$ Curve with the Position of the Absorption Bands for a Number of Materials

<i>Crystal</i>	<i>Energy at which decrease commences (eV)</i>	<i>Wave-length (in Å) corresponding to this energy</i>	<i>Observed upper wave-length limit of the optical absorption band (Å)</i>
NaCl	7.3 ± 0.13	$1,690 \pm 30$	1,700
KCl	7.1 ± 0.08	$1,740 \pm 20$	1,750
KI	4.8 ± 0.15	$2,570 \pm 80$	2,600
LiF	11.5 ± 0.15	$1,070 \pm 15$	1,080
NaF	9.2 ± 0.08	$1,340 \pm 15$	1,320
CaF ₂	10.4 ± 0.05	$1,190 \pm 20$	1,215

A remarkable feature of the results of Hilsch shown in Fig. 157 is the very high value of δ (which must be due almost entirely to electron reflection at these low values of E_p^0 for the compounds he investigated).

8. Reflection and secondary electron emission for primary electrons of higher energy

Although phenomena associated with the passage of higher energy electrons through solid material are somewhat outside the scope of this work, we shall describe briefly the phenomena observed in such cases.

As the electron energy increases the energy distribution of the secondary electrons varies little, most of the secondaries continuing to be emitted with an energy of only a few electron volts.

The value of δ continues to fall with increasing primary energy, but the fall becomes very slow. Thus the measurements of Trump and van de Graaff‡ show that, in the energy range from 50 keV to 300 keV, δ falls from 0.73 to 0.62 for tungsten, from 0.38 to 0.28 for steel, from 0.25 to 0.17 for aluminium, and from 0.13 to 0.05 for graphite.

Further, the importance of electrons leaving the surface with a high velocity (inelastically scattered or 'back-diffused' electrons) increases. This is clear from Fig. 158, which shows curves calculated by McKay§ from the data of Trump and van de Graaff for the ratio R_s of the number of secondaries of energy greater than 800 eV to the total number of emitted electrons.

If the material being investigated is in the form of a thin foil a few microns thick, and the primary electrons have an energy of a few tens of keV, low-energy secondary electrons may also be emitted from the other side of the foil. Such secondaries may, if the foil is of suitable thickness, be more numerous than those emitted from the entrance side of the foil. Further, their energy distribution shows a maximum

† *Zeits. f. Phys.* **77** (1932), 427.

‡ *J. App. Phys.* **18** (1947), 327.

§ *Advances in Electronics* (Academic Press Inc., New York, 1948).

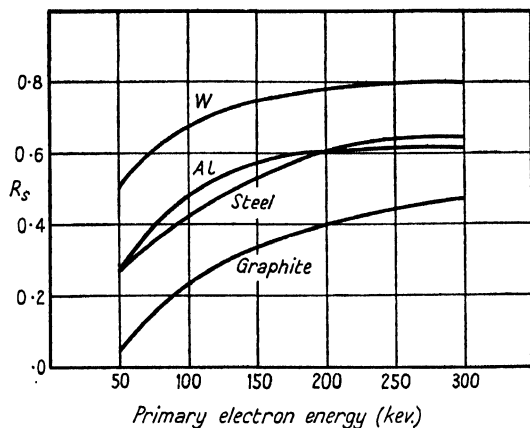


FIG. 158. Observed variation with primary energy of the ratio R_s of the number of secondary electrons with energy greater than 800 eV to the total number of secondary electrons emitted from W, Al, steel, and graphite bombarded with fast electrons.

at an energy several electron volts greater than for secondaries emitted from the entrance side.†

The detailed discussion of these phenomena is outside the scope of this book.

† Wecker, *Ann. der Physik*, **40** (1941), 405.

VI

ELECTRON COLLISIONS INVOLVING EMISSION OF RADIATION

1. Introduction

IN Chapter I it was mentioned, in the course of an analysis of the types of collision which would occur between an electron and an atom, that the emission of radiation could accompany such encounters. It is our purpose in this chapter to discuss such collisions. We shall first consider radiative impacts which lead to capture of the electron. Thus a positive ion may be neutralized by capturing an electron into a bound state, the surplus energy being emitted as radiation. Correspondingly, a neutral atom may capture an electron to form a negative ion though, in this case, as explained in § 2.4, the chance is limited by the absence of appropriate bound states of the negative ion. Capture processes such as these may be regarded as radiative transitions of an electron from an unquantized (free) state to a bound state. Radiative transitions between two free states are also possible in the presence of the field of an atom or molecule, neutral or ionized. Such transitions give rise, in particular, to the continuous X-ray spectrum, which will be discussed in §§ 3.3–3.5, and are an important source of absorption in stellar atmospheres.

2. Radiative capture of electrons

2.1. *The order of magnitude of the capture probability*

It is not difficult to see that the chance of radiative capture of an electron by an atom or ion is likely to be quite small. The measured lifetimes of the excited states of atoms show that an electron must remain in an excited state in the neighbourhood of an atom or ion as long as 10^{-8} sec. before there is a considerable chance of its undergoing a radiative collision. If τ sec. is the time of collision, i.e. the time during which an impinging electron is within the effective range of the atomic field, then the chance of emission of radiation during the encounter will be of order $10^8\tau$. For an electron of velocity of order 10^8 cm./sec. τ is of the order 10^{-15} sec., so that the chance of capture to a particular level in a collision is of the order 10^{-7} . Actually, for capture by positive ions, there are a number of accessible states into which capture may occur and this increases the chance quite considerably. The long-range Coulomb attraction also tends to concentrate the incident electron in

the neighbourhood of the charged ion, thereby further increasing the probability of capture. Even so, it still remains quite small. For capture by neutral atoms there are at most two accessible states and no long-range attraction so the chance is correspondingly very small.

There is very little experimental evidence available concerning the magnitude of radiative capture cross-sections for positive ions and none for neutral atoms, but indirect evidence in support of the theory may be obtained from a study of the inverse process—photo-ionization of a neutral atom or photo-detachment of electrons from negative ions:

$$\left. \begin{aligned} h\nu + A &\rightarrow A^+ + e \\ h\nu + A^- &\rightarrow A + e \end{aligned} \right\}. \quad (1)$$

Although the discussion of collisions between quanta and atomic systems is, in general, outside the scope of this book, we shall have occasion to refer to continuous absorption processes such as (1) in considering the validity of theoretical deductions concerning radiative capture.

2.2. *The theoretical formula*

The cross-section for radiative capture may be calculated by employing the quantum theory of radiative transition probabilities. According to this theory the transition probability is proportional to the square of the amplitude of the electric dipole moment averaged over the wave functions ψ_i , ψ_f of the initial and final state of the electron, i.e. to

$$\epsilon^2 \left| \int \psi_i^* \mathbf{r} \psi_f d\tau \right|^2, \quad (2)$$

where $\epsilon \mathbf{r}$ is the electric dipole moment, r being the distance of the electron from the centre of mass of the molecule. To obtain the cross-section it is only necessary to normalize the wave functions appropriately and insert the usual proportionality factor

$$64\pi^4 \nu^3 / 3hc^3, \quad (3)$$

where ν is the frequency of the emitted radiation and m is the mass of the electron. For radiative capture ψ_f is a wave function for a bound state and is normalized as usual, so that

$$\int |\psi_f|^2 d\tau = 1. \quad (4)$$

The wave function ψ_i for the initial free state will have the form, at a great distance r from the molecule, of a plane wave and the corresponding scattered wave. The amplitude of this plane wave must be chosen so as

to represent a flux of one electron/cm.²/sec. in the direction of the wave. If v is the initial velocity of the impinging electrons, then

$$\psi_i \sim v^{-1}[e^{ikz} + e^{ikr}r^{-1}f(\theta)], \quad (5)$$

where $k = mv/\hbar$.

The same formulae may be applied to determine the cross-sections for radiative capture by positive ions or neutral molecules, the only difference, apart from the detailed form of the wave functions, being that in the former case there are a great number of levels into which the electron may be captured whereas in the latter there are two at most.

If the wave functions ψ_i , ψ_f are accurate, the formula can be relied upon to give the radiative capture cross-section correctly, provided the wave length of the emitted radiation is small compared with the dimensions of the atom in the state to which capture takes place, a condition satisfied in all cases of practical importance. Hence there is no difficulty in obtaining accurate data for radiative capture by bare nuclei, but for all other cases only approximate wave functions ψ_i , ψ_f are available and this sometimes limits the attainable accuracy very severely. We shall therefore first discuss radiative capture by protons.

2.3. Radiative capture of electrons by protons

The most detailed calculations of the cross-sections for capture of electrons by protons have been made by Bates, Buckingham, Massey, and Unwin.[†] They used a formula given by Oppenheimer[‡] for the cross-section for capture to a state of given total quantum number n summed over all the sub-states of different azimuthal number l . Their results are given in Table I.

For the deepest states the capture cross-section varies nearly as E^{-1} at low electron energies E . The cross-section summed over all final states increases somewhat more rapidly as E decreases, owing to the increased contribution from highly excited states. Even at room-temperature energies the cross-section is still quite small, being about 3×10^{-19} cm.², of which about one-quarter is contributed from capture to the ground state. It is to be expected then that, in a spectrum arising from population of excited states by radiative capture of electrons, a 'recombination spectrum', lines due to transitions from highly excited states should be comparatively strong. This is a general feature of such spectra.[§]

It is sometimes of interest to know how the cross-section depends on

[†] *Proc. Roy. Soc. A*, **170** (1939), 322.

[‡] *Zeits. f. Phys.* **55** (1929), 725.

[§] See, for example, Paschen, *Sitz. Preuss. Akad. Wiss.* **16** (1926), 135.

TABLE I

Cross-sections for Radiative Capture of an Electron to Various States of a Hydrogen Atom

Electron energy (eV)	0.28	0.13	0.069	0.034
<i>Total quantum number of atomic state into which electron is captured</i>	<i>Cross-section in 10^{-21} cm.²</i>			
1	8.10	16.63	32.80	66.95
2	4.24	8.93	17.70	36.52
3	2.70	5.91	12.04	24.88
4	1.88	4.24	8.84	18.59
5	1.36	3.20	6.89	14.85
6	0.99	2.49	5.51	12.25
7	0.73	2.00	4.52	10.31
8	..	1.62	3.81	8.75
9	..	1.31	3.23	7.55
10	..	1.04	2.74	6.50
11	..	..	2.33	5.72
12	..	..	2.00	4.52
13	..	..	1.72	4.03
14	0.15	..	1.47	3.62
15	..	..	..	3.25
16	..	..	..	2.91
17	..	..	..	2.62
18	..	..	..	2.35
19	..	..	..	2.09
20	..	0.215	..	..
∴				
28	..	..	0.302	..
∴				
40	..	..	..	0.432
Sum for all final states	23.0	53.7	119	272

TABLE II

Variation of Radiative Capture Cross-section with Azimuthal Quantum Number of the Final State

Electron energy (eV)	0.28	0.13	0.069	0.034
<i>Quantum numbers of final states</i> <i>n l</i>	<i>Cross-section in 10^{-21} cm.²</i>			
2 0	1.20	2.45	4.80	9.81
2 1	3.04	6.48	12.90	26.71
3 0	0.402	0.826	1.62	3.30
3 1	1.15	2.46	4.95	10.11
3 2	1.15	2.62	5.47	11.47

the azimuthal quantum number of the final state. This may be done by using the formulae given by Stueckelberg and Morse† and by Wessel.‡ It is found that the major contributions come from the largest values of l . This may be seen from Table II.

2.4. Radiative capture by neutral hydrogen atoms

The problem of the capture of electrons by neutral hydrogen atoms is the simplest one for which approximate wave functions must be used. There are two points of difference from the corresponding problem for protons. Whereas in the latter case there are an infinite number of stationary states into which the electron may be captured, the H^- ion has only one stable bound state, of $1S$ type. The second difference is that between the long range of the Coulomb field which a proton exerts on the electron and the short range of the average field of the neutral atom. This has a profound influence on the behaviour of the cross-section in the limit of very slow electrons. We have seen that the cross-section for capture into a particular level by a proton increases as E^{-1} for low electron energies E . For capture by a hydrogen atom, on the other hand, the cross-section vanishes as $E^{\frac{1}{2}}$ in this limit. This behaviour is characteristic of all cases in which an electron is captured into an s orbital of a negative ion.

Quite accurate values are available for the cross-section for radiative capture by neutral hydrogen atoms. This is because the inverse photo-detachment process



has proved to be of great importance in the interpretation of the solar continuous emission spectrum. Much attention has therefore been devoted to obtaining the best possible values for the cross-section Q_a for this process in the wave-length range, 16,000 to 4,000 Å, of astrophysical importance. The cross-section Q_c for radiative capture, by a hydrogen atom, of electrons of velocity v , in which radiation of frequency ν is emitted, is related to that Q_a for the inverse process, absorption of a quantum of frequency ν by a H^- ion resulting in emission of an electron of velocity v , by the usual relation

$$Q_c = \frac{h^2 \nu^2}{m^2 v^2 c^2} \frac{g^-}{g_0} Q_a, \quad (6)$$

where g^- , g_0 are the statistical weights 1 and 2 respectively of the ground state of H^- and of H .

† *Phys. Rev.* **36** (1930), 16.

‡ *Ann. der Physik*, **5** (1930), 611.

Table III gives values of the radiative capture cross-section Q_c derived, using this relation, from the cross-sections calculated by Chandrasekhar.†

TABLE III

Cross-sections for Radiative Capture of Electrons by Neutral Hydrogen Atoms

<i>Electron energy</i> (eV)	<i>Capture cross-section</i> in 10^{-21} cm. ²
0.136	0.170
0.272	0.223
0.475	0.257
0.677	0.266
0.949	0.264
1.22	0.254
1.36	0.249
2.03	0.202
6.77	0.122
10.84	0.081
23.7	0.033

The main difficulty in obtaining reliable results is the sensitivity to the assumed form of the wave function ψ_f for the bound state of the H^- ion. Even the elaborate approximate wave function obtained by Henrich,‡ which probably gives the electron affinity of the H atom correct to 0.5 per cent., is not accurate enough. Although it is a good approximation at nuclear separations which give a large contribution to the binding energy it is not accurate enough at the larger separations which make substantial contributions to the mean dipole moment integral (2). To overcome this difficulty Chandrasekhar transformed the integral (2) into one involving the mean electronic momentum. When exact wave functions are used this gives the same results, but will not do so in general when the functions are only approximate. The contributions from the large nuclear separations are much less than in the mean dipole moment integral and the inaccuracy of Henrich's wave function at these separations is no longer important.

It will be noted by comparison of Tables I and III that the cross-section for capture into the ground state of a hydrogen atom is considerably greater, at all electron energies, than that for capture into the ground state of a negative hydrogen ion. This is because the long-range Coulomb field of the proton is much more effective in concentrating the electron wave in its vicinity than is the screened field of the hydrogen atom.

† *Ap. J.* **102** (1945), 223.

‡ *Ibid.* **99** (1944), 59, 318.

Some further remarks on the astrophysical applications of the inverse process are made in § 2.6.

2.5. Radiative capture by heavier ions and atoms

The cross-section $Q_c(Z, n, l, v)$ for capture of electrons of velocity v by a bare nucleus of charge Ze into a state of quantum numbers n, l is related to that $Q_c(1, n, l, v)$ for capture into the corresponding state of a hydrogen atom by†

$$Q_c(Z, n, l, v) = Z^2 Q_c(1, n, l, v). \quad (7)$$

If the nucleus is partially screened by s bound electrons, the outermost occupied orbital having quantum numbers n_0, l_0 , the cross-section for capture into a level with quantum numbers n, l with $n > n_0$ is still given approximately by (7), but a special calculation must be made to obtain the cross-section for capture into an orbital with quantum number n_0 . Just as for H^- the problem of calculating this cross-section is the same as that of calculating the continuous radiative absorption cross-section of the ion, with $s+1$ bound electrons in its ground state. Thus the cross-section for capture of electrons by O^+ into the ground orbital of O is essentially the same problem as that of calculating the continuous absorption coefficient of atomic oxygen for radiation of the appropriate frequency.

The accuracy attainable in such calculations depends on the sensitivity of the integral (2) to the detailed character of the wave functions. A comprehensive discussion of the possibilities has been given by Bates.‡ Table IV summarizes his conclusions together with the calculations, if any, which are available for each particular case.

The most important result of these calculations is that the cross-section for capture of an electron to the ground state of a heavy ion is of the same order of magnitude as for capture by a proton. Thus the cross-section for capture of an electron of 0.03 eV energy to a level of the lowest configuration of O is found to be $3.6 \times 10^{-20} \text{ cm}^2$ which is not very different from the corresponding value $6.7 \times 10^{-20} \text{ cm}^2$ for capture to the ground state of H . It was at first supposed that the cross-section for capture to the ground state of a heavy atom should be much larger than for hydrogen on the assumption that it could be obtained approximately by substituting for Z in (7) the effective nuclear charge acting on the electron in its final bound state. This is not so because the wave function ψ_i does not correspond to the same effective nuclear charge.

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

‡ *M.N.R.A.S.* **106** (1946), 432.

This point is of importance in interpreting observed recombination phenomena (see Chap. X, § 3.2).

TABLE IV

Summary of Available Data on Cross-sections for Radiative Capture of Electrons into the Ground States of Various Positive Ions and of the Likely Accuracy attainable

<i>Ion capturing the electron</i>	<i>References to calculations available</i>	<i>Likely accuracy</i>
<i>Singly charged ions</i>		
H ⁺	1	Exact
He ⁺	2	Fair—improvement possible
Li ⁺ , Na ⁺	3	Fair improvement possible
K ⁺	4	Poor—improvement very difficult
Rb ⁺ , Cs ⁺	..	Poor
Be ⁺	5	Fair improvement possible
Mg ⁺	..	Fair
Ca ⁺	6	Fair
Sr ⁺ , Ba ⁺	..	Poor
B ⁺ , C ⁺ , N ⁺ , O ⁺ , F ⁺ , Ne ⁺	7	Fair improvement possible
A ⁺ , Si ⁺ , P ⁺ , S ⁺ , Cl ⁺ , Ar ⁺	..	Fair
Remaining elements	..	Poor
<i>Doubly charged ions</i>		
He ⁺⁺	1	Exact
Li ⁺⁺	8	Poor—improvement possible
Ba ⁺⁺ , Mg ⁺⁺	..	Fair
Ca ⁺⁺	6	Poor—improvement very difficult
Sr ⁺⁺ , Ba ⁺⁺	..	Poor
B ⁺⁺ , Ar ⁺⁺	..	Fair
Ca ⁺⁺ , In ⁺⁺	..	Poor
C ⁺⁺ , N ⁺⁺ , O ⁺⁺ , F ⁺⁺ , N ⁺⁺ , Na ⁺⁺	9	Fair—improvement possible
Si ⁺⁺ , P ⁺⁺ , S ⁺⁺ , Cl ⁺⁺ , K ⁺⁺	..	Fair
Remaining elements	..	Poor

References

1. See § 2.3.
2. Wheeler, *Phys. Rev.* **43** (1933), 258; Vinti, *ibid.* **44** (1934), 524.
3. Li: Hargreaves, *Proc. Cambridge Phil. Soc.* **25** (1928), 75; Trumphy, *Zeits. f. Phys.* **71** (1931), 720. Na: Trumphy, *loc. cit.*; Rudkjøbing, *Publ. Kbh. Obs.* **18** (1941), 1.
4. Phillips, *Phys. Rev.* **39** (1932), 905; Bates, *Proc. Roy. Soc. A*, **188** (1947), 350.
5. Bates, *M.N.R.A.S.* **106** (1946), 423.
6. Bates and Massey, *Proc. Roy. Soc. A*, **177** (1941), 329.
7. Bates, *M.N.R.A.S.* **100** (1939), 25. O: Bates, Buckingham, Massey, and Unwin, *Proc. Roy. Soc. A*, **170** (1939), 322; Yamanouchi and Katani, *Proc. Phys. Math. Soc., Japan*, **22** (1940), 60; Bates and Seaton *M.N.R.A.S.* **109** (1949), 698.
8. Bates, *M.N.R.A.S.* **106** (1946), 432.
9. *Ibid.* 433.

The most extensive calculations for capture of electrons by neutral atoms other than hydrogen are those of Bates and Massey† for oxygen.

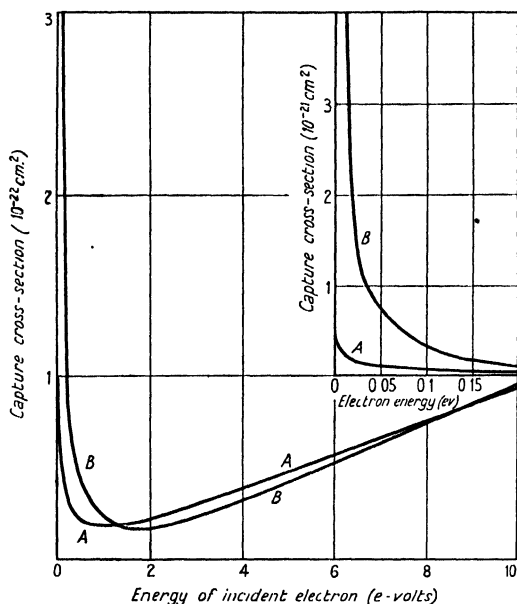


FIG. 159. Capture cross-section for electrons in atomic oxygen as a function of electron energy. Curve *A* is calculated for the theoretically estimated polarizability of atomic oxygen. Curve *B* is calculated for a polarizability just large enough to introduce a stable excited level of O^- .

Special interest attaches to this case because of the possible importance of negative oxygen ions in the ionized regions of the earth's upper atmosphere.‡ The problem is complicated by the possible existence of the excited state of O^- with very small binding energy (see Chap. IV, §§ 6.32, 6.5, 6.6). The electron configuration of this state is probably $(1s)^2(2s)^2(2p)^43s$. If this is so, the interaction between an oxygen atom and an electron must be such that a resonance effect appears in the wave function ψ_i . The resulting capture cross-section would be much larger than would be the case if the weakly bound state were non-existent. The difficulty is enhanced by the failure of any but empirical theory to provide a weakly bound excited state for O^- . Bates and Massey therefore introduced an empirical polarization interaction between

† *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

‡ See Massey, *Negative Ions*, Cambridge, 2nd edition, Chap. V.

an O atom and an incident electron. By varying the magnitude of the empirical polarizability they were able to vary the binding energy of the excited state at will and thus to correlate the capture cross-section with this binding energy. Fig. 159 illustrates the capture cross-section calculated for two values of the empirical polarizability. The first is what would be expected from the theoretically estimated polarizability of atomic oxygen but would not give rise to a stable excited state, while the second is slightly in excess of that just necessary to introduce a stable level.

In this case the electron is bound into a p orbital and the capture cross-section behaves like E^{-1} for small electron energies E .

Calculations have also been carried out for capture by neutral chlorine† and sodium,‡ but they must be regarded as illustrative of possibilities rather than as accurate predictions for the particular cases.

2.6. Evidence concerning the accuracy of calculated capture cross-sections

The only direct measurement of a cross-section for radiative capture is that of Mohler.§ He investigated the intensity of the continuous spectrum radiated by the positive column of an arc discharge in caesium vapour and obtained therefrom an estimate of the cross-section for capture by Cs^+ of 0.3 eV electrons into the $6p$ level of caesium. The method was as follows.

The intensity $I(\nu) d\nu$ of radiation with frequency between ν and $\nu + d\nu$ emitted per c.c. by radiative capture to a particular level from a plasma containing N_e electrons and positive ions per c.c. is given by

$$I(\nu) d\nu = h\nu N_e^2 v Q_c(v) f(v) dv. \quad (8)$$

v is the velocity of an electron whose capture to the level concerned gives rise to radiation of frequency ν so that

$$h\nu = h\nu_0 + \frac{1}{2}mv^2, \quad (9)$$

where $h\nu_0$ is the binding energy of the final state. $f(v) dv$ is the fraction of electrons with velocity between v and $v + dv$ and $Q_c(v)$ is the cross-section for radiative capture of electrons with velocity v to the level concerned.

In the positive column of an arc discharge the electrons have a Maxwellian distribution of velocities with an effective temperature T_e in excess of the gas temperature, so that

$$f(v) = (m/2\pi kT_e)^{1/2} v^2 \exp\{-mv^2/2kT_e\}. \quad (10)$$

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

‡ K. Huang, *Ap. J.* **101** (1945), 196.

§ *J. Res. Bureau Standards*, **10** (1933), 771.

If $I(\nu)$, N_e , and T_e can be measured and the source of the radiation identified, $Q_c(\nu)$ can therefore be obtained. N_e and T_e may be determined in the usual way by use of Langmuir probes. In Mohler's experiments the intensity of the continuum in the neighbourhood of the $6p$ limit of caesium was measured so that it is plausible to assign its source as mainly from radiative capture to the $6p$ level.

As a check the variation of the intensity with electron density and caesium vapour pressure was observed. It was found that the intensity increased with the vapour pressure showing that some three-body effects were contributing. To eliminate these, the limiting value of the intensity for zero vapour pressure was determined by a short extrapolation of the observed results and found to be proportional to N_e^2 . It was also verified that, under these conditions, the variation of intensity with wave-length was as given by (8) with the value of T_e obtained from the probe measurements.

The intensity of the continuum was measured at a wave-length corresponding to capture of an 0.3 eV electron to the $6p$ level ($\lambda = 4,400 \text{ \AA}$) and gave for the effective collision area $Q_c = 1.7 \times 10^{-21} \text{ cm}^2$. This is of the same order of magnitude as that calculated for capture by protons.

Apart from this measurement the only data which can be directly compared are the observations of the continuous absorption cross-sections for potassium. Unfortunately, this is a case in which great sensitivity of the theoretical prediction to the details of the approximate wave functions is to be expected. Nevertheless, theory and experiment both agree in finding abnormally low cross-sections and Bates† has shown, by introducing an empirical polarization term as in the calculations for radiative capture by atomic oxygen (see § 2.5), that the observations of Ditchburn, Tunstead, and Yates‡ fall within the theoretical possibilities. The experimental study of absorption by neon offers the best chance of a thoroughly detailed check on the theory.

No continuum attributable to the capture of electrons by neutral atoms has ever been observed in the laboratory.§ This is not inconsistent with the weak intensity expected under experimental conditions. On the other hand, indirect evidence of the validity of the theory for capture by a hydrogen atom is provided by the observed intensity variation of the solar continuous emission spectrum between wave-lengths of 4,000 and 18,000 $\text{\AA}$. From this, the variation with wave-length of the continuous absorption coefficient of matter in the solar photosphere may

† *Proc. Roy. Soc. A*, **188** (1947), 350.

‡ *Ibid.* **181** (1943), 386.

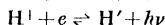
§ See Massey, *Negative Ions*, Cambridge, 2nd edition, 1950, Chap. III, § 2.

be derived. It was found impossible to identify the source of the absorption in the wave-length range mentioned until Wildt suggested† that it might be due to absorption by the negative hydrogen ion. An appreciable proportion of photospheric matter should be in the form of this ion as hydrogen is by far the most abundant element in the sun. Wildt's suggestion has been verified quantitatively‡ when account is also taken of absorption due to free-free transitions of electrons in the presence of hydrogen atoms (see § 3.2).

The only evidence supporting the theoretical calculations for the total capture cross-section comes from very indirect astrophysical considerations concerning the electron density in interstellar space. This may be determined in two distinct ways. Stromgren§ obtained it from the observed intensity of the H_α line emitted by interstellar matter. He assumed that all the electrons are derived from hydrogen so that the electron density N_e is nearly equal to that $N(H^+)$ of hydrogen ions and much greater than that $N(H)$ of neutral hydrogen atoms. By studying the rates of processes leading to the formation and destruction of excited hydrogen atoms the equilibrium constant

$$K = N_e N(H^+)/N(H'),$$

for the reaction



could be determined. Knowing $N(H')$ from the intensity of the H_α line this gave $N_e N(H^+)$ which is $\approx N_e^2$. In this way N_e was found to be about 3/c.c. On the other hand, Struve|| estimated N_e from the measurements of Dunham†† on the interstellar absorption lines of calcium which gave the ratio of the concentration $N(Ca^+)$ of Ca^+ ions to that $N(Ca)$ of neutral Ca atoms. The value of

$$N(Ca^+)N_e/N(Ca),$$

the equilibrium constant for the reaction



can be obtained from the Saha formula,‡‡ provided allowance is made for electrons reaching the ground state of Ca by first being captured to excited states and then dropping to the lowest state by successive emission of radiation. This introduces into the usual Saha formula a factor $Q_e(g)/Q_e(t)$, where $Q_e(g)$ is the cross-section for capture to the ground state of normal calcium and $Q_e(t)$ the total cross-section for capture into any bound state. In order that the two estimates of N_e should agree it is necessary that $Q_e(g)/Q_e(t)$ should be about 10, which is of the same order as the calculated ratio (see Table I for electrons of about 0.3 eV energy) for hydrogen.

Thus the evidence, though still very incomplete, suggests that no important error is present in the theory. Further discussion of a related matter, the nature of the recombination process in a dense discharge plasma, is given in Chap. X, § 3.6.

† *Ap. J.* **89** (1939), 295; **93** (1941), 47.

‡ See Deutsch, *Rev. Mod. Phys.* **20** (1948), 388 or Massey, *Negative Ions*, Cambridge, 2nd edition, 1950 Chap. V.

§ *Ap. J.* **89** (1939), 526.

|| *Proc. Nat. Acad. Sci., Wash.* **25** (1939), 36.

†† *Publ. Astr. Soc. Pacif.* **49** (1937), 26.

‡‡ Saha, *Phil. Mag.* **40** (1920), 472, 809; *Proc. Roy. Soc. A*, **99** (1921), 135.

3. Radiation in free-free transitions—bremsstrahlung

3.1. Introduction—theoretical formulae

A completely free electron may not radiate energy as this would involve violation of the conservation of linear momentum. In the presence of another body, such as an atom or ion, which may take up momentum, radiation may occur so that the electron suffers an inelastic collision in which the kinetic energy is transferred into radiant energy instead of energy of internal motion of the atom or ion. Classically the process is one of emission of radiation due to the acceleration of the electron by the atomic field. It is often referred to as *bremsstrahlung*. An encounter of this sort may be regarded as one in which the electron makes a transition between two states of the continuous spectrum in the field of the atom or ion, and a formula similar to that for radiative capture, in which the transition is from a free to a bound state, may be used.

Owing to the continuous distribution of the positive energy states in the field of an atom or ion, an electron may lose any fraction of its initial energy in such a radiative process. The frequency of the quanta emitted will range from zero up to a certain maximum frequency ν_0 which corresponds to the loss of the entire energy of the electron. If ϵV_0 , ϵV are respectively the initial and final energy of the electron, the frequency of the radiated quantum will be given by $h\nu = (V_0 - V)\epsilon$, the maximum frequency being given by $h\nu_0 = V_0\epsilon$.

The probability of a radiative encounter of this type may be specified in terms of an effective cross-section $q_\nu d\nu$ for a collision between the electron and ion in which a quantum of energy $h\nu$ is radiated. This may be analysed in terms of a differential cross-section $I_\nu(\theta, \phi; \vartheta, \phi')$, which is such that $I_\nu d\omega d\Omega/q_\nu$ is the chance that, in an encounter in which a quantum $h\nu$ is radiated, the electron is deviated through (θ, ϕ) into the solid angle $d\omega$ and the quantum is emitted in the direction (ϑ, ϕ') within the solid angle $d\Omega$. Thus

$$q_\nu = \iint I_\nu d\omega d\Omega, \quad (11)$$

and I_ν provides a complete specification of the angular distribution of of the emitted quantum as well as the angular distribution of the scattered electron.

It may be shown by various methods† that

$$I_\nu(\theta, \phi; \vartheta, \phi') = \frac{\epsilon^2 \hbar \nu k_n^2}{4\pi^2 m^2 c^3} \left| \int \psi_f^* \exp\{-2\pi i \nu \mathbf{n} \cdot \mathbf{r}/c\} \mathbf{s} \cdot \nabla \psi_i d\tau \right|^2, \quad (12)$$

† Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. XV; Heitler, *The Theory of Radiation*, 2nd edition, Chap. III.

where $\mathbf{n}$ and $\mathbf{s}$ are unit vectors in the direction of emission and of polarization of the emitted quantum, $k_n \hbar$ the momentum of the scattered electron, and ψ_i, ψ_f are the initial and final wave functions of the electron.

If the frequency of the radiation is not too great the retardation term $\exp\{-2\pi i \nu \mathbf{n} \cdot \mathbf{r}/c\}$ will be close to unity for those values of $\mathbf{r}$ for which the other terms occurring in the integral are appreciable. Replacing $\exp\{-2\pi i \nu \mathbf{n} \cdot \mathbf{r}/c\}$ by unity and using the relation

$$\int \psi_f^* \nabla \psi_i d\tau = (4\pi^2 m v / \hbar) \int \psi_f^* \mathbf{r} \psi_i d\tau$$

gives

$$I_\nu(\theta, \phi; \vartheta, \phi') = (\nu^3 k_n^2 / \hbar c^3) |\mathbf{s} \cdot \mathbf{M}|^2, \quad (13)$$

where

$$\mathbf{M} = e \int \psi_f^* \mathbf{r} \psi_i d\tau. \quad (14)$$

This reduces the formula to a form which is the extension of that given in (2) for free-bound transitions. In (14), however, both ψ_i and ψ_f represent states of positive energy and are normalized so as to have the asymptotic form (5).

Summing (13) over both directions of polarization for a fixed direction of the vector $\mathbf{n}$ gives, for the differential cross-section for a collision in which a quantum is emitted in the direction making an angle between ϑ and $\vartheta + d\vartheta$ with the direction of the incident electron, which is taken as that of the x -axis,

$$I_\nu(\theta, \phi; \vartheta) \sin \vartheta d\vartheta d\omega$$

$$= (2\pi \nu^3 k_n^2 / \hbar c^3) \{ |M_x|^2 \sin^2 \vartheta + \frac{1}{2} (|M_y|^2 + |M_z|^2) (1 + \cos^2 \vartheta) \} \sin \vartheta d\vartheta d\omega, \quad (15)$$

M_x, M_y, M_z being the rectangular component of the vector $\mathbf{M}$.

Free-free transitions in the fields of neutral atoms are of interest in connexion with the inverse process—absorption of light by an electron of positive energy in the neighbourhood of an atom. This is an important absorption mechanism in stellar atmospheres. The most important practical examples of free-free transitions are those which give rise to continuous X-radiation.

3.2. Free-free transitions in the fields of neutral atoms

In § 2.4 it was pointed out that absorption by negative ions of hydrogen plays a vital role in determining the quality of the solar emission spectrum in the wave-length range from 4,000 to 12,000 Å. It was found, however, that a further source of absorption must become dominant at wave-lengths above 12,000 Å. This has been identified as due to free-free transitions of electrons in the fields of hydrogen atoms. The first

calculations of these contributions to the continuous absorption coefficient, made by Wheeler and Wildt,[†] have been refined by Chandrasekhar and Breen[‡]. These improved calculations extend the good agreement between the theoretical and observed absorption coefficients of the solar photosphere up to the longest wave-lengths observed (see Fig. 160). From these calculations the cross-sections for the inverse process of radiative emission may be derived, but little interest attaches to them in view of the difficulty of any experimental verification.

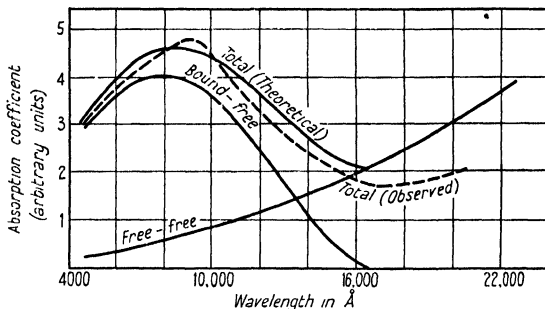


FIG. 160. Illustrating the contributions to the solar absorption coefficient of bound-free and free-free absorption processes for electrons in the fields of neutral hydrogen atoms.

Full line curves calculated on the assumption of a photospheric temperature of $6,300^{\circ}\text{K}$.

----- values for the total absorption coefficient derived from the observations of Chalonge, Kourganoff, and Peltey.[§]

A theoretical survey of the possible forms taken by the cross-sections for emission of *bremsstrahlung* by electrons in encounters with neutral atoms has been given by Nedelsky^{||} using the same approximate representation of the atomic fields as did Allis and Morse in their theory of elastic scattering (see Chap. III, § 2.35).

3.3. The experimental study of continuous X-radiation

The continuous spectrum of X-radiation is of great practical importance and its properties have been studied over a long period by many investigators. Most of the measurements have involved the use of thick targets, however, and although they may be of considerable practical importance, they shed little light on the fundamental process involved because of the complexity of the phenomena associated with the passage of the electron beam through the target material.

[†] *Ap. J.* **95** (1942), 281.

[§] *C.R. Acad. Sci.* **223** (1946), 272.

[‡] *Ibid.* **104** (1946), 432.

^{||} *Phys. Rev.* **42** (1932), 641.

Reliable measurements of the continuous X-radiation from a thin target are few and there remains considerable scope for work in this field. Problems which have been the subject of investigation in such experiments are:

- (a) the measurement of the distribution of intensity in the continuous X-ray spectrum excited by homogeneous electrons;
- (b) the variation with electron energy of the intensity of continuous X-radiation in a definite frequency range (thin target X-ray isochromat);
- (c) the dependence of X-ray continuous spectrum intensity on atomic number of the target material;
- (d) the degree of polarization of the emitted X-radiation, and its variation with frequency and electron energy; and
- (e) the variation of intensity of the emitted radiation with direction of emission relative to the direction of the incident electron beam and the dependence of this directional distribution on frequency and electron energy.

3.31. *Experimental arrangements.* The type of arrangement used for the study of the intensity of the continuous X-radiation from thin targets is shown in Fig. 161. This is the apparatus used by Harworth and Kirkpatrick† for thin targets of nickel.

A very similar arrangement has been used to study characteristic radiation from thin targets in the experiments of Webster and his colleagues (see Chap. II, § 3.1).

The target T , consisting of a film of nickel about 200 Å thick formed by evaporation on a cellulose acetate backing foil, was mounted inside a hollow aluminium cylinder C which screened the fragile target from the destructive effects of bursts of gas in the apparatus. Electrons from the cathode K were focused through a hole in the anode A and fell on the target. By means of a small bias voltage applied between the filament and shield of the cathode, the focal spot on the target could be maintained about 1 cm. in diameter for all accelerating potentials. The position of the cathode was adjustable by means of the sylphon bellows B .

The X-rays passed out through the window W and were collimated by means of the slit S so that a beam was selected making an angle of 93.5° with the direction of the cathode rays. The intensity of the beam was measured by means of the ionization chamber I . The length of exposure was defined by the clock-controlled shutter D . Before entering the argon-filled ionization chamber the X-rays passed through filters F .

† Ibid. **62** (1942), 334.

First an iron filter was used to absorb selectively the Ni K radiation from the target. In order to select a narrow frequency range of the continuous spectrum of reasonable intensity, Ross's method of balanced filters was used. The principle of this method has been described in Chap. II, § 3.2.

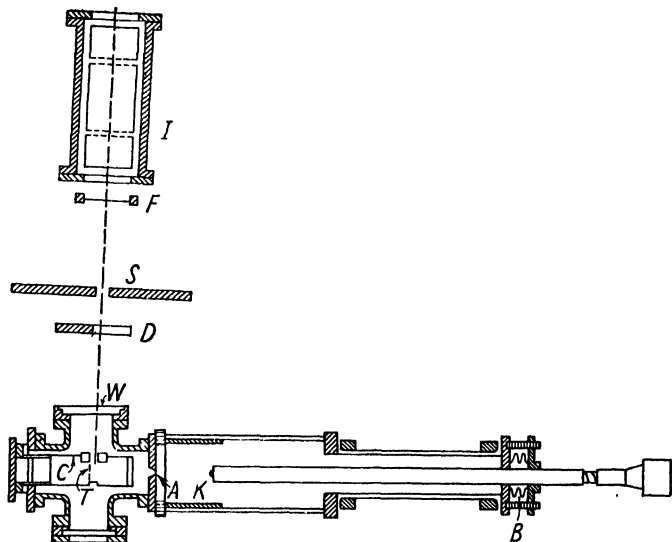


FIG. 161. Apparatus of Harworth and Kirkpatrick for studying the X-ray continuous spectrum from thin targets.

Balanced filters of Ag and Pd selected a small band of wave-lengths near $0.497 \text{ \AA}$, while another pair of Se and As filters selected a narrow band near $1.01 \text{ \AA}$. After a series of measurements the effect of stray radiation not originating at the targets was allowed for by repeating the measurements with the target removed. Under no conditions did this correction exceed 3 per cent. of the thin target intensity.

Corrections were made for the finite thickness of the target using methods similar to those described in Chap. II, § 3.1. The calculated path length of electrons exceeded the target thickness by about 1 per cent. at 50 kV, and by about 8 per cent. at 15 kV.

With this apparatus, relative measurements were made of the intensity of radiation in the bands defined by the Ross filters, for different electron energies. Absolute measurements of these intensities have been made with a similar apparatus by Smick and Kirkpatrick† for nickel and by Clark and Kelly‡ for aluminium.

† *Phys. Rev.* **60** (1941), 162.

‡ *Ibid.* **59** (1941), 220.

A similar type of arrangement was used much earlier for similar measurements with aluminium by Kulenkampff,[†] using as target an aluminium foil about 6,000 Å thick. For a target of this thickness true thin target conditions are not obtained. In Kulenkampff's arrangement the angle between the emitted X-ray beam and the direction of the incident electrons could be varied in order to study the angular distribution of the emitted X-radiation.

The excitation of the nucleus In^{115} by hard X-rays has been used by several investigators[‡] as a detector of X-radiation of a definite frequency from a thin target. Metastable indium decays to normal indium, with the emission of γ -rays and internal conversion electrons, with a half-life of 4.1 hours. The first activation level from which it can be produced has an excitation energy of 1.04 ± 0.02 MeV and a width of only 4 millivolts. As a result it can be used to study X-rays in an extremely narrow frequency band at 0.0118 Å.

In the experimental arrangement of Miller and Waldman[§] a foil of gold, thickness 0.02 mm., was placed on one side of a carbon disk thick enough to absorb electrons of about 2 MeV energy. On the other side was mounted a thin indium foil which was water-cooled. X-rays excited in the gold foil on the carbon disk activated the indium. To correct for the excitation by X-rays produced in the carbon a second experiment was carried out without the gold foil. The activity of the indium was measured by a Geiger counter. For electrons of energy above 1 MeV the gold foil acted as a true 'thin target'.

This method is adapted to the measurement of thin target X-ray isochromats for electrons in the energy range 1.04 to 1.42 MeV. At 1.42 MeV a second activation level of In^{115} can be excited so that the measurements at higher energies no longer refer to a single wave-length band.

The degree of polarization of the emitted X-radiation has been studied by Piston^{||} and by Boardman^{††} using an apparatus shown diagrammatically in Fig. 162.

Electrons from the cathode C were incident on the thin target T . The continuous X-radiation produced passed out through aluminium windows A which were made long in order to give a wide beam of radiation to increase the intensity. The X-rays were incident on a paraffin

[†] *Ann. der Physik*, **87** (1928), 597.

[‡] Collins and Waldman, *Phys. Rev.* **59** (1941), 109; Miller and Waldman, *ibid.* **75** (1949), 425; Korsunsky, Walther, Ivanov, Zypkin, and Ganenko, *J. Phys. U.S.S.R.* **7** (1943), 129.

[§] *Loc. cit.*

^{||} *Phys. Rev.* **49** (1936), 275.

^{††} *Ibid.* **60** (1941), 163.

scatterer S , in the form of a surface of revolution coaxial with the target and cathode of the tube. Radiation scattered through 90° entered the ionization chamber I_2 . In Piston's arrangement the X-rays incident on S made an angle of 105° with the direction of the electron beam.

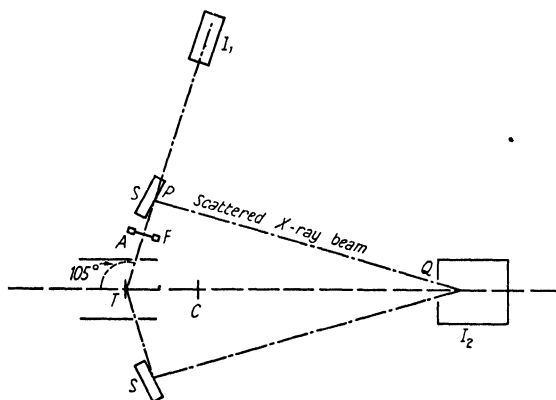


FIG. 162. Illustrating Piston's apparatus for studying polarization of the X-ray continuous radiation.

A narrow band of wave-length about $0.18 \text{ \AA}$ was selected by interposing balanced filters F , of Ta and W, between the window A and the scatterer S . The intensity of the X-radiation in this band was monitored by allowing some to pass through a small hole in the scatterer S into the ionization chamber I_1 . If X and Y are respectively the fractions of the radiation polarized with electric vector parallel and perpendicular to the direction of the scattered X-ray beam PQ , the intensity measured by I_1 is proportional to $X+Y$, that measured by I_2 is proportional to Y . The degree of polarization, P , of the radiation emitted in the direction AI_1 is given by†

$$P = \frac{X-Y}{X+Y} = 1 - \frac{2Y}{X+Y}.$$

This can be written $1 - mI_2/I_1$, where I_1 and I_2 are the ionization currents measured by the two chambers and m is a constant. The polarization could clearly be determined absolutely by using the same chamber for the measurement of Y and $X+Y$. However, such a measurement is made difficult for thin targets because of the low intensities involved.

† The quantity of physical interest is the degree of polarization of the radiation emitted at right angles to the direction of the electron beam. Geometrical considerations prevented its direct measurement, but it can be deduced from the measurements of the polarization in a direction making an angle of 105° with the incident beam.

For a thick aluminium target an absolute determination of the polarization has been made by Cheng. Piston substituted a thick aluminium target for his thin foils and used the results of Cheng's† measurements to determine the constant m .

Corrections had to be made for the finite size of target, window, and scatterer, as a result of which the angle of scattering varied between 87° and 93° . Corrections had also to be made for the finite thickness of the targets. As a result of scattering in such targets, the electrons will not all be moving parallel to the direction of incidence when they undergo radiative collisions and this will reduce the degree of polarization to be expected.

Piston used an aluminium target $7,000 \text{ \AA}$ thick and a silver target $1,700 \text{ \AA}$ thick, and electrons of energy 70 to 120 keV. Under these conditions the most probable angle of deflexion for electrons in the Al target was 6° – 11° and in the Ag target 12° – 22° . Similar measurements were made by Boardman using targets of Ni, Ag, and Pb less than $1,000 \text{ \AA}$ thick. Polarization measurements were also made earlier by Kulenkampff‡ with the aluminium foil $6,000 \text{ \AA}$ thick.

3.4. *Calculated intensity of emission of the continuous X-ray spectrum*

The formulae (11)–(15) have been applied to the problem of emission of continuous X-radiation by several authors.§ In most cases the screening by the electrons of the Coulomb field of the nucleus has been neglected. Under the conditions of most of the experiments this is certainly justified for the radiation near the high-frequency limit. In this case most of the radiative scattering will occur when the electrons are inside the K -shell. With this assumption ψ_i and ψ_f are the appropriate wave functions for electrons with positive energy in the Coulomb field of a nucleus of atomic number Z . The quantities M_x , M_y , M_z have been evaluated, using these functions, by Sommerfeld and his collaborators.

An alternative approximate method, introduced by Sauter,|| is to use for the functions ψ_i , ψ_f those given by Born's approximation (see Chap. III, § 2.43) for the motion of the electron in the Coulomb field. This method, which is valid when $2\pi Ze^2/hv \ll 1$, v being the velocity of the electron after the emission of *bremsstrahlung*, has the advantage that it provides a simpler expression for the radiant intensity and can be

† *Phys. Rev.* **46** (1934), 243.

‡ *Phys. Zeits.* **30** (1929), 513.

§ Sommerfeld, *Ann. der Physik*, **11** (1931), 257; Scherzer, *ibid.* **13** (1932), 137; Sommerfeld and Maue, *ibid.* **23** (1935), 589; Elwert, *ibid.* **34** (1939), 178; Weinstock, *Phys. Rev.* **61** (1942), 584; Kirkpatrick and Wiedmann, *ibid.* **67** (1945), 321.

|| *Ann. der Physik*, **18** (1933), 486; **20** (1934), 404.

extended without difficulty to allow approximately for screening by the atomic electrons. It will not give accurate results near the high-frequency limit.

The effect of the retardation term, omitted in obtaining (14), has been considered by Sauter.† It introduces a correction of the same order of magnitude as that due to relativity and has an important influence on the directional distribution of the emitted quanta.

For the study of X-radiation the relevant cross-section is that,

$$I(\vartheta, \nu) \sin \vartheta \, d\vartheta d\nu,$$

for emission of a quantum of frequency between ν and $\nu + d\nu$ in a direction making an angle between ϑ and $\vartheta + d\vartheta$ with the direction of the incident electron beam. To obtain this, an integration must be carried out over all directions of the scattering of the electron.

$$\text{Writing} \quad L_x^2 = \int_0^{2\pi} \int_0^\pi |M_x|^2 \sin \theta \, d\theta d\phi, \text{ etc.}, \quad (16)$$

we have $I(\vartheta) = (2\pi\nu^3 k_n^2 / \hbar c^3) \{L_x^2 \sin^2 \vartheta + \frac{1}{2}(L_y^2 + L_z^2)(1 + \cos^2 \vartheta)\}$

or, writing

$$I_{x,y,z} = (2\pi\nu^3 k_n^2 / \hbar c^3) L_{x,y,z}^2, \\ I(\vartheta) = I_x \sin^2 \vartheta + \frac{1}{2}(I_y + I_z)(1 + \cos^2 \vartheta). \quad (17)$$

The evaluation of the integrals (16) is a lengthy process since it has not been found possible to obtain a closed formula for $|M_x^2|$. However, these integrations have been carried out numerically in a number of cases from Sommerfeld's data for M_x , M_y , and M_z by Elwert,† Weinstock,† and by Kirkpatrick and Wiedmann.†

It is found that the quantities $I_{x,y,z}$, which determine the total intensity emitted per unit frequency range in the X-ray spectrum, are functions of V_0/Z^2 and ν/ν_0 only, so long as only the scattering by a true Coulomb field is considered and no account taken of screening. If screening is allowed for by Sauter's method, it is found that Z occurs in other combinations than the ratio V_0/Z^2 , but this is only of importance in the long-wave limit of the spectrum.

Using the exact Sommerfeld formulae, Kirkpatrick and Wiedmann† calculated $I_{x,y,z}$ for a large number of values of V_0/Z^2 and ν/ν_0 . Fig. 163 shows their values of I_x and I_y ($= I_z$) at the extreme short-wave limit of the spectrum $\nu/\nu_0 = 1$ as a function of V/Z^2 . Similarly this figure shows also the same quantities calculated at the extreme long-wave limit $\nu/\nu_0 = 0$, using Sauter's method to allow for the effect of screening.

† Loc. cit.

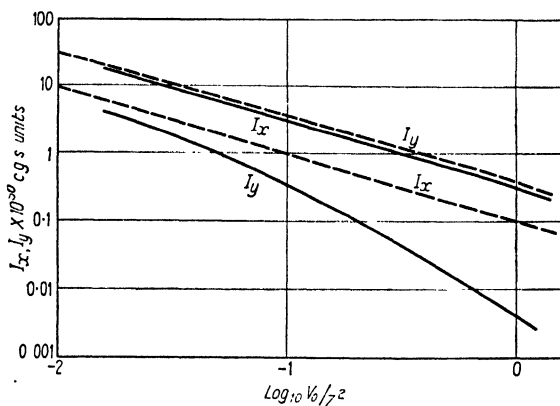


FIG. 163. I_x , I_y calculated as functions of $\log_{10} V_0/Z^2$ (V_0 in e.s.u.). The units of I_x , I_y are ergs per steradian per unit frequency interval per bombarding electron per atom per sq. cm. of target. — — — I_x , I_y at short-wave limit; — — — — I_x , I_y at long-wave limit.

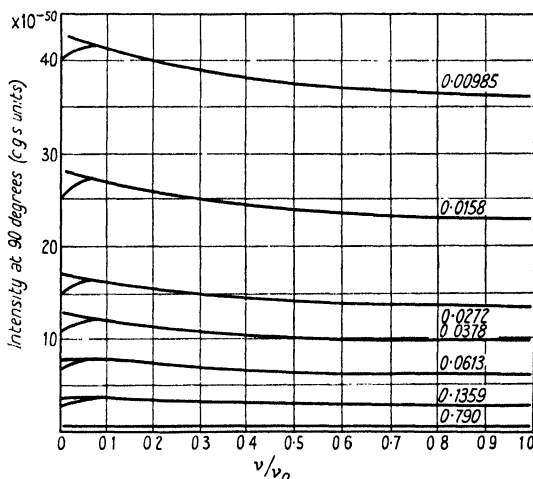


FIG. 164. Intensity emitted at right angles to the incident electron beam as a function of v/v_0 . The numbers on the curves refer to different values of V_0/Z^2 . The units of intensity are as in Fig. 163. The two parts of the curve at low frequencies refer to different values of Z . For $V_0/Z^2 = 0.1359$ the lower and upper curves refer to values of Z of 8 and 25 respectively. For $V_0/Z^2 = 0.00985$ the corresponding values of Z are 58 and 92.

From the exact calculations Kirkpatrick showed that, to a rough approximation, I_x and I_y , for constant v/v_0 , are inversely proportional to V_0/Z^2 , this proportionality being much better in the case of I_x than

of I_ν . I_x is nearly constant for a large range of ν/ν_0 except near the long-wave limit. I_ν decreases with increase of ν/ν_0 .

Using these values of I_x , I_ν Fig. 164 shows the total intensity in ergs per steradian per unit frequency interval per bombarding electron per atom per cm^2 , emitted at 90° to the direction of bombardment, as a function of ν/ν_0 for a number of values of V_0/Z^2 . As pointed out above, at small values of ν/ν_0 , and a given value of V_0/Z^2 , I_x and I_ν depend upon Z . For $V_0/Z^2 = 0.1359$, the lower and upper curves refer to values of Z of 8 and 25 respectively. For $V_0/Z^2 = 0.00985$, the corresponding values of Z are 58 and 92.

3.5. Discussion of results of experiments on the continuous X-ray spectrum

3.51. Distribution of intensity in the X-ray spectrum. As early as 1917 D. L. Webster† suggested that the observed shape of the continuous X-ray spectrum from a thick target could be explained on the assumption that the distribution in intensity from a thin target increased to a sharp maximum at the short-wave-length limit of the spectrum and then decreased with increasing λ like $1/\lambda^2$, i.e.

$$\left. \begin{aligned} I_\lambda d\lambda &= a d\lambda/\lambda^2 & (\lambda > \lambda_0) \\ &= 0 & (\lambda < \lambda_0) \end{aligned} \right\}, \quad (18)$$

or, expressed in terms of a frequency distribution,

$$\left. \begin{aligned} I_\nu d\nu &= b d\nu & (\nu < \nu_0) \\ &= 0 & (\nu > \nu_0) \end{aligned} \right\}, \quad (19)$$

where a and b are constants.

Accurate measurement of the intensity distribution from thin targets is very difficult. The very low intensities preclude the use of a diffraction method for obtaining a spectrum. The only method available is then that of balanced filters, and so far this has been used only to obtain I_ν at two or three points on a distribution. Early experiments by Nicholas‡ appeared to indicate a constant I_ν over a wide range of frequency. The more recent work of Harworth and Kirkpatrick§ using thin nickel targets and radiation in two narrow frequency ranges centred about $0.497 \text{ \AA}$ and $1.010 \text{ \AA}$ indicates that I decreases with increasing frequency.

The theoretical curves of Fig. 164 also show I_ν decreasing with increase

† *Phys. Rev.* **9** (1917), 220.

‡ *Bur. Stand. J. Research*, **2** (1929), 837. Similar results were obtained by Kulenkampf, *Ann. der Physik*, **87** (1928), 597, and Duane, *Proc. Nat. Acad. Sci. U.S.A.* **15** (1929), 805.

§ *Phys. Rev.* **62** (1942), 334.

of ν , but much less rapidly than would be needed to explain Harworth and Kirkpatrick's results (see § 3.53.)

3.52. Absolute intensity in the X-ray spectrum. Two absolute measurements of intensity are available for comparison with the calculations. Smick and Kirkpatrick† measured the absolute intensity of X-radiation in a narrow frequency range of the continuous spectrum centred about $1.431 \text{ \AA}$ at an angle of 88° , using a nickel target of thickness $500 \text{ \AA}$ and 15 kilovolt electrons. Under these conditions $\nu/\nu_0 = 0.575$, $V_0/Z^2 = 0.0637$, where V_0 is expressed in e.s.u. According to the calculations of Fig. 164, the total intensity should be about 6×10^{-50} in the above units, while the measured value was found to be 2.2×10^{-50} in these units. Much better agreement was obtained with the measurements of Clark and Kelly‡ on aluminium using electrons of energy 31.7 keV , a band of continuous spectrum centred about $0.474 \text{ \AA}$, and an angle of observation of 60° . The calculated value in this case comes out at $4.23 \times 10^{-51} \text{ erg}$, etc., as compared with a measured value of $6.17 \times 10^{-51} \text{ erg}$, etc., the estimated error being ± 33 per cent.

3.53. Variation of intensity with electron energy for a definite frequency band. The shape of the variation of intensity with electron energy for a definite frequency band is given fairly well by theory. Thus Fig. 165 shows the curves obtained for nickel by Harworth and Kirkpatrick§ for two frequency bands centred about wave-lengths of $0.497 \text{ \AA}$ and $1.010 \text{ \AA}$ respectively. These curves show that, when the tube potential is increased through the value $V_{\min}$ which is just sufficient to excite the frequency band in question, the intensity rises sharply to a maximum and then decreases, approximately proportional to $1/V_0$, for further increase of the tube potential V_0 .

The broken lines of Fig. 165 show the calculated curves for thin nickel targets. The curve for radiation centred about a wave-length of $0.497 \text{ \AA}$ is arbitrarily adjusted to fit the experimental curve at one point. Then without any further adjustment, the theoretical curve for $1.010 \text{ \AA}$ is as shown. The shape of both curves shows good agreement between theory and experiment, but the relative intensities for the two frequencies are not in very good agreement with theory, as pointed out above (§ 3.51).

Sommerfeld|| has compared similar results obtained by Kulenkampff from an aluminium foil target with theory for a number of different angles of emission. On the whole the agreement is also good in this case except that the observed curves do not continue to increase to a sharp maximum

† Ibid. **60** (1941), 162.

§ Loc. cit.

‡ Ibid. **59** (1941), 220.

|| *Ann. der Physik*, **11** (1931), 257.

when the cathode-ray energy approaches the value corresponding to the critical frequency of the radiation concerned. This, however, is to be expected because Kulenkampff's target was too thick to be regarded as a true thin target.

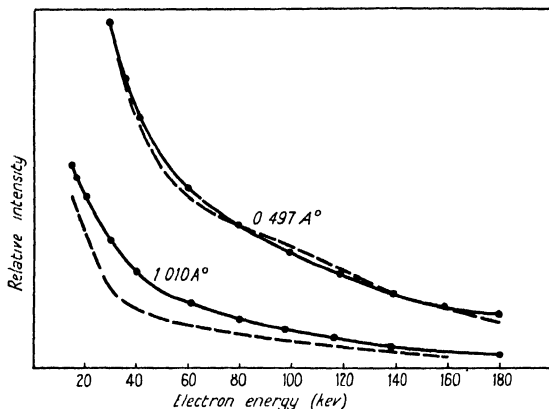


FIG. 165. Intensity of X-ray emission at a given frequency as a function of electron energy for nickel. The minimum energies required to excite the two bands of radiation shown are 12.2 keV and 24.9 keV respectively. ———— observed; - - - - theoretical.

For high-energy electrons experiments have been carried out using indium foil detectors and a very narrow band of X-rays of wave-length $0.0118 \text{ \AA}$ from a thin gold target.† Korsunsky and co-workers found the X-ray intensity to increase with electron energy near the threshold in good agreement with the relativistic calculations of Bethe and Heitler.‡ Miller and Waldman, on the other hand, found the intensity to be almost independent of electron energy. The Bethe-Heitler calculations use Born's approximation which is not expected to be very good for an element as heavy as gold.§ The detailed discussion of phenomena at these energies is outside the scope of this book.

3.54. Dependence on atomic number of target material. For incident electrons of a given energy Fig. 166 shows the expected variation of the total continuous X-ray intensity per unit frequency range emitted in all directions as a function of Z^2 for cathode rays of energy 30 keV and a thin target. The units are the same as for Fig. 163. The curves refer to

† Miller and Waldman, *Phys. Rev.* **75** (1949), 425. Korsunsky, Walther, Ivanov, Zypkin, and Ganenko, *J. Phys. U.S.S.R.* **7** (1943), 129.

‡ *Proc. Roy. Soc. A*, **14** (1934), 83.

§ Guth (*Phys. Rev.* **59** (1941), 325), by applying a correction to the Bethe-Heitler theory, was able to account for an X-ray intensity nearly independent of electron energy.

a number of frequencies of the continuous spectrum. It is clear that the intensity increases roughly with the square of the atomic number.

No measurements are available for thin targets, but a great deal of work has been carried out on the efficiency of production of continuous X-radiation from thick targets of different materials. Beatty showed in

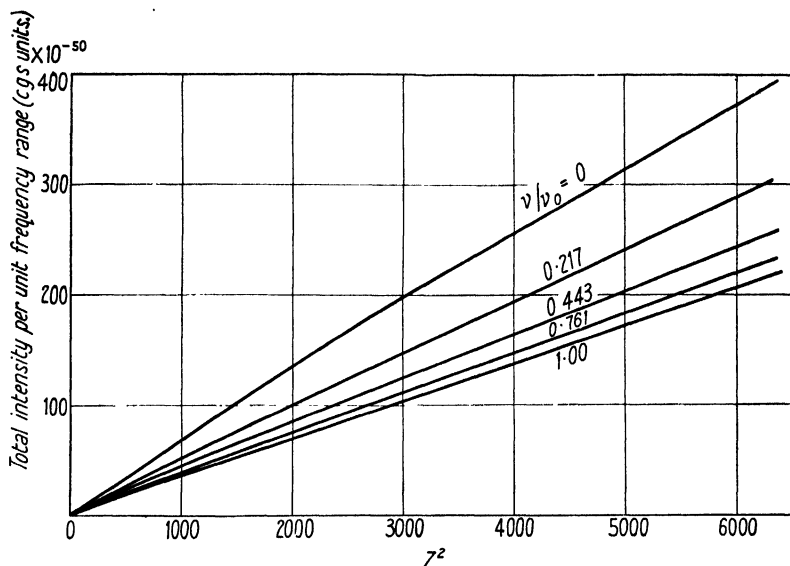


FIG. 166. Calculated variation of the total intensity of continuous X-radiation with Z^2 for electrons of energy 30 keV. The units are as in Fig. 163.

1913† that the total intensity was practically proportional to the atomic number of the target material. Defining the efficiency, η , of X-ray production for a thick target as the ratio of the energy emitted as X-rays to the incident cathode-ray energy, Compton and Allison‡ analysed all the experimental evidence on η and gave a value $1.1 \times 10^{-9} ZV$ as accurate to within about 20 per cent. Here V is the energy in electron volts of the cathode rays incident on the target. Kirkpatrick and Wiedmann have estimated the efficiency of production of continuous X-radiation by thick targets in the following way. They calculated

$$\delta R = h \int_0^{\nu_0} \int_0^{\pi} \nu I(\vartheta, \nu) \sin \vartheta \, d\vartheta \, d\nu,$$

where δR is the total continuous X-ray energy radiated per atom/cm.²

† *Proc. Roy. Soc. A*, **89** (1913), 314.

‡ *X-rays in Theory and Experiment* (Macmillan, London, 1935), p. 90.

for an electron of energy E . Then, following E. J. Williams,[†] they wrote for the total energy loss δE per atom per cm.²

$$\delta E = 5.62Z\beta^{-1.4} \times 10^{-30} \quad \text{for } \beta > 0.50,$$

$$= 4.07PZ\beta^{-2} \times 10^{-31} \quad \text{for } \beta < 0.30,$$

where P is a dimensionless quantity involving the oscillator strengths of the electrons in the atoms of the target material and $\beta = v/c$, v being the electron velocity. An expression for δE for $0.30 < \beta < 0.50$ was obtained by graphical interpolation. The ratio dR/dE is the 'thin target efficiency'. If E_0 is the energy of incidence of the electrons on the target, the 'thick target efficiency', η is given by

$$\eta = \frac{1}{E_0} \int_0^{E_0} \frac{dR}{dE} dE.$$

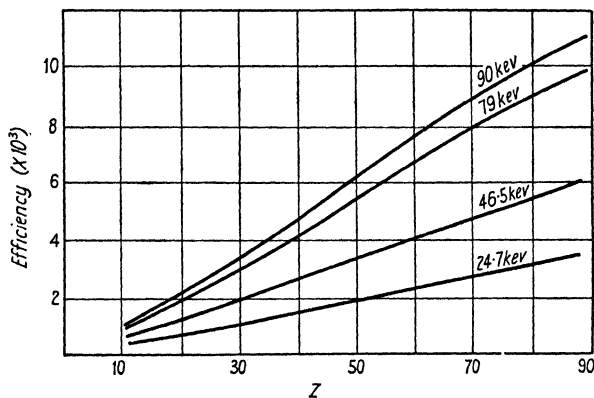


FIG. 167. Calculated 'thick target' efficiencies of X-ray emission as a function of atomic number for a number of different cathode-ray energies.

Fig. 167 shows the calculated thick target efficiencies as a function of atomic number for a number of different cathode-ray energies. It is seen that the efficiency is approximately proportional to the atomic number of the target material and to the energy of the incident cathode ray, in agreement with the experimentally derived formula given by Compton and Allison. However, the theoretical thick target efficiencies are about 20 per cent. greater than those expected from the Compton-Allison formula.

3.55. Polarization of the emitted radiation. If an electron suffers a head-on collision with a target atom so that all the acceleration of the

[†] *Proc. Roy. Soc. A*, **130** (1931), 310.

electron is parallel to its direction of motion, one would expect classically that the radiation emitted at right angles to the direction of incidence would be polarized in the incident direction. On the other hand, for very distant collisions, in which the main component of the acceleration is perpendicular to the direction of motion, it would be expected that the radiation emitted at right angles would be polarized with the electric vector perpendicular to the direction of incidence. For other collisions, in which the acceleration is neither parallel nor perpendicular to the incident direction, the polarization should be incomplete.

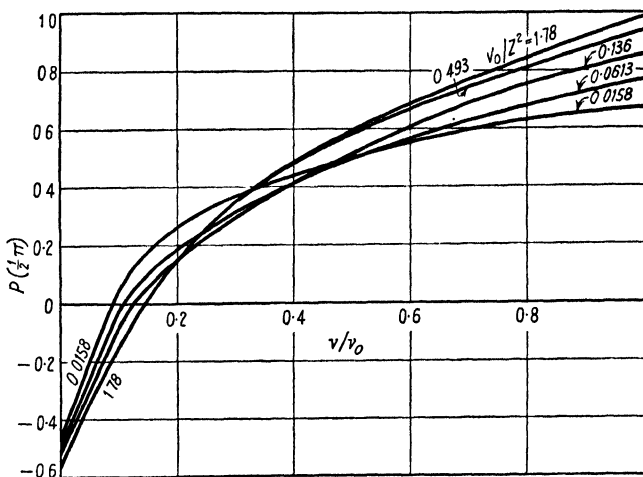


FIG. 168. Calculated degree of polarization $P(\frac{1}{2}\pi)$ of radiation emitted at 90° to the incident electron beam as a function of ν/ν_0 for a number of values of V_0/Z^2 .

Inspection of Fig. 163 shows that the behaviour expected from the quantum theory is somewhat similar. Thus I_x , the component along the direction of incidence, is much more important than I_y at the high-frequency limit where, on the classical picture, one would expect complete polarization, while I_y predominates at the low-frequency limit. According to the quantal calculations the polarization is not complete at either limit.

The degree of polarization at 90° , $P(\frac{1}{2}\pi)$, may be defined by the ratio $(I_x - I_y)/(I_x + I_y)$. Calculated values of $P(\frac{1}{2}\pi)$ as a function of ν/ν_0 are represented in Fig. 168 for a wide variety of values of V_0/Z^2 . At the high-frequency limit the polarization is the more complete the larger the value

of V_0/Z^2 . At the low-frequency limit $P(\frac{1}{2}\pi)$ is always negative, in agreement with the classical picture. Scherzer† investigated the limiting case $V_0/Z^2 = 0$ and showed that in this case $P(\frac{1}{2}\pi)$ should be 0.6 for the entire spectrum. The calculations of Kirkpatrick and Wiedmann seem to be approaching this limiting condition as $V_0/Z^2 \rightarrow 0$.

The early experiments on the polarization gave conflicting results. This seems to have been caused by the use of targets of finite thickness. Thus Dasannacharya,‡ who studied the polarization of radiation emitted from aluminium targets of a range of thicknesses down to 6,000 Å, found the polarization increased as the target was made thinner. This effect arises from the scattering of the cathode rays in the target material so that a great deal of the radiation coming from some depth in the target is produced by electrons that are not moving parallel to the direction of incidence.

As expected, the polarization is not uniform for all frequencies of the emitted radiation. If the lower frequencies are filtered out the measured polarization is increased.

Table V shows the results of the measurements of Piston on the degree of polarization of continuous radiation in the band of wave-lengths from 0.176 Å to 0.184 Å emitted at 105° to the incident direction for targets of Al and Ag and a variety of incident electron energies. The minimum cathode-ray energy required to excite this wave-length band is 69 keV.

TABLE V

Calculated Polarization of X-radiation emitted at 90° to the Direction of the Electron Stream compared with Measurements on Al and Ag

Target material Tube voltage (kV)	Al (7000 Å thick) (Piston)	Al Theoretical (Kirkpatrick and Wiedmann)	Ag (1700 Å thick) (Piston)	Ag Theoretical (Kirkpatrick and Wiedmann)
69	..	..	0.89 ± 0.05	0.92
70	0.95 ± 0.06	0.97	0.83 ± 0.06	0.91
75	0.77 ± 0.10	0.92	0.61 ± 0.06	0.88
80	0.63 ± 0.09	0.90	0.49 ± 0.06	0.78
90	0.60 ± 0.08	0.85	0.39 ± 0.06	0.68
100	0.51 ± 0.07	0.77	0.35 ± 0.06	0.60
120	0.31 ± 0.10	0.60	0.28 ± 0.06	0.54

It is seen from this table that the polarization is practically complete when the cathode-ray energy is such that the wave-length band being studied lies at the short-wave-length limit of the spectrum. As the cathode-ray energy is increased and the wave-length band investigated

† *Ann. der Physik*, **13** (1932), 137.

‡ *Phys. Rev.* **36** (1930), 1675.

moves farther away from the short-wave limit the degree of polarization decreases to quite small values.

The calculations of Kirkpatrick and Wiedmann are compared in Table V with the measurements of Piston. Piston's targets were probably too thick to give true thin target conditions, but it might have been expected that agreement with the theory would be better than is indicated by the table. The observed polarizations are considerably smaller than those calculated except at the high-frequency limit. Some of the discrepancy may be accounted for by the fact that Piston observed his radiation at an angle of 105° with the direction of the cathode-ray beam, but this is quite insufficient to account for all the discrepancy.

Results similar to those of Piston had also been obtained previously by Kulenkampff for a band of longer wave-length ($0.40 \text{ \AA}$) from an aluminium foil $7,000 \text{ \AA}$ thick. Kulenkampff's measurements show a departure from the calculated polarization similar to that shown by the results of Piston.

More recently, Boardman† has investigated the polarization of the X-radiation emitted from thin targets of Ni, Ag, and Pb less than $1,000 \text{ \AA}$ thick in a band centred around $0.180 \text{ \AA}$. For lead, Boardman obtained 0.75 for the degree of polarization at the short-wave limit. The calculated value under these conditions is about 0.70 .

3.56. Directional distribution of the emitted radiation. The non-relativistic theory of the continuous X-ray spectrum takes account only of dipole transitions and predicts an angular distribution of intensity of emitted radiation per unit solid angle at an angle θ of the form

$$I(\theta) = (I_x - I_y)\sin^2\theta + 2I_y,$$

giving a maximum at right angles to the incident radiation. When account is taken of retardation effects (including terms of the first order in $\beta = v/c$, where v is the electron velocity), Sommerfeld‡ showed that a maximum intensity of radiation was to be expected in the forward direction, at an angle Θ with the direction of incidence, where

$$\cos\Theta = 2\beta/(1 - I_y/I_x).$$

A directional distribution of this type was found by Kulenkampff§ and Duane.|| A comprehensive study of the directional distribution of the continuous radiation from a target of magnesium less than $1,000 \text{ \AA}$

† *Phys. Rev.* **60** (1941), 163.

‡ *Ann. der Physik*, **11** (1931), 257.

§ *Ibid.* **87** (1928), 597.

|| *Proc. Nat. Acad. Sci. U.S.A.* **13** (1927), 662; **14** (1928), 450.

thick has been made by Böhm.[†] In these measurements the Ross filter method was employed to isolate a small region of the spectrum. Fig. 169 shows some typical polar curves obtained by Böhm. Fig. 169 (a)

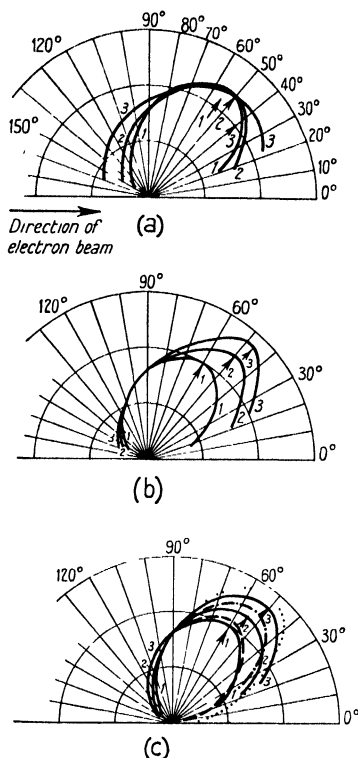


FIG. 169. Directional distribution of continuous X-rays emitted from a thin magnesium target:

(a) electron energy 31 keV: (1) $\lambda = 0.43 \text{ \AA}$, (2) $\lambda = 0.65 \text{ \AA}$, (3) $\lambda = 1.60 \text{ \AA}$;

(b) $\lambda = 0.65 \text{ \AA}$, electron energy: (1) 20 keV, (2) 31 keV, (3) 40 keV;

(c) distribution at high-frequency limit: (1) 20 keV, (2) 31 keV, (3) 40 keV.

Broken curves show the angular distributions calculated from Scherzer's theory. ——— 20 keV; — · — · — 31 keV; · · · · · 40 keV. The arrows show the directions of maximum intensity.

shows the intensity per unit solid angle of the radiation emitted in different directions for a cathode-ray energy of 31 keV and mean wavelengths of $0.43 \text{ \AA}$, $0.65 \text{ \AA}$, and $1.60 \text{ \AA}$. For these three cases the direction of maximum intensity makes angles of 55° , 50° , and 40° respectively with the direction of incidence of the electron beam, indicating that the

[†] *Ann. der Physik*, **33** (1938), 315.

direction of maximum intensity tends to shift towards larger angles as the wave-length decreases.

Fig. 169 (b) shows the intensity distribution for a mean wave-length at 0.65 Å excited by potentials of 20, 31, and 40 kV respectively. As the electron energy increases the maximum moves towards smaller angles.

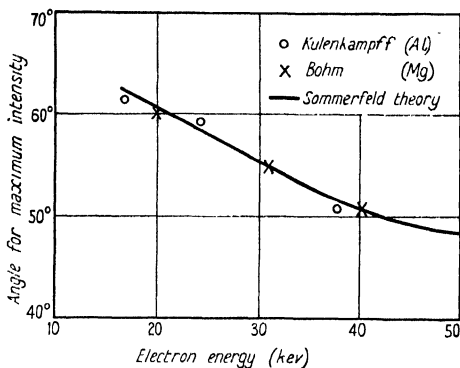


FIG. 170. Illustrating the variation with electron energy of the angle between the direction of the electron beam and that of maximum emission of radiation at the high-frequency limit. Measured values for Al (6,000 Å thick) (Kulenkampff). Measured values for Mg (1,000 Å thick) (Bohm). — — — theoretical curve.

Fig. 169 (c) shows the intensity distribution at the high-frequency limit for potentials of 20 kV, 31 kV, and 40 kV. The broken curves in this figure show the theoretical directional distribution deduced by Scherzer,[†] allowing for relativistic effects. The agreement is seen to be very good in this case. It is clear that the curves of Fig. 169 (c) pass through zero for angles of 0° and 180°. This does not appear to be the case for wave-lengths away from the high-frequency limit.

The remarkable agreement between the experiments and the theory at the high-frequency limit is shown in Fig. 170, where the angle of maximum intensity at the high-energy limit is compared with Sommerfeld's theory. Fig. 170 includes also Kulenkampff's[‡] measurements using an Al foil, 6,000 Å thick. At long wave-lengths, however, the calculated direction of maximum intensity comes out smaller than that observed.

It is clear that the amount of observational data on the continuous X-ray spectrum is still rather meagre and many more measurements are needed under true thin target conditions. The agreement between the non-relativistic theory and the data available, although qualitatively reasonable, is not yet good in quantitative detail.

[†] Ibid. 13 (1932), 137.

[‡] Loc. cit.

VII

COLLISIONS BETWEEN ATOMS UNDER GAS-KINETIC CONDITIONS

1. Introduction—Classification of possibilities

WE now begin the consideration of impact phenomena in which both colliding systems are of atomic mass. In dealing with electron impacts it was convenient to discuss the investigation of collisions involving electrons of homogeneous energy before going on to consider phenomena in which electron swarms are concerned. We adopt the opposite order for atomic collisions. This is largely because the experimental study of collisions involving ions or neutral molecules of homogeneous velocity is much more difficult than for electrons. There is also the advantage of having available the highly developed gas-kinetic theory.

A wide variety of phenomena can be classified within the heading of this chapter. Collisions between atomic or molecular systems include a number of additional possibilities which do not arise in electron impacts. In general we still have the distinction between elastic and inelastic collisions according as energy is or is not exchanged between the relative translational motion and internal motion of either or both colliding systems. If it is not, then the collision is elastic, otherwise inelastic.

Inelastic collisions between atoms or molecules may involve a change of the electronic, vibrational, and/or rotational states of either or both colliding systems. The latter possibility, that the internal motion of both may change, does not occur with electron impacts.

We may classify the possibilities according to the scheme in Table I. The colliding systems are denoted by A and B or, if the molecular character needs to be emphasized, by AC and BD . Electronic excitation is denoted by a ' as in A' , that of vibration and/or rotation by a *, and the change of kinetic energy of relative translation, or energy discrepancy, by ΔE . The physical phenomena in which the particular kind of collision is important under gas-kinetic conditions are also listed in the table. It will be appreciated that this can only be so if the kinetic energy of relative motion is increased by the collision, or if it is decreased by an amount comparable with the temperature energy $\frac{3}{2}\kappa T$.

There is one point about the classification which might be raised. If in the transfer collisions (f) or (h) the translational energy change is zero, should they be regarded as elastic or inelastic? If the atoms A and

B are identical there is no means of determining experimentally whether there has been any transfer of excitation or of charge. It is strictly correct, then, to consider the transfer processes as contributing to the elastic collisions. In dealing, for example, with the diffusion of meta-stable He atoms or of He⁺ in He this must be allowed for (see §§ 6.5, 6.7). If the atoms are not identical but isotopic the energy discrepancy may be very small, but it is finite and the process is observable. In this case it is best to consider the process as it really is, an inelastic one.

TABLE I

Summary of Atomic and Molecular Collision Processes

General nature of collision	Detailed description	Symbolic representation	Examples of physical phenomena in which effective
Elastic		$A + B \rightarrow A + B$ (a)	Viscosity, diffusion and thermal diffusion of gases. Mobility of positive ions in gases
Inelastic, in which one colliding system does not change its state of internal motion	Electronic excitation	$A + B \rightarrow A + B' + \Delta E$ (b)	Deactivation of metastable atoms by atom impact
	Ionization	$A + B \rightarrow A + B^+ + e$ (c)	
	Excitation of vibration and/or rotation	$A + BD \rightarrow A + BD^* + \Delta E$ (d)	Dispersion of high-frequency sound. Rate of unimolecular reactions
	Electronic and vibrational excitation	$A + BD \rightarrow A + BD^* + \Delta E$ (e)	
	Transfer of electronic excitation	$A' + B \rightarrow A + B' + \Delta E$ (f)	Quenching of resonance fluorescence. Sensitized fluorescence
		$A' + B \rightarrow A + B' + e + \Delta E$ (g)	Excitation of spark lines by foreign gases
Inelastic, in which both colliding systems change their state of internal motion	Charge transfer	$A^+ + B \rightarrow A + B^+ + \Delta E$ (h)	
		$A^+ + B \rightarrow A + B^+ + \Delta E$ (i)	Excitation of spark lines by foreign gases
		$A^+ + B^- \rightarrow A' + B' + \Delta E$ (j)	Mutual neutralization of positive and negative ions
	Transfer of vibration or rotation	$AC^* + BD \rightarrow AC + BD^* + \Delta E$ (k)	
	Interchange of electronic and vibrational excitation	$AC'' + BD \rightarrow AC + BD^* + \Delta E$ (l)	Photochemical phenomena
		$A' + BD \rightarrow A + B + D + \Delta E$ (m)	Photochemical phenomena
		$A' + B' \rightarrow AB^+ + e + \Delta E$ (n)	Photo-ionization. The inverse process is one of electron ion recombination
	Atomic rearrangement collisions	$AC + BD \rightarrow AB + CD$ (p)	Chemical reactions

We now proceed to separate discussion of the different physical phenomena in their relation to the particular collision processes. For reasons of space we must exclude from consideration all chemical reactions of the atomic rearrangement type. Reference may be made to chemical text-books, such as *The Theory of Rate Processes* by Eyring, Laidler, and Hirschfelder, for a detailed discussion of these phenomena.

Consideration of processes which can lead to recombination will be deferred to Chapter X. Effects arising from the impact of atoms or molecules, with gas-kinetic velocities, on a surface are discussed in Chap. IX, § 10.

2. General nature of the interaction between atoms

We shall give here a brief summary of the general nature of atomic interactions as indicated from theory as this is important for the interpretation of many collision phenomena with which we are concerned in this chapter.

We consider first two atoms in their ground states with completely filled outer shells, such as two rare gas atoms. At large separations r an attractive interaction,

$$V(r) \sim -C/r^6, \quad (1)$$

exists which is usually known as the van der Waals attraction. This arises from a dynamic polarization of one atom by the other, the electrons tending to revolve in their orbits in the respective atoms in such a relative phase that their average separation over a period of time is as large as possible. Various approximate theoretical methods† have been given for the estimation of C for a given pair of atoms, in terms of such properties as their polarization. These methods are not very accurate, particularly for complex atoms.

The expression (1) is really the first term in an asymptotic series and, as the atoms approach, additional attractive terms varying as r^{-8} , r^{-10} , etc., should be included. It is doubtful how useful the addition of such terms is, because, for values of r at which they are becoming appreciable, the chemical (or intrinsic) forces are also coming into play. These forces are strongly repulsive when the atoms have completely filled outer shells and fall off exponentially with distance. They arise from a combination of direct Coulomb forces, averaged over the charge distribution of the atoms, with forces arising from the exchange of electrons between the atoms‡ (see Chap. IV, § 5.1).

The combination of the van der Waals and chemical forces gives an interaction of the shape illustrated in Fig. 171. Gas-kinetic studies at ordinary temperatures yield information mainly about the depth and shape of the attractive potential where the minimum energy is of the order κT . They can also give information about the slope of the repulsion. Detailed prediction of atomic interactions at separations

† Mott and Sneddon, *Wave Mechanics and its Applications*, Oxford, 1948, § 32.

‡ Ibid., § 33.

effective in gas-kinetic collisions has been confined mainly to the simplest atoms, such as helium, and even then it is not certain how the different contributions to the interaction should be combined at separations near the potential minimum. For trial purposes, in attempting to derive the interaction from experimental results, an interaction of the form

$$\lambda r^{-s} - \mu r^{-t} \quad (2)$$

is often used, the first term representing the chemical repulsion, the second the van der Waals attraction. The four parameters λ , μ , s , and t can then be chosen to give the best agreement with observed data. The repulsive term may be replaced by the exponential form $Ae^{-r/a}$ which receives some justification from the quantum theory of the valence force. Examples of the use of various empirical expressions which give the correct general shape for the interaction will be given below (see §§ 4, 5, 6.4, 6.5).

The only essential modification which is introduced if one of the atoms is replaced by an ion such as Li^+ is the addition of an attraction of the form

$$V \sim -\alpha\epsilon^2/r^4, \quad (3)$$

due to the polarization of the atoms by the ionic charge, α being the polarizability of the atom. α is given in terms of the dielectric constant K of the gas formed by the atoms at N.T.P. by the relation

$$\alpha = (K - 1)/8\pi N, \quad (4)$$

where N is the number, 2.7×10^{19} , of atoms per c.c. under these conditions. Some uncertainty arises in these cases as to when the polarization saturates, i.e. at what values of r the interaction (3) ceases to increase as r is reduced. If this does not occur before the chemical repulsion dominates the situation there is no difficulty but, if the polarization saturates at greater distances, the addition of the term (3) may seriously overestimate the depth of the potential minimum.

Attractive chemical forces do not usually arise in gas-kinetic collision studies as these are rarely concerned with unsaturated systems. They do play an important part, however, in phenomena determined by the interaction of an atom with an ion, or excited atom, of its own kind, e.g.

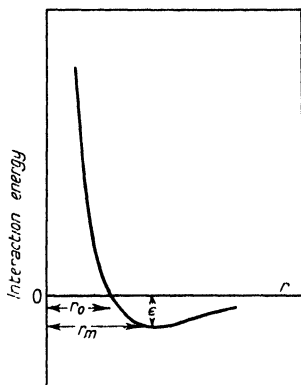


FIG. 171. Variation of the interaction energy with distance r between two atoms, with filled outer electron shells.

of He with He^+ or of He with He' . In such cases there are two possible interactions, one of which arises when the electron distribution is symmetrical, the other when it is antisymmetrical with respect to the nuclei. These two interactions may be represented for our purposes in the form

$$V = V_0(r) \pm v(r), \quad (5)$$

the alternative signs for $v(r)$ corresponding to the two cases. $V_0(r)$ has much the same form as the interaction between normal atoms. In general $v(r)$ is of such magnitude as to produce, in one of the two cases, an attractive energy of a few electron volts, much greater than that due to the van der Waals forces. For an ion and an atom, both in their ground states, $v(r)$ falls off exponentially with r , though more slowly than the repulsive part of $V_0(r)$. An example is provided by the interactions between H and H^+ illustrated in Chap. IV, Fig. 112. An important instance where this effect must be taken into account is discussed in § 6.52. On the other hand, for a normal and excited atom $v(r)$ falls off as r^{-p} if the transition from the excited to the ground state is associated with an electric $(p-1)$ -pole moment. Thus for a normal He atom and one in a p state $v(r)$ falls off as r^{-3} , both interactions being thus of very long range. If the transition is associated with no moment, i.e. is of $s-s$ type, $v(r)$ again falls off exponentially though more slowly than $V_0(r)$. The same applies if the transition involves electron exchange between the two atoms, e.g. in the interaction between a normal and a metastable helium atom in the 2^3S state (see § 6.7). The matter is further discussed in § 7.4, in which the existence of the two interactions is related to the phenomena of transfer of excitation or of charge on collision between a normal and excited atom.

The above considerations apply strictly only if one of the atoms or ions concerned possesses a completely filled outer shell of electrons. In all the cases which we shall be discussing below this condition is fulfilled. If it is not, more possibilities arise than we have discussed above, including in particular the occurrence of attractive chemical forces between neutral atoms.

3. Elastic collisions of gas atoms—General discussion

3.1. *Cross-sections effective in scattering, viscosity, and diffusion*

The definitions of total and differential elastic collision cross-sections given in Chap. I, § 2, for electron impacts apply equally well to collisions between atoms or molecules. It is necessary only to allow for the fact that the colliding systems are now of comparable mass. The motion of the centre of mass must be separated out so that the angle of scattering

θ is the angle the direction of relative motion is turned through by the collision.

In dealing with electron collisions we introduced, in addition to the differential and total cross-sections $I(\theta)$ and Q_0 , a momentum loss cross-section defined by

$$Q_d = 2\pi \int_0^\pi (1 - \cos \theta) I(\theta) \sin \theta d\theta. \quad (6)$$

This cross-section is the appropriate one for dealing with electron diffusion phenomena. In the same way the diffusion coefficient for a mixture of gases depends on the momentum loss cross-section defined by (6), θ having the same significance as above.

According to the theory of Chapman† and Enskog‡ the coefficient of diffusion is given by

$$D = \frac{3\pi^{\frac{1}{2}}}{16(n_1 + n_2)P_{12}} \left\{ \frac{2(M_1 + M_2)}{M_1 M_2} \kappa T \right\}^{\frac{1}{2}} (1 - \epsilon_0)^{-1}, \quad (7)$$

where
$$P_{12} = 2 \int_0^\infty v^5 Q_d(1, 2) \exp\left\{-\frac{1}{2} \kappa T (M_1 + M_2) v^2\right\} dv. \quad (8)$$

M_1, M_2 are the masses of the atoms of the respective gases, and n_1, n_2 their concentrations in number of atoms/c.c. $Q_d(1, 2)$ is the cross-section (6) for collision of an atom of each kind with relative velocity v . T is the absolute temperature. ϵ_0 is a correction depending on the nature of the collisions and the concentrations n_1, n_2 . It is never greater than 0.136 and can generally be ignored.

If the diffusion cross-section is constant or is replaced by a suitable mean value $\bar{Q}_d$ the formula (7) gives

$$D = \frac{3}{8} \left(\frac{\pi \kappa T (M_1 + M_2)}{2 M_1 M_2} \right)^{\frac{1}{2}} \frac{1}{(n_1 + n_2) \bar{Q}_d}.$$

Since the mean relative velocity of two gas molecules is given by

$$\bar{v} = \left[\frac{8 \kappa T (M_1 + M_2)}{\pi M_1 M_2} \right]^{\frac{1}{2}}$$

we have

$$D = \frac{3\pi}{32} \frac{\bar{v}}{(n_1 + n_2) \bar{Q}_d}.$$

When $n_1 = n_2$, as for diffusion of electrons in a gas, we have

$$D = \frac{3\pi}{32} \frac{\bar{v}}{n_2 \bar{Q}_d} \simeq \frac{\bar{v}}{3n_2 \bar{Q}_d},$$

which is the expression used in Chap. II, § 5.2.

† *Phil. Trans. A*, **216** (1916), 279; **217** (1916), 115.

‡ *Inaug. Diss.* (Upsala, 1917).

The mobility k of an ion in a pure gas at specified temperature and pressure is given by the relation

$$k = eD/\kappa T, \quad (9)$$

where D is given by the formula (7). It is thus determined, as for electrons, by the momentum loss cross-section for collisions between an ion and a gas atom. Standard conditions for specifying the mobility are usually taken as atmospheric pressure and a temperature of 18°C .

The phenomenon of thermal diffusion† is rather more complicated and depends not only on the cross-section for collisions between dissimilar atoms but also on those $Q_d(1, 1)$, $Q_d(2, 2)$ for atoms of the same kind.

A further cross-section Q_μ arises in the theory of the viscosity μ and heat conductivity σ of gases.‡ According to the theory of Chapman§ and Enskog|| the coefficient of viscosity μ of a gas at temperature T is given by

$$\mu = \frac{10\kappa^3 T^3}{M^2} \left(\frac{4\pi\kappa T}{M} \right)^{\frac{3}{2}} \frac{1+\epsilon}{\pi R_{11}}, \quad (10)$$

where M is the mass of a gas atom and ϵ is a correction which is never greater than 0.017. R_{11} is given by

$$R_{11} = \frac{1}{2} \int_0^\infty v^2 Q_\mu \exp\{-Mv^2/4\kappa T\} dv,$$

where

$$Q_\mu = 2\pi \int_0^\pi I(\theta) \sin^3\theta d\theta. \quad (11)$$

This cross-section gives greater weight to large angle deviations than Q_d , as would be expected from the following considerations. The greater the rate at which energy is equalized by sharing in collisions the smaller the viscosity and heat conductivity. If energy is equalized after impact of two similar molecules the angle of scattering is 90° . Collisions for which $\theta \simeq 90^\circ$ are therefore more effective in stifling conductivity than any others. Hence the weighting by $\sin^2\theta$ in (11). On the other hand, diffusion is most retarded by collisions in which back scattering occurs, i.e. $\theta \simeq 180^\circ$. This is allowed for in (6) by the weighting factor $\sin^2 \frac{1}{2}\theta$.

Even with an extended range of interaction between gas atoms the cross-sections Q_d and Q_μ have finite values on the classical as well as on the quantum theory. This is because of the reduced emphasis on small

† Chapman, *Phil. Trans. A*, **217** (1916), 115.

‡ These are connected, for monatomic gases, by the relation

$$\sigma = (1+\delta) \frac{5}{2} c_v \mu \quad (12)$$

where δ is a small correcting term and c_v is the specific heat at constant volume (see Kennard, *Kinetic Theory of Gases*, McGraw-Hill, New York, 1938, p. 179).

§ *Phil. Trans. A*, **216** (1916), 279; **217** (1916), 115.

|| Inaug. Diss. (Upsala, 1917).

angle deviations. In most gas-kinetic phenomena classical methods give results of sufficient accuracy in the theory of viscosity and diffusion. The only exceptions are the lightest gases at very low temperatures. On the other hand, the total elastic cross-section Q_0 is *never* given correctly on classical theory. For an extended range of interaction it gives an infinite value whereas the quantum theory normally gives a finite value. Even for rigid spherical atoms of radius $\frac{1}{2}a$ for which the classical value of Q_0 is πa^2 , the quantum theory gives a different value for *all* velocities of relative motion. Thus for all collisions between atoms Q_0 can only be calculated from quantum theory. We shall now examine these questions in a little more detail.

3.2. Quantal and classical cross-sections for rigid spherical atoms

The collision between two rigid spherical atoms of radius $\frac{1}{2}a$ and of mass M may be regarded in the same way as the collision of a particle of mass $\frac{1}{2}M$ with an infinitely massive rigid spherical obstacle of radius a . For such a collision the interaction energy is given by

$$\left. \begin{aligned} V &= 0 & (r > a) \\ &\rightarrow \infty & (r \leq a) \end{aligned} \right\} \quad (13)$$

The classical cross-section is πa^2 . The quantal formula is the same as that given in Chap. III, § 2.21:

$$Q_0 = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l. \quad (14)$$

The wave number $k = \frac{1}{2}Mv/\hbar$, where v is the relative velocity of the colliding atoms. η_l is the phase shift produced in the de Broglie waves for the relative motion associated with angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$.

The discussion of the formula (14) follows on similar lines to that of Chap. III, § 2.22. We first suppose that the relative velocity is so low that ka is very small. Under these conditions those waves for which $l > 0$ will hardly be affected by the inaccessible region $r < a$. The wave with $l = 0$ is a sine wave which, because of this inaccessibility, must vanish at $r = a$ instead of at $r = 0$, i.e. a phase change $\eta_0 = -ka$ is produced. Hence, in the limit $k \rightarrow 0$,

$$\begin{aligned} Q_0 &\rightarrow \frac{4\pi}{k^2} k^2 a^2 \\ &= 4\pi a^2, \end{aligned} \quad (15)$$

four times the classical value.

A difference between classical and quantal values is to be expected

when the wave-length λ is long compared with the dimensions of the scattering obstacle. However, it is not difficult to show that, even in the limit of very short wave-lengths, the quantum value does not tend to πa^2 but to twice that value.

If λ is large all the phase shifts η_l for which $ka > l$ will be large. We may break up the sum in (14) into two parts so that

$$Q_0 = \frac{4\pi}{k^2} \left(\left| \sum_{l=0}^{l_0} + \sum_{l_0}^{\infty} \right| \right) (2l+1) \sin^2 \eta_l, \quad (16)$$

with $l_0 \simeq ka$. The second sum may be neglected because the phases η_l are very small for $ka < l_0$. In the first, $\sin^2 \eta_l$ will fluctuate rapidly with l as, for $l < l_0$, $\eta_l \gg \pi$. It is therefore a good approximation to replace $\sin^2 \eta_l$ by its mean value of $\frac{1}{2}$ and write

$$\begin{aligned} Q_0 &\simeq \frac{1}{2} \frac{4\pi}{k^2} \sum_{l=0}^{l_0} (2l+1) \\ &\simeq 2\pi l_0^2 / k^2 \\ &= 2\pi a^2. \end{aligned} \quad (17)$$

A more accurate analysis confirms this result.

In order to analyse the matter further it is instructive to examine, under the same conditions, the difference between the classical and quantum forms for the differential cross-sections. With classical mechanics the probability of scattering per unit solid angle is independent of angle in this case, so that

$$I(\theta) = \frac{1}{4} a^2. \quad (18)$$

The quantum expression for $I(\theta)$ has been given in Chap. III, § 2.41, and is

$$I(\theta) = \frac{1}{4k^2} \left| \sum \{ \exp(2i\eta_l) - 1 \} (2l+1) P_l(\cos \theta) \right|^2. \quad (19)$$

At $\theta = 0$, $P_l(\cos \theta) = 1$ independent of l , so

$$I(0) = \frac{1}{4k^2} \{ \left| \sum (2l+1)(\cos 2\eta_l - 1) \right|^2 + \left| \sum (2l+1) \sin 2\eta_l \right|^2 \}.$$

We may now adopt the same procedure as for Q_0 by summing up to $l = l_0$ and ignoring all higher terms. Furthermore, because of interference, the second sum will be negligible compared with the first: $\sin 2\eta_l$ will fluctuate violently in sign whereas $\cos 2\eta_l - 1$ is one-signed and has a mean value of -1 . This gives

$$I(0) \simeq l_0^4 / 4k^2 = \frac{1}{4} k^2 a^4. \quad (20)$$

This is $k^2 a^2$ times greater than the classical value at that angle, the ratio tending to infinity as $\lambda \rightarrow 0$. The large value arises from the coherence

of the harmonics which all have the same sign at $\theta = 0$ (see Fig. 68, Chap. III).

As θ increases first P_0 and then successively lower-order harmonics change sign and produce interference so that the value of $I(\theta)$ rapidly falls. For large values of θ it may be shown† that the classical expression (17) for $I(\theta)$ holds. As θ decreases this will remain approximately true until the coherence effect becomes pronounced. This can be taken as the

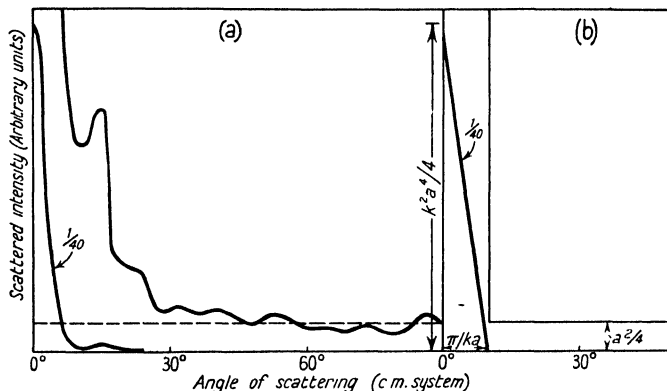


FIG. 172. Angular distribution of scattered atoms for the rigid sphere model ($ku = 20$).

- (a) - - - classical distribution; ——— distribution calculated by quantum theory.
 (b) Schematic angular distribution.

angle for which P_0 has its first zero, i.e. approximately $\pi/l_0 = \pi/ka$. This gives the schematic form of $I(\theta)$, according to quantum theory, which is illustrated in Fig. 172 (b), namely

$$I(\theta) = \frac{1}{4}a^2[k^2a^2 - (k^2a^2 - 1)(ka\theta/\pi)] \quad (\theta < \pi/ka) \\ = \frac{1}{4}a^2 \quad (\theta > \pi/ka) \quad \left. \vphantom{I(\theta)} \right\} \quad (21)$$

With this rough approximation we have, for large ka ,

$$2\pi \int_{\pi/ka}^{\pi} I(\theta) \sin \theta d\theta \simeq \pi a^2, \quad 2\pi \int_0^{\pi/ka} I(\theta) \sin \theta d\theta \simeq \pi a^2,$$

indicating that the doubling of the classical cross-section comes from the increased scattering at small angles. As λ decreases the angular range over which the classical formula is valid increases, but the quantum excess over the classical value at very small angles also increases so that the cross-section remains doubled.

† Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. VII.

A more accurate analysis confirms this description. Fig. 172 (a) illustrates the function $I(\theta)$ calculated by Massey and Mohr† without approximation for the case $ka = 20$, showing that the schematic representation (21) reproduces the main features.

The doubling of the total cross-section by the wave theory was first pointed out by Massey and Mohr† and a detailed discussion in terms of diffraction theory has been given by Wergeland.‡

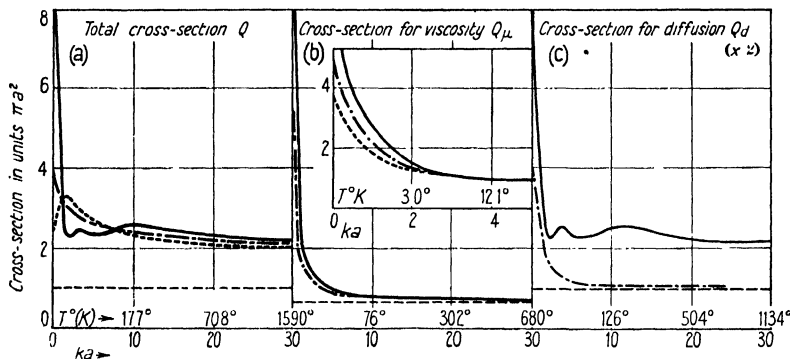


FIG. 173. Cross-sections calculated using the rigid sphere model.

(a) Total collision cross-section, Q .

(b) Cross-section for viscosity, Q_μ .

(c) Cross-section for diffusion, $Q_d (\times 2)$.

----- classical; — quantum theory for dissimilar atoms; — quantum theory for identical atoms obeying the Bose-Einstein statistics. - - - - - quantum theory for identical atoms obeying Fermi-Dirac statistics.

As the diffusion and viscosity cross-sections Q_d and Q_μ attach much less weight to small angle deviations it is not surprising that in the short wave-length limit the quantal and classical formulae for these cross-sections agree. Fig. 173 illustrates the variation of Q , Q_d , and Q_μ with relative velocity according to the quantum theory. The temperature scales indicate the range in which quantum effects are likely to be important for helium. They are calculated for an atomic radius

$$\frac{1}{2}a = 1.05 \text{ \AA}.$$

For Q_μ and Q_d the corresponding relative velocity is that which is most effective in determining viscosity and diffusion phenomena at the temperatures indicated while for Q it is equal to the R.M.S. velocity at the temperature. It will be seen that, below 80° K, the quantum

† *Proc. Roy. Soc. A*, **141** (1933), 434.

‡ *Skrift. Norske Videns. Akad., Oslo, Mat-Nat. Klasse*, 1945, No. 9.

theory must be used. For heavier gases, on the other hand, quantum effects are negligible at temperatures down to the liquefying points.

3.21. The effect of symmetry. In considering collisions of similar atoms a further quantal effect is introduced. This arises from the need to satisfy certain symmetry requirements.† Thus if the atoms obey Bose-Einstein statistics the wave function representing the relative motion must be unchanged when the atoms are interchanged. This requires that, in the formula for the differential cross-section, all harmonics of odd order must be excluded. This will be so for normal helium atoms with nuclei He^4 . On the other hand, for collisions between helium atoms possessing He^3 nuclei, which obey Fermi-Dirac statistics, a different modification is introduced. For this case

$$I(\theta) = \frac{3}{4}I_o(\theta) + \frac{1}{4}I_s(\theta), \quad (22)$$

where I_o includes only the odd-order harmonics, I_s only the even order.

The effect of these symmetry requirements on the cross-sections Q_μ and Q , for the rigid sphere case, is illustrated in Fig. 173.

Halpern and Gwathmey‡ have discussed the modifications introduced in more complicated cases such as collisions between hydrogen molecules.

3.3. Cross-sections for extended range interactions

For actual atoms the interaction energy has not the form (13) but is finite at all finite values of r . As, however, it exhibits a steeply rising repulsion for $r < r_0$ (see Fig. 171), a number of the general conclusions derived from the study of the rigid sphere model remain true. Thus the classical theory may be used for the discussion of viscosity and diffusion except for helium at low temperatures. It is never valid for the determination of total collision cross-sections. In fact with the form (2) for V no classical value exists. The quantum theory predicts an angular distribution of the form (21) where the range a is of the order r_0 . This may be made use of in designing experiments to measure Q as it makes possible an estimate of the angular resolving power required to give a result effectively independent of the geometry of the apparatus (see § 5.12).

3.31. Classical formulae. The classical formula for the differential cross-section is given by

$$I(\theta) d\omega = \frac{p}{\sin \theta} \frac{dp}{d\theta} d\omega, \quad (23)$$

$$\theta = \pi - 2 \int_{r_0}^{\infty} \frac{dr}{r\phi(r)}, \quad (24)$$

† For a detailed discussion see Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, 1949, Chap. V.

‡ *Phys. Rev.* **52** (1937), 944.

where
$$\phi(r) = \left\{ \frac{r^2}{p^2} - 1 - \frac{r^2}{p^2 E} V(r) \right\}^{\frac{1}{2}}. \quad (25)$$

In this form E is the kinetic energy of relative motion before and after the collision, $V(r)$ the interaction energy between the atoms when at a distance r apart, and r_0 is the positive zero of the denominator, or the largest such zero if more than one exists.

A proof of this result is given in *The Theory of Atomic Collisions*, by Mott and Massey, 2nd edition, Chap. VII. The parameter p which occurs is usually referred to as the impact parameter. It is the perpendicular distance from the centre of mass to the asymptote of the initial relative orbit and, in classical theory, bears a single-valued relation to the angle of scattering.

The condition of validity of the classical formula for scattering at an angle θ is best given in terms of an angle

$$\eta_l = \frac{1}{4}\pi + k \left[\frac{1}{2}p\pi - r_0 + \int_{r_0}^{\infty} (pr^{-1}\phi(r) - 1) dr \right], \quad (26)$$

where $l = kp$ and k is the wave number of the relative motion. This is the 'classical approximation' to the phase angle η_l which appears in the quantum scattering formula (19) (see Chap. III, § 2.23 and equation (15)). Let l_0 be the value of l for which

$$\frac{\partial \eta_l}{\partial l} = \frac{1}{2}\theta.$$

Then the formula (23) will be valid for scattering at an angle θ if l_0 and η_{l_0} are both $\gg 1$. This condition is bound to be violated for any value of k and form of $V(r)$ if θ is small enough.

On substitution of (23) in (7) and (10) the classical formulae for the diffusion and viscosity coefficients D and μ become

$$D = \frac{3}{64} \left\{ \frac{\pi}{2} \frac{M_1 M_2}{(M_1 + M_2) \kappa T} \right\}^{-\frac{1}{2}} \frac{(1 - \epsilon_0)^{-1}}{J(n_1 + n_2)}, \quad (27)$$

$$\mu = \frac{5}{8} \left(\frac{M \kappa T}{\pi} \right)^{\frac{1}{2}} \frac{(1 + \epsilon)}{I}, \quad (28)$$

where

$$J = - \int_0^{\infty} \int_0^{\infty} x^2 e^{-x} p \cos^2 \frac{1}{2} \alpha \, dp dx, \quad (29)$$

$$I = - \int_0^{\infty} \int_0^{\infty} x^3 e^{-x} p \sin^2 \alpha \, dp dx, \quad (30)$$

$$\alpha = 2 \int_{r_0}^{\infty} \frac{dr}{r \phi(r)}. \quad (31)$$

3.32. Quantal formulae. When the classical formulae of the last section are not valid the full quantal expression (19) for $I(\theta)$ must be used. If the colliding atoms are similar the appropriate symmetry modifications, as discussed in § 3.21, must also be included. The phases η_l may be calculated, when $V(r)$ is given, by direct numerical or mechanical integration of the Schrödinger equation for the motion, or by various approximate methods. In particular the expression (26) may be used in most gas-kinetic conditions except when the phase is small. For details of the available methods see *The Theory of Atomic Collisions*, by Mott and Massey, Chap. VII.

A formula for the total cross-section Q for gas-kinetic encounters between atoms for which the asymptotic form of the scattering potential $V \sim -Cr^{-s}$ has been given by Massey and Mohr. It is

$$Q = \pi \frac{2s-3}{s-2} f^{2/(s-1)} (4\pi C/hv)^{2/(s-1)}, \quad (32)$$

where v is the velocity of the atoms and

$$\left. \begin{aligned} f(s) &= \frac{s-3}{s-2} \cdot \frac{s-5}{s-4} \cdots \frac{1}{2} \cdot \frac{\pi}{2} \quad (s \text{ even and } > 2) \\ &= \frac{s-3}{s-2} \cdot \frac{s-5}{s-4} \cdots \frac{2}{3} \quad (s \text{ odd and } > 3) \\ &= 1 \quad (s = 3); \quad \frac{\pi}{2} \quad (s = 2). \end{aligned} \right\}. \quad (33)$$

This is a good approximation provided C is not too small. In particular it should be applicable to collisions under gas-kinetic conditions at ordinary temperatures between all atoms other than helium.

3.4. Determination of atomic interactions from gas-kinetic collisions

Apart from establishing the general validity of the quantum picture, the main interest of gas-kinetic collision studies is to provide information about the function $V(r)$, the potential energy of two atoms at a distance r apart.

Most information about the interaction between like atoms has been derived from measurements of the viscosity and second virial coefficient,†

† It is interesting to note, however, that the quantal formula for the second virial coefficient B may be expressed in terms of the same phases η_l as those which occur in the formula (19) for the differential cross-section for collisions between the atoms concerned. In fact, for an assemblage of n molecules

$$BT^{\frac{3}{2}} = - \frac{nh^3}{(\pi M \kappa)^{\frac{1}{2}}} \left[\frac{1}{16} + \frac{M}{\kappa T} \int_0^\infty \Delta e^{-\frac{1}{2} M v^2 / \kappa T} dv + \Gamma \right], \quad \text{where} \quad \Delta = (1/\pi) \sum (2l+1) \eta_l.$$

The summation is over even values of l only if the atoms obey Bose-Einstein statistics. Γ only differs from zero if a bound state exists for the relative motion of the atoms. If E_0 is the binding energy of this state

$$\Gamma = e E_0 / \kappa T - 1.$$

For proof of this formula see Beth and Uhlenbeck, *Physica*, **4** (1937), 915.

an essentially static property, over a range of temperatures. The diffusion coefficient may also be used in principle for this purpose, but little has been done in this direction for neutral atoms. On the other hand, through the measurement of mobility, it provides a powerful method for investigating the interaction between an ion and an atom. The development of molecular ray technique in recent years has made possible the direct measurement of the total collision cross-section for various pairs of atoms.

It has been pointed out in the preceding section that the analysis of such measurements can only be carried out by use of quantal formulae. An alternative possibility is to measure, not the total collision cross-section, but the cross-section for collisions involving deviations *greater* than a well-defined angle θ_0 which is such that, for $\theta > \theta_0$, the classical formula (23) for $I(\theta)$ certainly holds. In this case a classical analysis may be used. This method has not been employed in molecular ray experiments but has been applied in experiments using beams of neutral atoms of homogeneous energy of the order 100 eV (see Chap. VIII, § 4.2, and § 4.12 of this chapter).

4. The interactions of atoms derived from viscosity and other data

A considerable contribution to our knowledge of the interactions between rare gas atoms has come from analysis of the observed viscosity of the particular gas and its variation with temperature, and we shall now give an account of the more recent work in this direction. Information about the interactions can be obtained by other methods of investigation such as the analyses of second virial coefficient and Joule-Thomson coefficient data as well as of the properties of the solidified gases (lattice constant and heat of sublimation). We shall compare the results of these methods with the conclusions obtained from the viscosity data but the detailed description of them is outside the scope of this book.

As pointed out earlier (§ 3.2), it is only for helium that quantum effects are important and then only at temperatures below 80° K.

4.1. *The interaction of helium atoms*

A great deal of work has been devoted to the accurate determination of the interaction energy of two helium atoms at separations of gas-kinetic importance. This is partly because of the importance of quantal modifications in this case and partly because of the need for accurate knowledge of the interaction in interpreting the remarkable phenomena exhibited by liquid helium.

4.11. The low-temperature evidence. There exist seven determinations of the viscosity,[†] three of the thermal conductivity,[‡] and nine of the virial coefficient of helium§ at temperatures below 20° K where quantum effects are large. The thermal conductivity measurements at 1°, 2°, and 3° K are not consistent with the comparable viscosity measurement at 2° K. According to the relation (12) (p. 368, 2nd footnote) the latter should be multiplied by a factor 1.84 to agree with the thermal conductivity results.

The first quantal analysis of the viscosity observations was made by Massey and Mohr in 1933,|| who showed that the approximate formula for the interaction,

$$V(r) = be^{-ar} - cr^{-6}, \quad (34)$$

where $b = 7.7 \times 10^{-10}$ ergs, $a = 4.6 \times 10^8$ cm.⁻¹, and $c = 1.47 \times 10^{-60}$ erg cm.⁶, given by Slater^{††} on theoretical grounds, while not correct, was a fair approximation. Various attempts to improve on (34) have been made,^{‡‡} using the second virial coefficient as well as the viscosity and thermal conductivity data. The most detailed analysis has been carried out by Buckingham, Hamilton, and Massey.§§ From their calculations an interaction may be derived which is reasonably consistent with the thermal conductivity and virial coefficient data but is not in agreement with the observed viscosity.

The behaviour at low temperatures is determined mainly by the attractive portion of the field and is very insensitive to the detailed form of the repulsion. For the further analysis it is convenient to write the interaction in the form

$$V(r) = -\epsilon f(r/r_m), \quad (35)$$

where f determines the form of the interaction and ϵ , the depth of the potential minimum, determines its strength for a given f . r_m is the value of r at which $V(r)$ is a minimum. Buckingham, Hamilton, and Massey|||| investigated a family of interactions of essentially the same form for values of $r > r_0$, the distance at which $V(r)$ changes sign (see Fig. 171),

[†] van Itterbeek and Keesom, *Physica*, **5** (1938), 257.

[‡] Ubbink and de Haas, *ibid.* **10** (1943), 465.

[§] Holborn and Otto, *Zeits. f. Phys.* **23** (1924), 77; **30** (1925), 320; **33** (1925), 1; **38** (1926), 359; Keesom and Kraak, *Physica*, **2** (1935), 37; Nijhoff, Keesom, and Ilin, *Proc. K. Wet. Amst.* **31** (1928), 408.

|| *Proc. Roy. Soc. A*, **144** (1934), 188.

^{††} *Phys. Rev.* **32** (1928), 349.

^{‡‡} Buckingham, *Proc. Roy. Soc. A*, **161** (1937), 117; de Boer and Michels, *Physica*, **5** (1938), 945; Hirschfelder, Ewell, and Roebuck, *J. Chem. Phys.* **6** (1938), 205; Margenau, *Phys. Rev.* **56** (1939), 1000.

^{§§} *Proc. Roy. Soc. A*, **179** (1941), 103.

|||| Loc. cit.

but different strengths ϵ . For $r < r_0$ all interactions with certain unimportant exceptions were taken to be equal to that given by (34). They also included the evidence obtained by de Boer and Michels† from an interaction of slightly different form. Fig. 174 illustrates, as functions

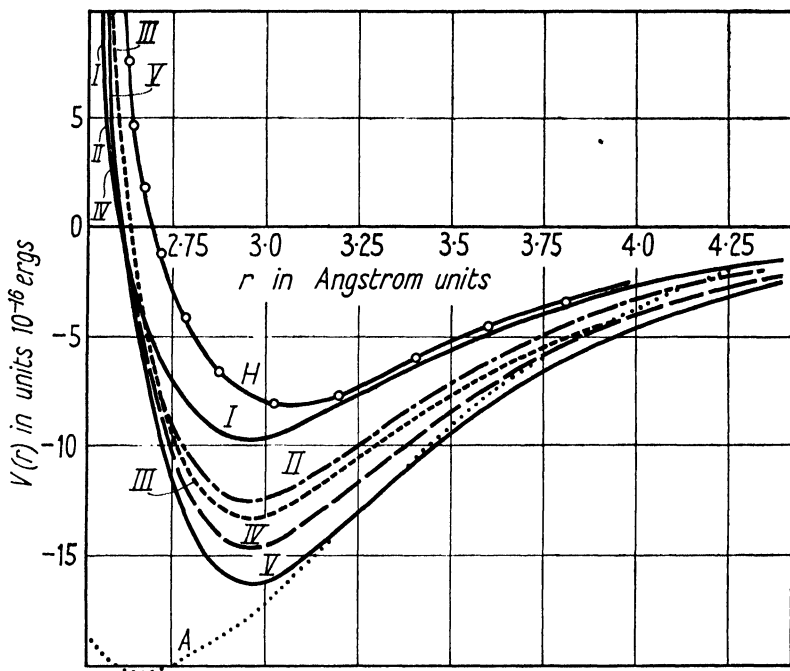


FIG. 174. Types of interaction energy function for two helium atoms.

- I. Interaction $V(r) = be^{-ar} - cr^{-6} - dr^{-8}$, with $a = 4.67 \text{ \AA}^{-1}$, $b = 6.5 \times 10^{-10} \text{ erg}$, $c = 1.48 \times 10^{-12} \text{ erg \AA}^6$, $d = 2.48 \times 10^{-12} \text{ erg \AA}^8$.
 - II. $V(r) = be^{-ar} - cr^{-6}$, with $a = 4.6 \text{ \AA}^{-1}$, $b = 7.7 \times 10^{-10} \text{ erg}$, $c = 1.47 \times 10^{-12} \text{ erg \AA}^6$.
 - III. $V(r) = \epsilon(r_0/r)^6((r_0/r)^6 - 2)$, with $\epsilon = 14.04 \times 10^{-16} \text{ erg}$, $r_0 = 2.874 \text{ \AA}$.
 - IV. As for interaction I, with $b = 9.75 \times 10^{-10} \text{ ergs}$, a, c, d as for I.
 - V. As for interaction II, with $a = 4.6 \text{ \AA}^{-1}$, $b = 10^{-9} \text{ erg}$, $c = 1.91 \times 10^{-12} \text{ erg \AA}^6$.
- A is the interaction of equation (37) of the text. H is the interaction of equation (39) of the text, with $\epsilon = 8.3 \times 10^{-16} \text{ erg}$, $r_0 = 2.7 \text{ \AA}$.

of r , the actual interactions used. The procedure was then to calculate the viscosity and second virial coefficients, μ and B respectively, as functions of the absolute temperature T for different values of ϵ and r_m . In doing this use was made of the fact that, if $\mu(T)$ and $\mu'(T)$ are the

† *Physica*, **5** (1938), 945, and **6** (1939), 409.

viscosity coefficients calculated from interactions with parameters r_m , ϵ and r'_m , $\epsilon(r_m/r'_m)^2$ respectively, then

$$\mu(T)T^{-1} = \mu'(T')T'^{-1}, \quad (36)$$

where $T' = (r_m^2/r'_m{}^2)T$. A similar relation holds for $B(T)T^{1/2}$.

To avoid varying too many parameters at once, the most detailed calculations were carried out for a fixed value of r_m . This was taken to be 2.943 Å, which is very nearly the value given by the interaction (34). The comparison with the rather meagre viscosity data in the temperature range 1.0°–5° K is given in Table II. The observed thermal conductivities have also been included by using the relation (12) (p. 368, 2nd footnote).

TABLE II

Comparison of Observed Values of μ with Values Calculated using the Interactions Shown in Fig. 174

μ in 10^{-7} c.g.s. units

T° K	Observed		Calculated interaction type				
	From viscosity	From thermal conductivity	I	II	III	IV	V
1.35	..	38.7	..	..	..	..	..
1.64	54.5	..	..	..	..	..	..
2.00	(65.0)	49.2	60.5	51.8	46.7	45.5	43.5
2.79	..	71.8	(84.8)	(78.0)	(67.0)	(65.5)	(64.5)
3.0	(92.5)	..	90.9	79.1	72.5	71.3	71.3
4.23	127	..	..	..	..	..	..
5.0	(153)	..	140	133	..	126	128

Interpolated values are indicated by brackets.

It will be seen that, while the interaction I (Fig. 174) gives the best agreement with the directly measured viscosity, that derived from the measured thermal conductivity is in best agreement with interaction III (Fig. 174). On the other hand, an earlier investigation by Buckingham and Massey† showed that the interaction V (Fig. 174) gives good agreement over the temperature range from 15° to 20° K. No measurements are available in the range 5°–15° K.

Fig. 175 illustrates the observed virial coefficient data together with a 'smoothing' function (K, K.W.) introduced by Keyes to represent the available results between 2° K and 650° K. Comparison with the calculated curves corresponding to the different interactions of Fig. 174 shows that the best agreement is likely to be with an interaction III and IV of that figure. This is consistent with the thermal conductivity measurements, but not with the viscosity measurements either in the

† *Proc. Roy. Soc. A*, **168** (1938), 378.

2° – 5° K or 15° – 20° K range. More measurements of all three sets of quantities are clearly required although, meanwhile, an interaction between II and IV of Fig. 174 would seem to be the most likely.

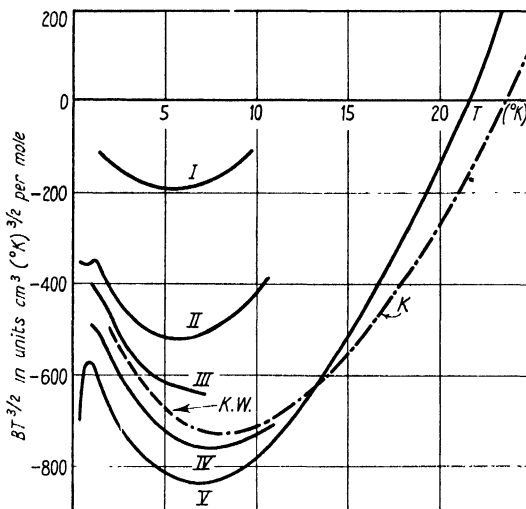


FIG. 175. Second virial coefficient, B , for He, calculated using the various interactions shown in Fig. 174. The broken curve represents an average of the experimental results.

Before considering the evidence from measurements at temperatures above 50° K it is of interest to see the extent to which the quantum statistics obeyed by the atoms affect the cross-sections. Fig. 176 illustrates cross-sections Q and Q_{μ} calculated by Massey and Buckingham† for helium, assuming interaction V, Fig. 174, and different statistics for the atoms. The symmetry properties are seen to be unimportant except at very low temperatures. Too much significance should not be placed on the forms of the separate curves as they are sensitive to the detail of the interaction assumed. In particular, the behaviour at very low temperatures depends strongly on whether or not the attraction is large enough to introduce a stationary state. It is certain that not more than one such state exists, and if so it must possess a very small binding energy. Of the interactions illustrated in Fig. 174, I, II, and probably III give no stable state. For IV and V a stable state exists, the corresponding binding energies being 0.004κ and 0.06κ respectively.

† *Proc. Roy. Soc. A*, **168** (1938), 378.

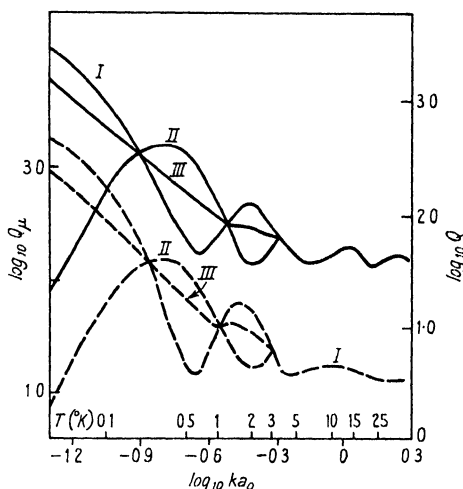


FIG. 176. Cross-sections for helium atoms calculated using interaction V of Fig. 174 with different assumptions concerning the statistics obeyed by the atoms ($a_0 = 0.528 \text{ \AA}$).

— total cross-section, Q ; --- viscosity cross-section, Q_μ .

I. Bose-Einstein statistics.

II. Fermi-Dirac statistics.

III. Classical (Maxwell-Boltzmann) statistics.

4.12. The evidence from temperatures above 20° K . The most recent analyses of the viscosity of helium in the range of temperature for which classical theory is valid are those of Amdur† and Hirschfelder, Bird, and Spotz.‡

Amdur used an interaction suggested by Margenau§ which has the form

$$V(r) = [7.70e^{-4.60r} - 5.60e^{-5.33r} - 0.0139r^{-6} - 0.030r^{-8} - 0.035r^{-10}] \times 10^{-10} \text{ ergs}, \quad (37)$$

r being measured in $\text{\AA}$. The first term is the same as the repulsive term in Slater's interaction (34), but it is softened by an additional attraction of exponential form. The usual van der Waals term, varying as r^{-6} , is supplemented by two additional terms to represent higher approximations. The interaction is illustrated, for $r > r_0$, in Fig. 174 (curve A).

To calculate the viscosity Amdur used a somewhat indirect procedure which requires justification. He did not calculate the viscosity

† *J. Chem. Phys.* **15** (1947), 482.

‡ *Ibid.* **16** (1948), 968.

§ *Phys. Rev.* **56** (1939), 1000.

cross-section Q_μ directly but evaluated a so-called classical total collision cross-section Q_{cl} defined by

$$Q_{cl} = 2\pi \int_{\theta_0}^{\pi} I_{cl}(\theta) \sin \theta d\theta, \quad (38)$$

where $I_{cl} d\omega$ is the differential cross-section given by classical theory (see (23), (24), (25) of this chapter) and θ_0 is the minimum angle for which the classical approximation is valid. Following the argument outlined in § 3.3, a was taken as π/k , where a is an effective collision radius, fixed by Amdur as the classical distance of closest approach, and $2\pi/k$ is the wave-length of the relative motion. Having calculated Q_{cl} it was then assumed that $Q_\mu = \frac{2}{3}Q_{cl}$ as it would be if the interaction were of the rigid sphere type (§ 3.2). In view of this procedure some doubt must be cast on the accuracy of Amdur's results in which he finds that (38) gives agreement within 5 per cent. with both the data on viscosity† and thermal conductivity‡ for temperatures between 20° and 200° K particularly in view of the importance of quantum corrections at the low temperatures.

Hirschfelder, Bird, and Spotz have carried through a detailed numerical tabulation of the viscosity cross-sections given by classical theory for two-parameter interactions of the form

$$V(r) = 4\epsilon\{-(r_0/r)^6 + (r_0/r)^{12}\}, \quad (39)$$

in which the depth of the potential minimum is ϵ and the zero of the interaction occurs at a separation r_0 . They give tables to cover a wide range of values of ϵ and r_0 . Applying their results to helium they find that the best agreement with the viscosity data between 80° and 1,000° K§ is obtained with $\epsilon = 6.03\kappa$ and $r_0 = 2.70 \text{ \AA}$. This interaction is illustrated in curve H of Fig. 174 and curve V of Fig. 177. The closeness of this agreement may be seen by reference to Table III.

Fig. 177 gives a comparison of the potentials (37) (curve IV) and (39) (curve V) with those obtained from other data. Curve I is the Slater interaction (34). Curve II is an interaction of the same form, but with slightly modified constants in the repulsive term found by Buckingham|| to give good agreement with second virial coefficient data over the

† Johnston and Grilly, *J. Phys. Chem.* **46** (1942), 948.

‡ Ubbink and de Haas, *Physica*, **10** (1943), 465 (up to 89° K); Eucken, *Phys. Zeits.* **12** (1911), 1101 (195° K).

§ Johnston and Grilly, loc. cit. (up to 300° K); Rammner and Beutling, *Zeits. f. Dampfessel u. Maschinetrieb*, **60** (1937), 620 (800° and 1000° K).

|| *Proc. Roy. Soc. A*, **168** (1938), 264.

TABLE III

Comparison of Observed Viscosity of Helium with that Calculated using the Interaction (39) due to Hirschfelder, Bird, and Spotz

(In units 10^{-7} gm. cm.⁻¹ sec.⁻¹)

T° K	Observed†	Calculated
80	821	827
100	947	957
120	1,068	1,086
140	1,182	1,197
160	1,290	1,305
180	1,395	1,413
200	1,496	1,509
220	1,595	1,605
240	1,692	1,700
260	1,789	1,789
280	1,888	1,877
300	1,987	1,964
800	3,840	3,665
1,000	4,455	4,237

† The observed values are those of Johnston and Grilly, *J. Phys. Chem.* **46** (1942), 948, except for the last two in the table which are given by Trautz and Zink, *Ann. der Physik*, **7** (1930), 427.

temperature range 71.5° to 673° K.† Curve III illustrates an interaction of the form (39) found by Hirschfelder, Ewell, and Roebuck‡ from the Joule-Thomson coefficients. To facilitate estimation of the region most effective in determining properties at a temperature T° K the interaction energy is given in Fig. 177 as a multiple of Boltzmann's constant. It appears from this that the weak attraction is not likely to have much influence on properties at temperatures greater than 20° K with which we have been concerned in this section, so that any lack of agreement between the interactions in this region is not very significant. However, even in the repulsive region a considerable spread in the derived results is evident. The need for further analysis and for more precise experimental data is clear.

To determine the interaction at distances less than 2 Å a different technique using atom beams of high energy must be employed. It is not to be expected that the derived interactions can be extrapolated to much smaller separations than those concerned in determining the data analysed. In this connexion, however, the exponential form of repulsion, as in the Slater interaction, has great advantages over the

† Holborn and Otto, *Zeits. f. Phys.* **23** (1924), 77; **33** (1925), 1 and **38** (1926), 359; Nijhoff, Keesom, and Iliin, *Proc. K. Wet. Amst.* **31** (1928), 408.

‡ *J. Chem. Phys.* **6** (1938), 205.

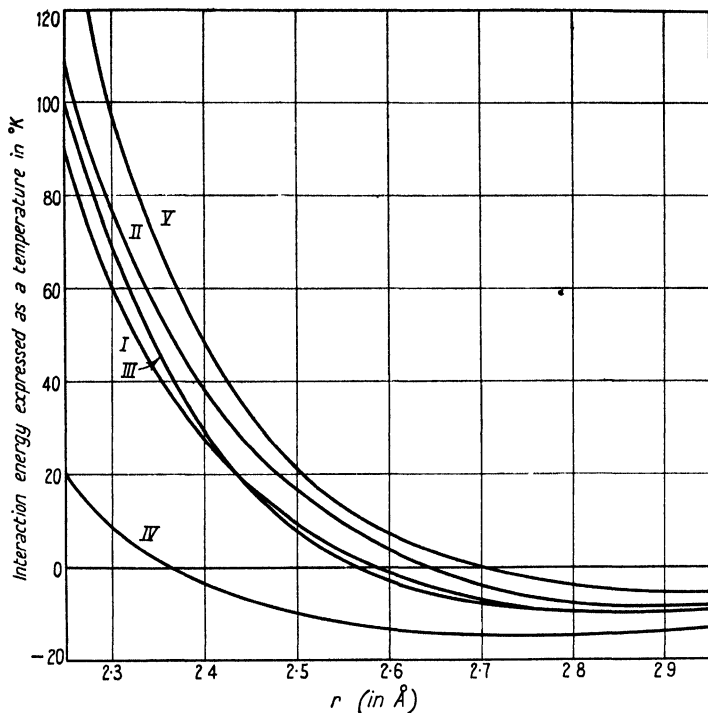


FIG. 177. Shape of the repulsive part of the interaction energy function for two helium atoms.

- I. The interaction (34) of the text (the same as interaction I of Fig. 174).
- II. Interaction of the same form as I, but with $b = 8.71 \times 10^{-10}$ erg.
- III. Interaction of the form of (39) of the text with constants adjusted to agree with data from the Joule-Thomson effect.
- IV. The interaction (37) of the text. This is the same function as curve A of Fig. 174.
- V. The interaction (39) of the text. This is the same function as curve H of Fig. 177.

inverse power law form as in (39). Thus Amdur and Pearlman† by a method described in Chap. VIII, § 4.22, have measured the cross-section for scattering of beams of helium atoms with energies between 300 and 1,000 eV by helium gas in which only deviations greater than 4.5° were counted as collisions. A completely classical theory could then be used for analysing the data (see Chap. VIII, § 4.22). It is found then that the repulsive term $8.71 \times 10^{-10} e^{-4.63r}$ in Buckingham's interaction, illustrated as curve II in Fig. 177, gives the correct order of the

† *J. Chem. Phys.* 9 (1941), 503.

interaction energy at the distances of approach, between 0.5 and 0.8 Å, effective in these experiments. Thus even at 0.55 Å it gives a repulsion only twice too large.

4.2. *The interaction of other rare gas atoms*

Hirschfelder, Bird, and Spatz† have applied their tabulation of the viscosity cross-sections for an interaction of the form (39) to analyse the viscosity data for neon and argon as well as helium, while Amdur has extended his method to all the rare gases.

A comparison of their results with other interactions which have been derived recently for neon and for argon is given in Table IV. The experimental data used and the form of the interaction assumed is given in each case. On the whole, for neon the position is fairly satisfactory if Amdur's interaction is ignored. This may be justified in view of the doubt about the accuracy of his method of calculating the viscosity cross-section. For argon the agreement between the interactions is not quite so good but still rather better than for helium.

5. The interactions between atoms from observed total cross-sections

5.1. *The measurement of total cross-sections by molecular ray methods*

The study of the scattering of atoms and molecules with gas-kinetic velocities may be carried out by methods which are the same in principle as those used for studying the total cross-sections for scattering of electrons. The electron beam must be replaced by a beam of gas atoms. It is necessary therefore to develop techniques for the production of such beams as well as methods for measuring the strength of the beam at any point. The beam must, of course, be unidirectional and the atoms composing it must not collide with each other. The conditions are therefore those of effusive flow of a gas. A molecular beam of this sort will differ from the electron beams of Ramsauer's experiments (Chap. I, § 3) in that the atoms within it will possess a Maxwellian distribution of velocities instead of a single definite velocity, but for many purposes this is not a serious defect. Methods of obtaining beams of neutral particles with homogeneous velocities have been devised, but in such beams the atoms have energies greatly in excess of ordinary thermal values. These methods will be described in Chap. VIII, § 2.7.

The first experimental production of a molecular beam was carried out by Dunoyer‡ in 1911, but the full development of the technique was

† Loc. cit.

‡ *Compt. Rend.* 152 (1911), 592; *Le Radium*, 8 (1911), 142.

TABLE IV

Atom	Form of interaction ($\times 10^{10}$ ergs) (r in Å)	Experimental data used	Position of zero, r_0 (Å)	Position of minimum r_m (Å)	Depth of minimum ϵ (10^{-15} ergs)	Asymptotic form $\sim C/r^6$ ($\times 10^{-40}$ erg cm. ⁶)	References to theoretical analysis
Ne 1.	$\epsilon \{-1.60f\{(r_m/r)^6 + 0.2(r_m/r)^3\} + 0.92 \exp\{-13.2(r/r_m - 1)\}\}$ with $f = 1$ for $r \geq r_m$; $f = \exp\{-4(r_m/r - 1)^3\}$ for $r < r_m$	(i) Lattice distance in solid Ne (ii) Heat of sublimation of solid Ne (extra- polated to 0° K) (iii) Second virial co- efficient (iv) Joule-Thomson co- efficient (extrapo- lated to zero density)	2.82	3.16	5.18	8.3	Corner, <i>Trans. Far.</i> <i>Soc.</i> 44 (1948), 914
2.	$4\epsilon\{-(r_0/r)^6 + (r_0/r)^{12}\}$	Viscosity	2.8	3.16	5.01	10.0	
3.	$4\epsilon\{-(r_0/r)^6 + (r_0/r)^{12}\}$	Viscosity and thermal conductivity	2.8	3.14	5.0	9.5	Hirschfelder, Bird, and Spotz, <i>J. Chem.</i> <i>Phys.</i> 16 (1948), 968
4.	$\{0.966e^{-2.37r} - 0.121r^{-6} - 0.179r^{-8} - 0.137r^{-10}\}$	Viscosity and thermal conductivity	2.7	3.24	4.0	12.1	Amdur, <i>ibid.</i> 190
A 1.	$\{13.4e^{-2.37r} - 1.1r^{-6}\}$	Joule-Thomson co- efficient (extrapolated to zero density)	3.38	3.86	15	110	Hirschfelder, Ewell, and Roebuck, <i>ibid.</i> 6 (1938), 205

2. $\epsilon\{-1.57f[(r_m/r)^6 + 0.2(r_m/r)^3] + 0.88 \exp\{-13.5(r/r_m - 1)\}\}$ with f as for interaction 1 for Ne	(i) Lattice distance in solid A	3.43	3.87	17.21	91	Corner, <i>Trans. Far. Soc.</i> 44 (1948), 914 Hirschfelder, Bird, and Spotz, <i>J. Chem. Phys.</i> 16 (1948), 968 Amdur, <i>ibid.</i> 190.
	(ii) Heat of sublimation of solid A (extrapolated to 0° K)					
	(iii) Second virial coefficient					
	(iv) Joule-Thomson coefficient (extrapolated to zero density)	3.44	3.87	16.47	99	
3. $4\epsilon\{-(r_0/r)^6 + (r_0/r)^{12}\}$	Viscosity	3.418	3.81	17.12	109	
4. $4\epsilon\{-(r_0/r)^6 + (r_0/r)^{12}\}$	Viscosity and thermal conductivity	3.46	3.80	17.30	75.5	
5. $\{8.30 \times 10^3 e^{-4.732r} - 0.755r^{-6} - 1.64r^{-8} - 1.85r^{-10}\}$						

carried out at Hamburg by Stern and his collaborators over the period from 1923 to 1933. It is not our intention here to describe the full technical details of molecular ray experiment. An excellent account has been given by Fraser in *Molecular Rays* (Cambridge, 1931) and *Molecular Beams* (Methuen, 1936). We shall, however, summarize the types of source and methods of detection before describing the most detailed applications of the method which have yet been made to the study of atomic collisions.

5.11. *The production and detection of molecular beams.* Three kinds of source have been developed: the oven source, the capillary source, and the filament source.

In the oven source, applicable to substances which are not gaseous at ordinary temperatures, the substance to be vaporized is placed in an oven. A small hole is made in one of the walls of the oven and molecules inside the oven, incident on this hole, escape and may be collimated to produce a molecular beam. If the flow through the hole is to be effusive, rather than hydrodynamic—that is, if the gas is to issue from the source in a molecular beam rather than in a turbulent jet, the pressure must be such that the mean free path of the molecules in the source, $\lambda > d$, where d is the diameter of the aperture.

In the capillary source, applicable to substances that are gaseous at ordinary temperatures, the source consists simply of a capillary tube. Gas from a reservoir passes through the capillary and reaches temperature equilibrium with its walls. Provided the pressure in the capillary is such that $\lambda > d$, where d is the diameter of the capillary, the flow through the end of the capillary is effusive and the molecules issuing can be collimated into a molecular beam.

In the 'filament' type of source molecules emitted from the surface of a heated filament or some other solid are collimated to produce a molecular beam.

Provided the flow is purely effusive, the intensity of the molecular beam may be calculated from the temperature and pressure of the source. The ordinary law of effusive flow gives for the number N of molecules effusing in unit time through an aperture of area A , $N = \frac{1}{4}n\bar{v}A$, where n is the number of molecules per c.c. and $\bar{v}$ the mean velocity. This expression should apply provided the hole has no appreciable thickness. In the oven type of source the additional requirement has to be satisfied that the surface of the charge is large compared with the area A of the aperture. If this condition is not satisfied the rate of effusion is determined by the rate of evaporation. The necessity of satisfying this

condition sometimes gives difficulty in the case of the vapour of metals that oxidize readily. A film of oxide may form over the metal, thus reducing the effective area of evaporation below that needed for the maintenance of the vapour pressure inside the oven at the magnitude given by the equilibrium vapour pressure at the corresponding temperature. Any estimate of n from the vapour pressure-temperature curve will then be incorrect and it will not be possible to estimate correctly the rate of effusion through the aperture.

Knowing the total rate of effusion, the intensity in a collimated beam can readily be calculated from the fact that, for a thin aperture, the number of molecules leaving per unit solid angle at an angle θ to the normal to the aperture is proportional to $\cos \theta$.

The methods of detection of slow molecular beams may be summarized as follows:

(a) *Condensation*, in which the molecular beam is condensed on a cooled surface and the beam is detected by the changed appearance of the surface, this change being sometimes enhanced by chemical means. This method of detection is qualitative, although attempts have been made to use it as the basis of a quantitative method by estimating the thickness of the deposit either by weighing or by optical means.

(b) *Chemical targets*, in which some specific type of molecular or atomic species can be detected by chemical action. The most widely known example of this method of detection is that of atomic hydrogen by a target of MoO_3 , giving a blue MoO_2 trace.

(c) *Manometric method*, in which the molecular beam enters a space closed except for the orifice by which the beam enters. The pressure in the space builds up until the rate of effusion of gas out through the orifice is equal to the rate at which gas is brought in by the beam. The pressure can then be measured by any suitable type of ion gauge.

(d) *Surface ionization detector*, available particularly for neutral beams of alkali atoms, which strike a suitable hot filament, undergo surface ionization, and are measured by the ion current between the hot surface and a suitable detector held at a negative potential with respect to it. When applicable this is by far the most convenient and accurate method.

For fuller information regarding these methods reference should be made to the two books of Fraser (loc. cit.).

5.12. The principle of the method for measuring total cross-sections. To determine the total cross-section for collisions between two kinds of gas atoms A and B , averaged over the distribution of relative velocities

fixed by the temperatures of the gases, a narrow molecular beam of the atoms A may be fired through the gas of atoms B contained in a small scattering chamber. The intensity of the beam is measured after passage through the chamber both when the gas B is absent (I_0) and when n_B atoms/c.c. are present (I). From the ratio I/I_0 of these intensities the average cross-section may be derived as follows.

Let the masses of the atoms A and B be M_A and M_B and the temperatures of the corresponding gases be T_A and T_B , respectively. The chance that an atom A , moving with velocity v , should pass through the chamber of length x , is given by

$$P(v) = \exp(-x/\lambda_v). \quad (40)$$

The free path λ_v is an average over the velocity distribution of the atoms B which is given, in terms of a mean effective cross-section $\bar{Q}_{AB}$, by†

$$\lambda_v = \pi^{\frac{1}{2}} w^2 / n_B \bar{Q}_{AB} \psi(w), \quad (41)$$

where

$$w = v(M_B/2\kappa T_B)^{\frac{1}{2}},$$

$$\psi(w) = w e^{-w^2} + (2w^2 + 1) \int_0^w e^{-z^2} dz. \quad (42)$$

The ratio I/I_0 will be equal to the probability $P(v)$ averaged over the velocity distribution of the atoms A , giving

$$I/I_0 = \overline{P(v)} = 2\alpha^2 \int_0^\infty \exp[-\{x n_B \bar{Q}_{AB} \psi(w)/\pi^{\frac{1}{2}} w^2\} - \alpha w^2] w^3 dw, \quad (43)$$

where

$$\alpha = M_A T_B / M_B T_A. \quad (44)$$

The determination of $\bar{Q}_{AB}$ from this formula is rather tedious. Remembering, however, that $\bar{Q}_{AB}$ is already a rather complicated average of the cross-section for a given relative velocity of the atoms A and B , a simpler procedure may be adopted without serious error. In this the mean value $\bar{P}$ is taken as approximately $\exp(-x/\bar{\lambda})$, where $\bar{\lambda}$ is the mean value of λ given by (41), i.e.

$$\begin{aligned} \bar{\lambda} &= (2\alpha^2 \pi^{\frac{1}{2}} / \bar{Q}_{AB} n_B) \int_0^\infty w^5 e^{-\alpha w^2} dw / \psi(w) \\ &= (2\pi^{\frac{1}{2}} / \bar{Q}_{AB} n_B) \bar{\psi}(\alpha), \text{ say.} \end{aligned} \quad (45)$$

Values of the function $\bar{\psi}(\alpha)$ have been given for the range of α important in practice.‡ These are reproduced in Table V.

In the remarkable experiments of Estermann, Foner, and Stern§

† Kennard, *Kinetic Theory of Gases*, McGraw-Hill.

‡ Rosin and Rabi, *Phys. Rev.* **48** (1935), 373.

§ Ibid. **71** (1947), 250.

TABLE V
The Function $\psi(\alpha)$

α	$\psi(\alpha)$	α	$\psi(\alpha)$	α	$\psi(\alpha)$
0	0.282	0.9	0.216	8	0.107
0.05	0.275	1.0	0.211	10	0.094
0.1	0.265	2.0	0.173	15	0.0813
0.2	0.256	3.0	0.155	21	0.0714
0.3	0.248	4.0	0.140	25	0.0643
0.545	0.236	5.28	0.127	30	0.0589
0.8	0.221	7.0	0.113	35	0.0548

(see § 4.13) the value of λ for a definite velocity v could be determined so that the formula (41) could be used directly.

It is important in planning experiments of this kind to ensure that the angular resolving power is great enough. As a guide for this purpose the schematic angular distribution, illustrated in Fig. 172 (b) for the collisions of rigid spheres, may be used. For the parameter a the sum of the gas-kinetic radii of the colliding atoms (determined from viscosity or other phenomena) may be substituted or, with possibly greater accuracy, $\sqrt{2}$ times this sum. It is then possible to determine the minimum angle of deviation θ_0 , which is to be counted as a collision in the actual apparatus, so that the ratio

$$\frac{\int_{\theta_0}^{\pi} I(\theta) \sin \theta \, d\theta}{\int_0^{\pi} I(\theta) \sin \theta \, d\theta}$$

is as near unity as is desired. If θ_0 is the minimum angle of deviation in degrees, measured in the laboratory system (see Chap. VIII, § 1.2),

TABLE VI

Angular Resolution in Apparatus for the Measurement of Total Collision Cross-section

θ_0 = minimum angle of deviation to be counted as a collision (measured in degrees in the laboratory system), if the error in the total cross-section is not to exceed 10 per cent.

Target atom	Energy of incident particle (lab. system) eV	θ_0 (degrees) (lab. system)							
		Incident atom							
		He	Ne	A	Li	Na	K	Rb	Cs
He	0.0255 (= 300° K)	3.6	..	..	1.5	0.73	0.50	0.36	0.27
	0.0862 (= 1,000° K)	2.0	..	..	0.80	0.40	0.27	0.20	0.15
	1 (= 11,600° K)	0.59	..	..	0.23	0.12	0.08	0.06	0.04
Ne	0.0255 (= 300° K)	..	1.4	..	1.4	0.62	0.40	0.27	0.19
	0.0862 (= 1,000° K)	..	0.75	..	0.75	0.34	0.22	0.15	0.11
	1 (= 11,600° K)	..	0.22	..	0.22	0.10	0.06	0.04	0.03
A	0.0255 (= 300° K)	..	..	0.70	0.87	0.41	0.27	0.19	0.14
	0.0862 (= 1,000° K)	..	..	0.30	0.48	0.23	0.15	0.10	0.08
	1 (= 11,600° K)	..	..	0.11	0.14	0.07	0.04	0.03	0.02

so that the error in the determination of the cross-section should not exceed 10 per cent.,

$$\vartheta_0 \simeq 277/a(MT)^{\frac{1}{2}}, \quad (46)$$

where M is the atomic mass of the incident atom, T the equivalent temperature (in °K) of the incident particles, and a is measured in Å. Table VI shows ϑ_0 for a number of different incident particle energies for some cases of scattering that have been investigated.

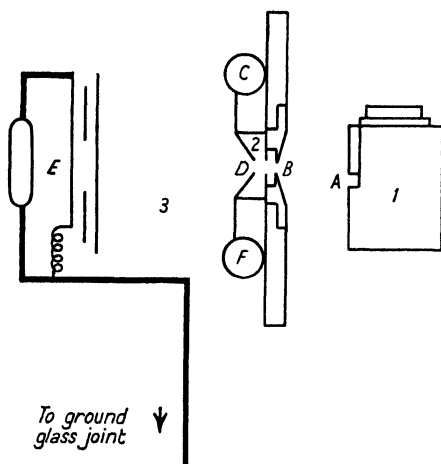


FIG. 178. Apparatus used by Rosin and Rabi for measuring total collision cross-sections for impacts of alkali metal and rare gas atoms.

5.13. The collision cross-sections of alkali metal atoms. The quantitative study of beams of alkali metal atoms is assisted by the convenience and accuracy of the hot-wire method of detection which can be used. For this reason all the measurements of cross-sections up to the present have been made using these atoms.

The earliest work, that of Broadway,[†] was concerned with the scattering of a beam of sodium atoms by a beam of mercury atoms. It was directed towards the establishment of the quantal result that

$$\lim_{\theta \rightarrow 0} I(\theta)$$

is finite, and for this purpose the scattering between angles of 0.2° and 1° was studied. Evidence in favour of the finite limit was found.

The most detailed study has been made by Rosin and Rabi,[‡] who measured the cross-sections for collision between the alkali and rare

[†] *Proc. Roy. Soc. A*, **141** (1933), 634.

[‡] *Loc. cit.*

gas atoms and provided strong evidence of the correctness of the quantum view-point. The apparatus they used is illustrated diagrammatically in Fig. 178. A molecular beam of alkali atoms issued from the oven 1 through the aperture and fore slit *A* and, passing through the image slit *B*, entered the scattering volume 2 containing the rare gas which was admitted through the inlet *C*. That part of the beam which had not suffered collision in the scattering volume passed out through *D* into a highly evacuated region 3. The intensity of this beam could then be surveyed by means of a fine tungsten filament *E* which could be rotated by means of a ground glass joint so as to traverse the beam. The pressure in the scattering chamber was measured by a McLeod gauge connected to the outlet *F*.

The slit *B* was 0.01 mm. wide and only 0.05 mm. long to reduce scattering within it. The beam was limited to a height of 0.25 mm. The length of path in the scattering chamber was 2 mm. and the beam passed into the detecting chamber through a channel, of 1 mm. length, of a shape specially designed to offer high resistance to gas flow. A tungsten filament of 0.02 mm. diameter, subtending an angle of $1.7'$ at the scattering chamber, constituted the detecting wire.

To make the measurements it was only necessary to sweep the detecting filament through the beam in the absence of the scattering gas and repeat the observations with the gas present at a measured pressure. The important result emerged that, although the magnitude of the beam was reduced by the scattering gas, its shape was practically unaltered. This is illustrated for a typical case, the scattering of sodium by argon, in Fig. 179. The significance of this absence of broadening is that the number of collisions involving a deviation through less than a few minutes of arc is a small fraction of the total number of collisions. This is in agreement with the quantum view-point but in complete contradiction to the classical theory, according to which at least 50 per cent. of the total scattering would take place between $1'$ and $10'$. It indicates

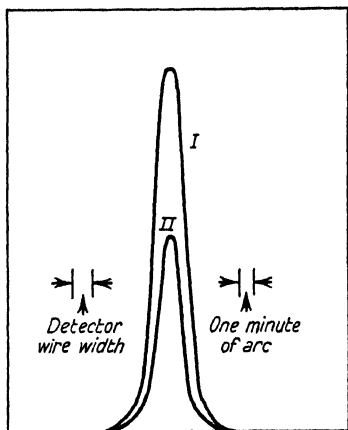


FIG. 179. Shape of beam of alkali metal in Rosin and Rabi's experiments.

I. Before absorption.

II. After absorption.

further that the angular resolving power of the apparatus is sufficiently high to give accurate values of the total cross-sections. In deriving the cross-sections in the manner explained in § 5.12 correction was made for the effect of the gas-pressure gradient in the channel between scattering and detecting chambers. The final values obtained are given in Table VII.

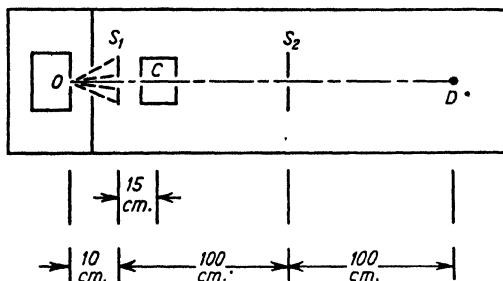


FIG. 180. Apparatus used by Estermann, Foner, and Stern for measuring total collision cross-sections for impacts of caesium atoms with rare gas atoms.

In spite of what has been said above, it is possible that the resolving power may not be quite high enough for the extreme case of caesium-helium collisions. For these the actual deflexion of the heavy atom from its original direction is only about 0.12 of the angle through which the relative velocity vector is turned. Taking $2'$ as the minimum deviation from the beam which could be observed, it follows that the minimum angle of deviation of the relative velocity vector which could be observed is about 0.25° , which is rather close to the mean value of π/ka which may be as small as 1° . The most recent investigations of Estermann, Foner, and Stern, in which a very high resolution was available, confirm this in finding a cross-section for caesium-helium collisions which is $2\frac{1}{2}$ times greater than that given by Rosin and Rabi,[†] considerably larger indeed than would have been anticipated (see § 5.2).

The measurements of Estermann, Foner, and Stern[†] were obtained with an apparatus in which they investigated the gravity deflexion of a beam of caesium atoms. Fig. 180 illustrates the principle of the method and the important dimensions. For the main purpose of the work the scattering chamber C was not included. Caesium atoms evaporated from the oven O were collimated by a fore slit S_1 and collimating slit S_2 each of 0.02 mm. width. The beam was detected by a tungsten wire detector

[†] Loc. cit.

D of 0.02 mm. diameter which could be moved parallel to itself in a vertical plane perpendicular to the undeviated beam. Owing to the long path length between S_2 and D an atom with the most probable velocity corresponding to a temperature of 450° K suffered a downward deflexion due to gravity of 0.174 mm. before arriving at the detector. Hence, as the detector traversed a vertical plane, the intensity of the beam observed varied in a manner determined by the velocity distribution of the atoms in the beam issuing from S_2 . The current observed at a particular setting of the detector was thus a measure of the flux of atoms with velocity lying within narrow limits.

In the first experiments of Estermann, Simpson, and Stern† the velocity distribution of the atoms was studied. To measure the effective cross-sections, or more correctly the free path λ_v of (41) for a fixed value of v , it was only necessary to introduce the scattering chamber C , the centre of which was 85 cm. from S_2 . A change in direction of the velocity of a beam atom through an angle 0.02/850 radians, $\simeq 5''$, prevented it from passing through so it would be regarded as scattered. This gave a very high resolving power which should have been completely adequate. The measurement of I/I_0 was then carried out in the usual way with different pressures of gas in C for different settings of the detector D corresponding to different velocities v of the beam atoms. This was done for collisions of the caesium atoms with helium, nitrogen, and caesium. The value obtained at the most probable velocity, for helium, is given in Table VII. It is seen to be about $2\frac{1}{2}$ times greater than that found by Rosin and Rabi.

For Cs-Cs collisions a special scattering chamber of monel metal was used and the pressure measured by an auxiliary detector which measured the efflux of vapour through a side slit and a collimating slit. The cross-section found at the most probable velocity is 2.35×10^{-14} cm.²

The size of the discrepancy between the two sets of measurements for Cs-He collisions is a little disturbing. It would not have been anticipated that the resolving power of Rosin and Rabi's experiments was so inadequate even in this case. This is supported by the absence of any broadening of the beam profile by the scattering in their experiments.

As a further confirmation of the adequacy of the resolution in other cases, Rosin and Rabi's results may be compared (see Table VII) with the later measurements of Rosenberg‡ (K in He and A) and the earlier

† *Phys. Rev.* **71** (1947), 238.

‡ *Ibid.* **55** (1939), 1267. Rosenberg also measured the cross-sections for K-H₂, K-D₂, K-N₂, K₂-He, K₂-H₂, and K₂-N₂ collisions.

measurements of Mais† (K in He, Ne, and A). Rosenberg's apparatus had an angular resolving power higher than that of Rosin and Rabi, whereas in Mais's experiments it was $4\frac{1}{2}$ times smaller, the minimum scattering angle detectable being $4\cdot5'$ of arc.

The agreement with Rosenberg's results is excellent. The values found by Mais are somewhat smaller, as would be expected from his poorer resolution, but they are close enough to suggest that the higher resolution in Rosin and Rabi's experiments would be adequate. However, it remains important to understand the discrepancy for Cs-He collisions. It will be shown in the next section that, whereas Rosin and Rabi's value is somewhat smaller than would have been expected from an approximate theory, the one obtained by Estermann, Foner, and Stern is much larger than anticipated.

5.2. Analysis of observed cross-sections—van der Waals forces between alkali and rare gas atoms

The interaction energy $V(r)$ between an alkali atom and a rare gas atom will have the asymptotic form

$$V(r) \sim -C/r^6,$$

where C is the van der Waals constant. It is to be expected that this attraction will be so large as to determine the scattering cross-section almost completely under the temperature conditions of Rosin and Rabi's experiment. The formula (32) given by Massey and Mohr (§ 3.32) may therefore be applied to determine the constant for the different pairs of atoms. The values obtained are given in Table VII.

It is possible to obtain approximate values for the constant C if the polarizabilities of the atoms concerned are known. The polarizabilities of lithium, potassium, and caesium have been measured directly, by molecular ray methods, by Scheffers and Stark,‡ and those of the rare gas atoms may be deduced from measurements of their refractivities.§ Those give, for the constants C , the values listed in Table VII. On the whole the agreement with those obtained directly from Rosin and Rabi's measurements is very encouraging and suggests that the power of the molecular ray method for investigating atomic interactions cannot easily be overestimated. On the other hand, it will be seen that for the Cs-He interaction the measurements of Estermann, Foner, and Stern give a very much larger value for C than that estimated theoretically. Although the latter estimate is not likely to be very accurate it is disappointing that such a large discrepancy exists, particularly in view of the satisfactory results for the other cases. Until this situation is clarified the results of the analysis of all cross-sections obtained from molecular ray experiments can only be accepted with caution.

It is of interest to note, in conclusion, that the power law followed by the interaction may be determined from a study of the variation of the cross-sections with temperature so that the method can readily give both the shape and strength of the interaction.

† *Phys. Rev.* **45** (1934), 773.

‡ *Phys. Zeits.* **35** (1934), 625.

§ C. and M. Cuthbertson, *Proc. Roy. Soc. A*, **84** (1911), 13.

TABLE VII

Observed Collision Cross-sections Q for Alkali Metal-Rare Gas Atom Impacts (in 10^{-16} cm.²) and the Derived van der Waals Constants C (in 10^{-60} cm.⁶)

Alkali metal atom	Rare gas atom							
	He		Ne		Ar		A	
	C		C		C		C	
	From observed Q	From polarizabilities	From observed Q	From polarizabilities	From observed Q	From polarizabilities	From observed Q	From polarizabilities
Li	106	17	120	32	303	188	188	125
Na	130	(26)	213	(51)	401	192	192	(200)
K	165, 170-8, † 150†	35	259, 239†	68	580, 587-1, † 400†	356	356	260
Rb	152	(40)	268	(77)	572	249	249	(290)
Cs	162 (440)§	44	287	87	572	235	235	325

† Measurement by Rosenberg (loc. cit.). ‡ Measurement by Mais (loc. cit.). § Measurement by Estermann, Foner, and Stern (loc. cit.).

All other observed values given are those obtained by Rosin and Rabi (loc. cit.).

6. The mobility of positive ions in gases

6.1. Introduction

A great deal of experimental and theoretical work has been devoted to the study of the mobility of positive ions in gases.† This work is not only important for providing a means of determining the interaction between an ion and atom at gas-kinetic separations but also because it makes possible the study of cluster formation due to attractive forces between ions and dipolar molecules. This latter effect plays an important part in the design of apparatus for mobility measurements. Cluster formation occurs so readily that, in order to measure the true mobility of unclustered ions, very special precautions must be taken to remove any polar impurities such as water vapour.‡ To reduce further the chance of clustering due to residual impurities the measurement should be made as soon as possible after the ions enter the gas. It is also very desirable to have some means available for testing whether any clustering has occurred. In the early experiments, in which these precautions were not taken, low values of the mobility were found which were practically independent of the nature of the initial ion, depending only on the gas concerned.§ Estimates of the mass of the ion made in terms of Langevin's theory (§ 6.41) indicated that cluster formation must have occurred. At this stage it was not clear whether the cluster was composed of atoms of the main gas or impurities. Experiments on the mobilities of electrons|| (see Chap. I, § 7) threw light on this point. It was found that, in moist air, the mobilities of both electrons and positive ions are small and nearly the same, indicating that clusters had formed. On drying the air the electron mobility increases to the normal value for electrons unaccompanied by molecular clusters. This shows that the molecules involved in the cluster are not those of the main gas but of the polar impurity, water. In these experiments the mobility of the positive ions was not increased by the drying, which must be effected to a much greater extent than for electrons—in diffusing a given distance positive ions take much longer than electrons and hence make many more collisions with impurity molecules. Evidence in favour of this was obtained from the experiments of Erikson†† on the variation of mobility of positive

† For a discussion of much of the experimental work see Tyndall, *The Mobility of Positive Ions in Gases*, Cambridge, 1938.

‡ Tyndall and Phillips, *Proc. Roy. Soc. A*, **111** (1926), 577; Erikson, *Phys. Rev.* **33** (1929), 403; **34** (1929), 635.

§ See, for example, Grindley and Tyndall, *Phil. Mag.* **48** (1924), 711.

|| See, for example, Franck and Pohl, *Verh. deut. phys. Ges.* **12** (1910), 291, 613; Townsend and Tizard, *Proc. Roy. Soc. A*, **87** (1912), 357; *ibid.* **A**, **88** (1913), 336.

†† *Loc. cit.*

ions with age. He was able to show that ions with age as short as $1/500$ sec. had a mobility about 25 per cent. higher than ions of the mobility usual when clustering is complete. Subsequent work has confirmed this.

6.2. Technique for measuring mobilities of unclustered positive ions.

6.21. The electrical shutter method. The most thorough study of the mobilities of unclustered ions has been carried out by Tyndall and his co-workers† using an apparatus based on a method first suggested by van de Graaff.‡

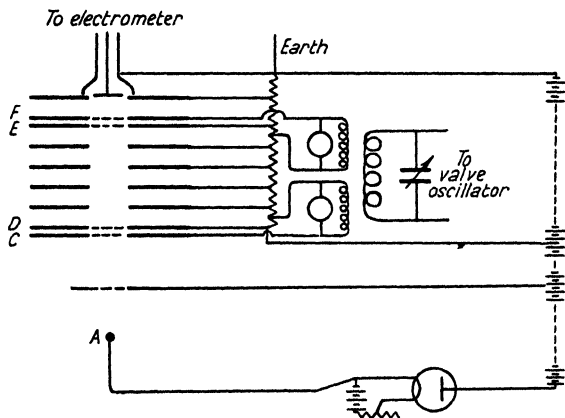


FIG. 181. Apparatus used by Tyndall and Powell for measuring ionic mobilities.

The principle is the same as that described in Chap. I, § 7.2, for measuring electron mobilities, but a different type of shutter is employed. Instead of an electron filter a pair of perforated electrodes such as CD in Fig. 181 are used. If an alternating potential is applied between these, ions are only allowed to pass through both during one half-cycle. To reduce the proportional time during which ions may pass through, a steady potential of magnitude slightly less than the peak alternating potential, and in a sense to oppose the passage of the ions, is applied. Fig. 181 illustrates the electrode arrangement. A is the ion source. CD and EF are the two shutters between which the electric field is maintained uniform by four equidistant guard rings.

Owing to the variable field between the plates of the shutter an end correction is required in order to obtain an absolute value for the

† See Tyndall, *Mobilities of Positive Ions in Gases*.

‡ *Phil. Mag.* 6 (1928), 210.

mobility. This correction does not affect relative values obtained with apparatus of given dimensions provided the ratio of main field to peak shutter potential is unchanged. To determine the correction only one absolute determination is required. This was carried out for helium ions in helium by Tyndall and Powell.† They used an apparatus in which the distance DE could be varied and measured the electrometer current for different distances DE and constant values of the frequency and main electric field. The current is a maximum when the distance DE is covered in a whole number of cycles. Hence the change in DF between two successive current maxima gives the distance the ions travel in a cycle, the end correction being eliminated.

Special precautions were taken to avoid impurities. The whole apparatus was constructed entirely of metal and of pyrex glass so that it could be thoroughly baked. Only specially purified gas was admitted, liquid-air traps being inserted between the apparatus and the last tap of the gas plant to exclude mercury and tap-grease vapours. In the most recent experiments‡ tap-grease contamination was entirely eliminated by replacing the taps by mercury traps. To reduce further the absolute concentration of impurity the work was carried out at relatively low pressures (3–60 mm. Hg). The length of path DF was usually about 1.5 cm. The alternating frequency ranged from 1,000 to 175,000 cycles/sec. so that drift velocities at values of F/p ranging from 2 to 50 volts/cm. at 3 mm. Hg could be studied. With this range available the age of the ions investigated was from 10^{-5} to 2×10^{-3} sec., within which no evidence of any clustering was found.

It is an advantage of the shutter method that this can be checked by observing whether the successive peaks of electrometer currents occur at frequencies which are accurately in the ratio 1:2:3, etc. The homogeneity of the ions can also be tested from the electrometer current-frequency curve as it essentially provides a mass spectrum in first, second, etc., orders.

The electron filter used by Bradbury and Nielsen as a shutter for electron mobility investigations (see Chap. I, § 7.2) has also been used for studying positive ion mobilities. It is rather less convenient for this purpose as it is necessary to employ very close spacing of the grid wires as well as high alternating potentials.

6.22. Micro-wave method. Recently, an interesting alternative method, applicable particularly to the measurement of the mobility of ions in

† *Proc. Roy. Soc. A*, **134** (1931), 125.

‡ Cf. Munson and Tyndall, *ibid.* **177** (1941), 187.

their own gas, has been developed in which micro-wave techniques are employed. The principle of the method is as follows.

If a plasma, consisting of positive ions A^+ and electrons, is produced in a gas within a container and the ionizing agency is cut off, the ion and electron density in the plasma falls steadily with time, partly because of recombination and partly from diffusion to the walls of the container. The diffusion loss is predominant at low pressures. By measuring the rate of decay of electron density in the plasma after the exciting source is cut off, the so-called ambipolar coefficient of diffusion of the electrons and ions may be obtained and from this the mobility of the positive ions. Micro-wave technique is especially suitable for measuring the rate of change of the electron density in the decaying plasma.

The ions and electrons in the plasma move under the combined action of concentration gradient and an electric field F . If n_e, n^+ are the respective concentrations of electrons and of positive ions and j_e, j^+ their corresponding particle current densities, then

$$\left. \begin{aligned} j_e &= -D_e \text{grad } n_e - k_e F n_e \\ j^+ &= -D^+ \text{grad } n^+ + k^+ F n^+ \end{aligned} \right\}, \quad (47)$$

where D_e, k_e and D^+, k^+ are the respective diffusion coefficients and mobilities of electrons and of positive ions. In a decaying plasma the only fields present are due to the space charge and, provided n_e and n^+ are not too small, the condition for preservation of a plasma,

$$|n^+ - n_e| \ll n_e,$$

is maintained. The currents j_e, j^+ may therefore be taken as equal and the field strength F eliminated from the equations (47) to give

$$j = -D_a \text{grad } n, \quad (48)$$

where j and n now refer either to positive ions or electrons and D_a , the ambipolar diffusion coefficient, is given by

$$D_a = (D^+ k_e + D_e k^+) / (k^+ + k_e). \quad (49)$$

In a decaying plasma, in which there is no source of ionization,

$$\text{div } j + \frac{\partial n}{\partial t} = 0,$$

so that

$$-D_a \nabla^2 n + \frac{\partial n}{\partial t} = 0.$$

Assuming an exponential rate of decay so that $n \propto e^{-t/\tau}$, we have

$$\nabla^2 n + n/\tau D_a = 0. \quad (50)$$

This equation must be solved subject to the conditions that n should be finite within the container and vanish at the walls. For a spherical container of radius R , a spherically symmetrical distribution of ion concentration must therefore satisfy these conditions and the equation

$$\frac{d^2}{dr^2}(rn) + rn/D_a\tau = 0.$$

This requires that $n = Br^{-1}\sin(1/D_a\tau)^{\frac{1}{2}}r$, (51)

where $(1/D_a\tau)^{\frac{1}{2}}R = s\pi$ ($s = 1, 2, \dots$), B a constant. (52)

The allowed values of τ correspond to different modes of diffusion. In general the concentrations n will be given by a linear combination of different modes determined by the distribution when the ionization is cut off. If it is assumed that at this time the distribution is that corresponding to the mode $s = 1$, then

$$\tau = R^2/\pi^2 D_a. \quad (53)$$

D_a could then be obtained if τ is measured. Similar considerations apply to containers of other shapes such as cylindrical containers.

To ensure that the lowest diffusion mode prevails the exciting source is arranged to give an ionization rate constant throughout the container. This generates the lowest mode in the steady state and after the excitation is cut off it persists during the decay period.

If the decay of electron density is observed after the electrons and ions have come into equilibrium with the gas and possess a Maxwellian distribution, then

$$D^+/k^+ = D_e/k_e = \kappa T/\epsilon,$$

so

$$D_a = 2D^+k_e/(k_e + k^+) \\ \simeq 2D^+$$

as $k_e \gg k^+$. Hence

$$k^+ \simeq \frac{1}{2}\epsilon D_a/\kappa T. \quad (54)$$

The decay time τ may be measured by observing the change in the resonant wave-length λ of a micro-wave cavity enclosing the container. It may be shown that†

$$\Delta\lambda = C\lambda^2(\Delta\bar{n}),$$

where $\Delta\bar{n}$ is the change in the mean electron concentration within the container and C is a constant determined by the distribution of electron density and of electric field within the cavity.

This technique has been applied by Biondi and Brown‡ to study the mobility of helium ions in highly purified helium contained in a quartz bottle which could be thoroughly baked. The helium was ionized by a

† Slater, *Rev. Mod. Phys.* **18** (1946), 481.

‡ *Phys. Rev.* **75** (1949), 1700.

250 micro-wave pulse from a 10 cm. wave-length magnetron. During the pulse a stationary charge distribution of concentration between 10^{10} and 10^{11} /c.c. was produced, corresponding closely to the lowest diffusion mode. The magnetron was then turned off for 11 milliseconds and measurements made during this interval of the change of electron concentration within the quartz bottle. A time of only about 50 micro-seconds is necessary for the electrons and ions to come into thermal equilibrium with the gas atoms, so that the measurements apply essentially to these conditions. To determine the rate of decay of electron density a weak continuous signal was fed to the cavity through a coaxial line in which a standing wave pattern is set up. The positions of the minima of this pattern will depend on the relation between signal frequency and the resonance frequency of the cavity. When these are equal the minima occur at certain 'resonance' positions which may be located by a suitable technique. If a probe is inserted in the line at a resonance position a minimum signal will be received by it when the signal frequency equals the resonance frequency of the cavity. This minimum may be made apparent in an oscilloscope. When observing the decay of electron density within the quartz bottle the cavity resonance frequency will be slowly changing. To measure the rate of change it is only necessary to vary the frequency of the continuous signal and observe the time at which each frequency is in resonance with the cavity, resonance being indicated by a minimum pick-up signal in the probe.

Correction must be made for the effect of volume recombination. At pressures greater than 20 mm. Hg this effect is predominant and measurements of the decay of electron density give the recombination coefficient α (see Chap. X, § 3.6). At pressures of 5 mm. Hg the recombination loss is relatively small and

$$\frac{dn_e}{dt} \simeq -(n/\tau) - \alpha n_e^2,$$

where τ is the decay time due to diffusion. To this approximation

$$n_e/(1 + \alpha \tau n_e) = [n_0/(1 + \alpha \tau n_0)] \exp(-t/\tau),$$

where n_0 is the electron concentration at $t = 0$. Assuming α to be independent of pressure, a rather doubtful assumption (see Chap. X, § 3.6), this relation may be used to correct the data for recombination loss.

As a check on the extent to which the lowest diffusion mode has been excited, the value found for D_a should be independent of the shape of the container. Biondi and Brown verified this for a spherical bottle of radius 1.25 cm. and two cylindrical bottles (one of radius $R = 1.9$ cm. and

height $H = 2.5$ cm., the other with $R = 0.95$ cm. and $H = 2.34$ cm.). It was verified also that D_a was inversely proportional to the pressures.

The results obtained for k^+ are discussed in § 6.51. The information obtained about the recombination coefficient is discussed in Chap. X, § 3.6. There is no doubt that much valuable information will be forthcoming from the applications of techniques such as this.

6.3. *Effect of charge transfer*

If ions A^+ drift through a gas of atoms B , which have a higher ionization potential than A , the charge exchange process,



is not energetically possible and does not complicate the interpretation of mobility data. Most attention has therefore been devoted to the study of the mobilities of alkali ions in various gases as in such cases charge transfer does not occur. A special case of interest arises when the ion drifts through its own gas. Such cases have been studied with the rare gas ions He^+ , Ne^+ , A^+ , Kr^+ , Xe^+ . If the ion A^+ is initially moving in a gas of atoms B with ionization potential less than that of A , the nature of the ions will change from A to B^+ as the stream ages and little of value may be derived from the study of such cases.

6.4. *The mobilities of ions in gases of higher ionization potential*

6.41. *Theoretical considerations.* When charge transfer cannot occur the classical formulae (27) and (9) may be applied provided the interaction energy between an ion and a gas atom is known. Alternatively, information about the interaction may be obtained from the observed mobilities and their temperature variation.

The general nature of the interaction between an atom and an ion has been discussed in § 2. At large separations the interaction has the form

$$V(r) \sim -\alpha\epsilon^2/r^4,$$

where α , the polarizability of the atom, is given in terms of the dielectric constant K of the gas at N.T.P. by the relation

$$\alpha = (K-1)/8\pi n,$$

where n is the number of gas atoms/c.c. at N.T.P. The interaction changes to a repulsion at a smaller distance. The simplest interaction including these features is the one used by Langevin†

$$\left. \begin{aligned} V(r) &= -\alpha\epsilon^2/r^4 & (r > r_0) \\ &\rightarrow \infty & (r < r_0) \end{aligned} \right\}. \quad (55)$$

† *Ann. Chim. Phys.* 5 (1905), 245.

The mobility k is given by $eD/\kappa T$, where D is the diffusion coefficient. Substituting the form (55) for $V(r)$ in the formulae (27), (28), (29), (30),

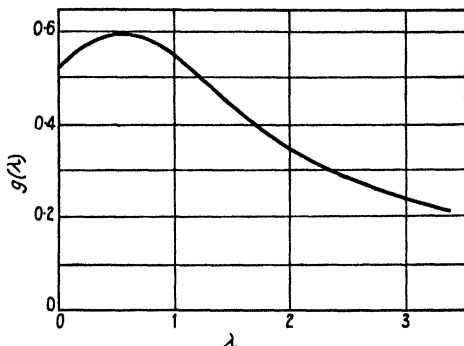


FIG. 182. The function $g(\lambda)$ appearing in Langevin's theory of ionic mobility.

(31), and (32) and taking the suffix 1 to denote properties of the gas atoms and 2 of the ions we find, after some reduction, that

$$k = (1 + M_1/M_2)^{\frac{1}{2}} \{\rho(K-1)\}^{-\frac{1}{2}} g(\lambda), \quad (56)$$

where

$$\lambda = (8\pi p r_0^4 / (K-1)\epsilon^2)^{\frac{1}{2}}, \quad (57)$$

$$g(\lambda) = 3/16\lambda f(\lambda), \quad (58)$$

$$f(\lambda) = \int_0^\infty \int_0^\infty x^2 e^{-x} p' \cos^2 \frac{1}{2} \alpha \, dp' dx, \quad (59)$$

$$\alpha = p' \int_0^\infty \frac{dr'}{\{r'^4 - p'^2 r'^2 + 1/\lambda^2 x\}^{\frac{1}{2}}}. \quad (60)$$

ρ is the density of the gas at N.T.P. and p the gas pressure. The function $g(\lambda)$ has been calculated numerically by Langevin and by Hassé and Cook.† It is illustrated in Fig. 182. It will be seen that, for small values of λ , $g(\lambda)$ varies slowly with λ so that for different ions in the same gas the mobility should be nearly proportional to $(1 + M_1/M_2)^{\frac{1}{2}}$. This is often useful in checking experimental results.

Hassé and Cook‡ have also considered an interaction of the form $\lambda r^{-8} - \mu r^{-4}$ in which both λ and μ are treated as parameters. This leads to a somewhat more complicated expression than (56), but for different ions in the same gas the most important factor determining the mobility is again $(1 + M_1/M_2)^{\frac{1}{2}}$.

† *Phil. Mag.* 12 (1931), 554.

‡ *Ann. Chim. Phys.* 5 (1905), 245.

6.42. The mobilities of the alkali ions—the interaction between an alkali ion and a rare gas atom. Because of the convenient sources available the most complete data have been obtained for ions of the alkali metals.

A number of measurements† of the variation of mobility with temperature have been carried out. In such work the experimental chamber was surrounded by a Dewar flask filled with liquid hydrogen, nitrogen, oxygen, or ethylene, for low temperatures, and by a suitable bath at high temperatures. The electrical leads passing from outside into the apparatus were made very fine to reduce heat conduction. In these experiments the hot ion source was placed 7.5 cm. above the shutter system, the ions being pulled down to it by an auxiliary field.

The measurements made of the mobilities of alkali ions in various gases at 760 mm. and 18° C. are given in Table VIII. The simple Langevin theory gives results in remarkably close agreement with these values for the rare gases if the observed values of the dielectric constant are used together with values of the radius r_0 derived from Slater's rules (see Chap. III, § 2.35). These rules enable one to estimate the radius of the outer electron shell in an atom or ion. r_0 is taken as the sum of these radii for the atom and ion concerned. The detailed nature of the agreement, which is exhibited in Table VIII, must, however, be largely fortuitous as study of the temperature variation reveals. On the other hand, it is such as to leave little doubt that the ions were really free from clustering.

Table IX gives the results of measurements of the temperature variation of the mobility of alkali ions in certain rare gases. From these data it is possible to test whether the interactions assumed by Langevin or by Hassé and Cook do represent good approximations and if so to determine the respective constants r_0 and λ , μ . It is then found that it is only for Cs^+ in He that good representation of the data may be obtained,‡ even with the best possible choice of the adjustable constants. For the Langevin interaction these are found to be $K-1 = 6.25 \times 10^{-5}$ (to be compared with the experimental value 6.8×10^{-5}) and $r_0 = 2.5 \times 10^{-8}$ cm. For Hassé and Cook's interaction the best fit is obtained with $\mu = 2.37 \times 10^{-43}$ and $\lambda = 4.9 \times 10^{-73}$ absolute units. This value of μ is about three times greater than would be given by the polarizability alone, showing that the usual van der Waals attractions are also effective.

† Na^+ in He, Cs^+ in He: Pearce, *Proc. Roy. Soc. A*, **155** (1936), 490. Li^+ -He, K^+ -A, Rb^+ -Kr, Cs^+ -Xe: Hoselitz, *ibid.* **177** (1941), 200.

‡ It seems probable from the nature of the variations that, for Li^+ and Na^+ in He, a good fit might still be obtained by an interaction of the form $\lambda r^{-s} - \mu r^{-4}$ with $s > 8$, but for K^+ in A, Rb^+ in Kr, and Cs^+ in Xe a more complicated interaction seems to be required.

TABLE VIII

Mobility of Alkali Metal Ions in cm./sec./volt/cm. at 760 mm. and 18° C.

Values derived from Langevin's theory are given in brackets.

Ion	Gas							
	He	Ne	A	Kr	Xe	H ₂	N ₂	CO
Li ⁺ unclustered	25.8 (22.9)	11.85 (12.0)	4.97 (5.17)	3.97 (4.17)	3.04 (3.19)	..	4.21	2.63
clustered	11.70	5.28	2.26	1.46	0.98	..	..	..
Na ⁺ unclustered	24.2 (20.0)	8.70 (8.20)	3.23 (3.44)	2.34 (2.50)	1.80 (1.88)	..	3.04	2.44
clustered	11.15	5.25	2.25	1.43	0.94	..	..	..
K ⁺ unclustered	22.9 (19.4)	8.0 (7.49)	2.81 (2.97)	1.98 (2.09)	1.44 (1.53)	13.5	2.70	2.32
clustered	11.85	5.26	2.19	..	0.92	..	..	..
Rb ⁺ unclustered	21.4 (18.5)	7.18 (6.73)	2.39 (2.57)	1.57 (1.66)	1.10 (1.17)	13.4	2.39	2.08
clustered	12.8	5.38	2.10	1.37	0.87	..	..	..
Cs ⁺ unclustered	19.6 (17.3)	6.50 (6.48)	2.24 (2.40)	1.42 (1.52)	0.97 (1.04)	13.4	2.35	1.98
clustered	13.9	5.48	2.18	..	0.83	..	..	..

TABLE IX

Variation of Mobility, at Constant Gas Density, with Temperature

Values in brackets for Li^+ in He are obtained from an absolute theoretical calculation by Meyerott (loc. cit.)

$T^\circ \text{K}$	Li^+ in He	Na^+ in He	Cs^+ in He	K^+ in A	Rb^+ in Kr	Cs^+ in Xe
20.5	20.0 (16.4)	..	..	..	..	..
78	21.8 (17.4)	..	17.5	1.30	..	..
90	22.2 (17.5)	18.5	18.0	1.52	1.15	..
195	23.9 (18.6)	20.9	19.2	2.34	1.57	1.02
273	..	..	..	..	1.575	1.005
291	25.8 (19.4)	22.8	18.9	2.81	1.58	1.01
370	..	..	..	..	1.59	1.01
389	27.8 (20.1)	24.0	18.1	..	..	..
400	..	..	..	3.07	..	..
450	..	..	..	..	..	1.03
455	..	..	..	..	1.64	..
460	..	..	..	2.95	..	..
477	..	24.6	..	..	..	..
483	29.2 (20.9)	..	..	..	..	..
492	..	..	17.4	..	..	..

As the observed variation (see Fig. 183) falls in between the best given by the respective theories, it is probable that the repulsive force should be rather 'harder' than assumed by Hassé and Cook.

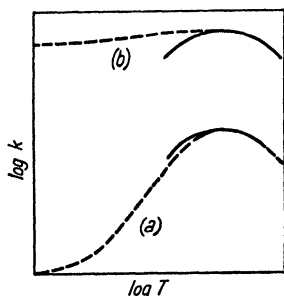


FIG. 183. Comparison of observed and calculated variation with temperature of the mobility k of Cs^+ ions in He. ——— observed results. The two curves represent the same experimental points displaced along the $\log k$ axis. - - - - - calculated curves: (a) Langevin theory, (b) theory of Hassé and Cook.

In all other cases the two theories give unsatisfactory results so that, to proceed farther, greater generality must be introduced in the assumed interactions.

An attempt has been made by Meyerott† to calculate the interaction between Li^+ and He from quantum theory, without any assumptions (see § 2). He finds that

$$V(r) = 1.6 \times 10^{-9} [e^{-5.8r} - 0.00147r^{-4} - 0.0105r^{-6}] \text{ ergs, } (61)$$

where r is measured in Å. With this interaction he calculated the mobility over the observed temperature range. In this calculation the quantal formula for $I(\theta)$ in § 3.32 was used, but for most of the temperature range the classical expressions (23-5) would have been sufficiently accurate.

The results obtained are given in Table IX. The agreement is not very satisfactory and suggests that the potential minimum is rather

† *Phys. Rev.* 66 (1944), 242.

deeper than it should be. Further evidence for this is provided from data on cluster formation by Li^+ in He at low temperatures (see § 6.62).

6.5. The mobilities of ions in their own gases

6.51. The experimental data. The first observations of the mobility of an ion in its own gas were made by Tyndall and Powell† in 1930, for helium. They used a radio-active source for the ions and obtained the value 13 cm./sec./volt/cm. under standard conditions. The work was repeated‡ using a glow-discharge source (see Chap. VIII, § 2) and the value 21.4 cm./sec./volt/cm. was obtained. This value, considerably higher than the earlier one, was considered the more reliable. On the other hand, Biondi and Brown, using the micro-wave method of measuring the ambipolar diffusion coefficient of ions in helium, obtained a value of 13.7 cm./sec./volt/cm. which is in close agreement with the earlier value (see also the discussion in § 6.3).

In all these experiments it is necessary to use very pure gases in the discharge so as to obtain a rare gas ion without admixture of other ions. It was not until 1939 that Munson and Tyndall§ obtained definite data for the mobilities of Ne^+ , A^+ , Kr^+ , and Xe^+ in their own gases. The results obtained are given in Table X.

TABLE X

Mobilities, k , of the Rare Gas Ions in their own Gases in cm./sec./volt/cm. at 760 mm. and 18° C.

<i>Ion</i>	<i>k observed</i>	<i>k_e estimated from alkali ion experiments</i>	<i>k/k_e</i>
He^+	21.4	25.6	0.84
Ne^+	6.23	8.7	0.70
A^+	1.93	2.81	0.70
K^+	0.94	1.57	0.60
Xe^+	0.65	0.97	0.66

It might have been expected, at first sight, that these mobilities should be nearly the same, apart from the mass factor $(1 + M_1/M_2)^{1/2}$, as those for the corresponding alkali ion in the same gas (i.e. He^+ in He should be closely comparable with Li^+ in He). In Table X the observed values for the appropriate alkali ion, corrected for the mass difference, are given as k_e . It will be seen that these estimated values are between 20 and 60 per cent. too large in all cases. This implies that the diffusion cross-section for collision between, say, He^+ and He is substantially larger than

† *Proc. Roy. Soc. A*, **129** (1930), 162.

‡ *Ibid.* **134** (1931), 125.

§ *Ibid.* **177** (1941), 187.

for Li^+ and He. As the most obvious difference between the two cases is the possibility of charge exchange in the former but not in the latter, it is probable that this effect is mainly responsible.

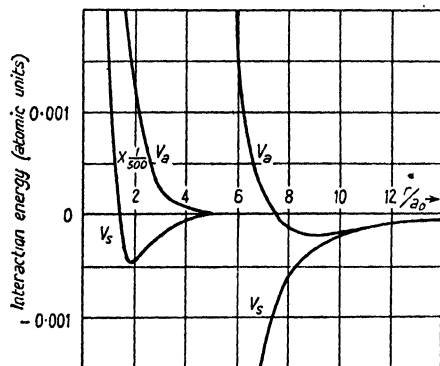


FIG. 184. Calculated interaction energies V_s and V_a between a normal helium atom and a normal helium ion.

6.52. Theory of the charge exchange effect. In developing the theory of the mobility of ions it has been assumed hitherto that there is only one possible interaction between an ion and an atom in their normal states. It has already been pointed out in § 2 that this is no longer true for an ion in its own gas. The interaction between an atom A and an ion A^+ in their normal states may take either one of two forms.† This is because the electronic wave function (see Chap. IV, § 5.1) may either be symmetric or antisymmetric with respect to interchange of the nuclei. The antisymmetric interaction V_a is very similar to the interactions assumed in discussing the mobility of alkali ions. While the symmetric interaction V_s also behaves at large separations as $-\alpha\epsilon^2/r^4$ it includes a strong attraction which persists to much smaller nuclear separations than for the antisymmetric case. In fact this interaction involves a chemical attractive force as well as a van der Waals and polarization attraction.

The two interactions have already been discussed for H_2^+ in Chap. IV, § 5.1, for which case they are illustrated in Fig. 113 of that chapter. The calculated interactions‡ for He_2^+ are given in Fig. 184.

The cross-section which should now be included for Q_d in the formula (7) is the mean of the two cross-sections $Q_d(a)$ and $Q_d(s)$ calculated for the separate interactions V_a and V_s respectively. Since V_s is so different

† It is assumed that either the ion or the atom has an outer closed shell of electrons (see § 2).

‡ Massey and Mohr, *Proc. Roy. Soc. A*, **144** (1934), 188.

from V_a and hence from the interactions determining the mobility of alkali ions in the rare gases, it is not surprising that the reduced mobilities k_e of Table X, derived from the latter, are considerably different from the observed mobilities given in that table. Moreover, since V_s includes a very strong attraction, the value of $Q_a(s)$ is likely to be considerably larger than $Q_a(a)$. This would result in a smaller mobility than expected, in agreement with the observed data.

So far in this theory there has been no direct mention of charge exchange. However, the difference $V_a - V_s$ arises solely from the possibility of an electron changing from one nucleus to the other without altering the energy of the system as a whole. The differential cross-section $I(\theta) d\omega$ for the collision can be regarded as made up of two parts $(I_0 + I_1) d\omega$, the first corresponding to a direct collision, the second to one involving charge exchange. If η_l, δ_l are the l th-order phases (see Chap. III, § 2.2) for the scattering by the fields V_a, V_s respectively, then

$$\left. \begin{aligned} I_0 &= \frac{1}{16k^2} \left| \sum (2l+1)(e^{2i\eta_l} + e^{2i\delta_l} - 2) P_l(\cos \theta) \right|^2 \\ I_1 &= \frac{1}{16k^2} \left| \sum (2l+1)(e^{2i\eta_l} - e^{2i\delta_l}) P_l(\cos \theta) \right|^2 \end{aligned} \right\} \quad (62)$$

Since I_1 is determined by the difference between the corresponding phases η_s, δ_s it only arises from the difference between V_a and V_s which in turn is a consequence of charge exchange. A further discussion is given in Chap. VIII, § 6.1.

The calculation of the mobility of He^+ in He has been carried out along these lines by Massey and Mohr.[†] They first determined the interactions V_a and V_s by a direct application of wave mechanics, obtaining the results illustrated in Fig. 184. $Q_a(a)$ and $Q_a(s)$ were calculated from the quantum formula (19) for $I(\theta)$ and on substitution in (9) gave the mobility as 12 cm./sec./volt/cm. under standard conditions. This is considerably smaller than the value 21.4 cm./sec./volt/cm. observed by Tyndall and Powell for the ions obtained from a glow discharge in helium. The reason for this discrepancy is still not clear. As the small value of the calculated mobility arises from the magnitude of V_s it might be that Massey and Mohr overestimated this interaction. They show, however, that it is unlikely that the error made in this respect could be large enough. Mott[‡] has suggested that the separation of the two interactions at the nuclear distances concerned may be less definite than

[†] Ibid.

[‡] See Tyndall, *The Mobility of Positive Ions in Gases* (1938), p. 36.

assumed as the frequency of electron exchange at such distances is quite small. Owing to the powerful attraction, however, the effect arises from rather smaller separations than would be expected from the relative kinetic energy. At these separations the splitting into V_a and V_s should be quite definite and as given by the usual theory. Meyerott† has drawn attention to the possibility that the ions investigated by Tyndall and Powell were really He_2^+ as it is known that quite a considerable proportion of such ions are formed in a helium glow discharge. The mobility of such ions might well be considerably larger than for He^+ because, for them, there is no interaction with He atoms of the same form as V_s but only as V_a . Some evidence in favour of this view-point is provided by the earlier observations of Tyndall and Powell using a radio-active source of He^+ ions, which gave a rather lower mobility (13 cm./sec./volt/cm.). The fact that the ambipolar diffusion method also gives the lower mobility, in agreement with these early observations and the theory, certainly suggest the possibility that in their later experiments Tyndall and Powell were not observing the mobility of He^+ ions.

6.53. *The effect of charge exchange on the mean velocity of positive ions moving through a strong electric field in their own gas.* The measurement of the mobility k of positive ions in a gas and the influence of charge exchange in such cases has been discussed in §§ 6.51, 6.52. The considerations of those sections apply when the electric field is so small that the mean energy in the direction of the electric field acquired by a positive ion between collisions is small compared with the mean energy of random motion. If this condition is not satisfied the drift velocity of the ions is no longer proportional to F/p . A variation of k with F/p at high values of F/p has been observed in several experiments.‡ For example, for K^+ ions in He and A Hershey§ found k to remain constant up to values of F/p of about 5 volt/cm./mm. Hg, to increase at first for higher values of F/p , and ultimately to decrease monotonically with further increase of F/p . For Hg^+ ions in Hg Kingdon and Lawton|| found the mean velocity u to be proportional to $(F/p)^{1/2}$ in the range of F/p from 20 to 6,000 volt/cm./mm. Hg.

A theory of this behaviour based on charge exchange has been given by Sena.†† It is applicable to the case of the motion of ions in their own gas under conditions in which collisions involving charge exchange are

† *Phys. Rev.* **66** (1944), 242.

‡ Mitchell and Ridler, *Proc. Roy. Soc. A*, **146** (1934), 911; Hershey, *Phys. Rev.* **56** (1939), 908.

§ Loc. cit.

|| *Phys. Rev.* **56** (1939), 215.

†† *J. Phys. U.S.S.R.* **10** (1946), 179.

predominant. The characteristic feature of such collisions is that the new ion is formed with very small initial energy so that the process can be regarded as though a single ion were moving but loses all its kinetic energy at each collision. If the thermal velocities of the neutral atoms can be neglected, the mean velocity u acquired between two collisions by an ion of mass M and charge ϵ in a field F is $(\epsilon F x / 2M)^{\frac{1}{2}}$, where x is the free path between the collisions.

Allowing for the distribution of free paths the mean velocity of motion of the ions in the direction of the field is

$$\begin{aligned} \bar{u} &= (\epsilon F / 2M l_0)^{\frac{1}{2}} \int_0^{\infty} x^{\frac{1}{2}} e^{-x/l_0} dx \\ &= \frac{1}{2} (\pi \epsilon F l_0 / 2M)^{\frac{1}{2}}, \end{aligned}$$

where l_0 is the mean free path for charge exchange. That is

$$\bar{u} = (95\pi\epsilon / MnQ_c)^{\frac{1}{2}} (F/p)^{\frac{1}{2}}, \quad (63)$$

where Q_c is the charge exchange cross-section and n the number of gas atoms per c.c. at a pressure of 760 mm. Hg. Since for charge exchange collisions between ions and atoms of the same gas Q_c would not be expected to vary much with energy in this range, this result is in good agreement with Kingdon and Lawton's observations.

From their measured mean velocity of 10^5 cm./sec. for a value of F/p of 1,000 volt/cm./mm. Hg, Sena deduced a value for Q_c of 5.3×10^{-15} cm.² for Hg^+ ions of energy 1.6 eV energy in mercury vapour. This appears reasonable (see § 10.2).

In the plasma of the glow discharge, values of F/p of the order of 100 volt/cm./mm. Hg are usual, so that the process suggested by Sena undoubtedly plays an important part in determining the mean energy of the positive ions. It is easy to show, moreover, that, if such a mechanism is valid, the fraction of ions with an energy of drift motion between E and $E + dE$ is given by

$$(1/\epsilon F l_0) \exp\{-E/\epsilon F l_0\} dE. \quad (64)$$

6.6. Study of cluster formation

The refinements of technique introduced by Tyndall and his collaborators have made possible a quantitative study of certain aspects of cluster formation. They have been able to observe the effect on the mobility of adding small measurable admixtures of polar substances to gases which were effectively pure.

6.61. *The clustering of water molecules.* The most thorough study of this kind has been made by Munson and Tyndall† using water as the polar substance. The apparatus used was substantially the same as that with which the main mobility measurements were carried out except that, before the ions were allowed to pass

† *Proc. Roy. Soc. A*, **172** (1939), 28.

through the regions between the shutters, which were 1 cm. apart, they were aged by passage for 3 cm. through an ageing field. In most of the experiments the ratio F_1/F_2 of the ageing field F_1 to the field F_2 between the shutters was maintained constant while both were varied. With this arrangement a study was made of the mobilities of the alkali ions in the rare gases containing measured admixtures of water vapour. Special technique using optical magnification with a Rayleigh gauge† had to be employed to measure the partial pressure of the added water vapour, which was, in certain experiments, as low as 4×10^{-4} mm. Hg.

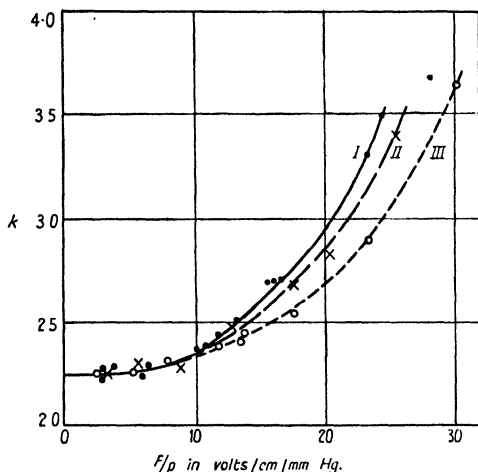


FIG. 185. Observed mobility of Li^+ ions, in A in the presence of water vapour, as a function of F/p .

- | | | |
|-------------------------------------|---|------------------------|
| I. 0.008–0.43% H_2O | • | } Experimental points. |
| II. 1.3% H_2O | × | |
| III. 2.8% H_2O | ○ | |

It was found that only two groups of ions were obtained in each case, one having the full mobility and consisting of unclustered ions, the other with a lower mobility consisting of clustered ions. The mobility of this latter group was found, for a given F/p (see Fig. 185), to be smaller the smaller the percentage of water vapour. However, this effect became less marked as F/p was reduced so that, in the limit of vanishing F/p , the mobility of the clustered ion was independent of the percentage of water vapour. This shows that the size of the cluster formed is independent of the concentration of water vapour if the ions are very slow. As the water-vapour concentration was reduced, at small F/p , the current due to clustered ions became relatively smaller, but in no case were any ions of intermediate mobility observed. The measured values of the mobilities for the fully clustered ions (in the limit of very small F/p) are given in Table VIII.

These results suggest that the chance of attaching the first water molecule is quite low, but once one such molecule is attached the chance of attaching others is so much increased that the final cluster builds up very rapidly. Presumably

† Schrader and Ryder, *Phys. Rev.* 13 (1919), 321.

the first attachment can only take place in a three-body collision. Once this occurs the structure is so complex that the excess energy acquired in attaching a second molecule is redistributed among the many internal degrees of freedom and may be dissipated gradually in subsequent collisions. In support of these ideas the fraction of ions clustered for a given F/p is observed to increase with the pressure of the main gas. On the other hand, the chance of three-body encounters, under many conditions in which appreciable clustering was observed, was very small. Thus perceptible clustering occurred in xenon with 0.005 per cent. water in which the chance of a three-body collision between an ion, a water molecule, and a gas molecule during the life of an ion was as low as 10^{-4} .

By applying Langevin's theory, assuming no increase in the effective diameter r_0 , an upper limit of about 6 is found for the number of clustered molecules in the saturated condition. A closer estimate for Li^+ suggests that the actual number is about 4, in agreement with the predictions of Bernal and Fowler† concerning hydration of ions in electrolytes. On the other hand, the latter authors predicted no attachment to Cs^+ , whereas clustering certainly occurred even for these ions.

The reason for the observed increase in mobility of the clustered group with F/p is not clear, but must be due in some way to the increased mean energy of the ions which corresponds to a temperature increase.

6.62. *The appearance of clustered alkali ions in pure rare gases.* It was found by Hoselitz,‡ in the course of an investigation of the mobility of Li^+ in Xe, that a group of ions of smaller mobility than the main group was always present and did not disappear after the most careful purification. It was suspected that these ions really arose from addition of one or more xenon atoms to the lithium ion. Confirmation of this possibility was obtained by observation of a similar group when studying the mobility of Li^+ in He at liquid-hydrogen temperatures at which all polar impurities would have been frozen out. A detailed study§ of the effect was therefore carried out on similar lines to the work described in § 6.61.

The fraction c of clustered ions was observed as a function of F/p and extrapolated to zero F/p . From the observed mobilities an estimate could be made by Langevin's method of the number of clustered atoms. Application of the usual formulae of statistical mechanics then gives an estimate of $\sum D_r/r$, where D_r is the energy required to remove an atom from a cluster containing r atoms. The results of such an analysis are given in Table XI for lithium ions in various rare gases. They form a consistent set in that the dissociation energy increases with the mass of the rare gas atom. The values found for helium are considerably smaller than would have been expected from the Li^+ -He interaction calculated by Meyerott (§ 6.42).

6.63. *Cluster formation with negative ions.* Negative ions form clusters in the same sort of way as positive ions. A study of the formation of clusters by negative ions formed by electron attachment in O_2 , air, N_2O , and NH_3 in the same gases has been made by Nielsen and Bradbury.||

6.7. Elastic collisions of metastable atoms with normal gas atoms

The cross-section for collision between a metastable atom and a gas atom of the same kind may be determined in much the same way as that

† *J. Chem. Phys.* **1** (1933), 515.

‡ *Proc. Roy. Soc. A*, **177** (1941), 200.

§ Munson and Hoselitz, *ibid.* **172** (1939), 43.

|| *Phys. Rev.* **51** (1937), 69.

TABLE XI

Effect of Clustering on the Mobility of Li⁺ Ions in the Rare Gases

Gas	Temperature ° K	k/k_0	$c/(1-c)$	n	D (eV)
He	20	1.10	> 3	1.8	> 0.016
	77	..	≈ 1	..	≈ 0.07
	90	..	< 1	..	< 0.08
Ne	90	1.98	> 10	..	> 0.13
	195	..	< 0.1	..	< 0.16
A	195	2.38	> 10	2.7	> 0.25
	290	..	< 0.33	..	< 0.29
Kr	290	3.09	> 10	2.6	> 0.31
	360	..	< 2	..	< 0.35
Xe	290	3.84	> 20	2.6	> 0.42

 k, k_0 = mobility of unclustered and clustered ion respectively. c = fraction of clustered ions. n = upper limit to average number of gas atoms attached to each ion. D = mean energy to extract one atom from cluster.

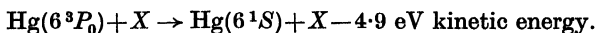
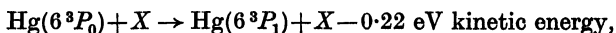
for collisions between an atom and an ion of the same kind. Corresponding to the possibility of transfer of excitation on collision, there are two possible interactions between a metastable helium atom (He') and a normal helium atom. The total cross-section is the mean of the cross-sections due to each interaction separately. Alternatively the cross-section can be regarded as the sum of one corresponding to direct scattering and another due to transfer of excitation. Direct measurement of the total cross-section under gas-kinetic conditions is very difficult because of the very high angular resolution required.† There is more hope of measuring the diffusion coefficient and hence the diffusion cross-sections. Just as for the collision between an ion and an atom of the same kind (see § 6.5), this should be appreciably larger than that for two normal atoms.

† Experiments have been carried out by Dorrestein and Smit (*K. Wet. Amst.* 41 (1938), 725), using the apparatus described in Chap. II, § 5.4, in which a wide beam of metastable helium atoms issuing from a collision chamber, in which they were produced by electron excitation of normal atoms, was allowed to pass through helium gas in a side tube. Its intensity after this passage was measured by the electron emission produced in a platinum collector (see Chap. IX, § 6.1). An effective absorption cross-section was obtained by determining the variation of the emitted current from the collector as the gas pressure and path length in the collector were varied. It is probable that this cross-section is effectively that for transfer of excitation between the incident metastable and struck gas atoms. With the poor resolution afforded by the collector, metastable atoms suffering small deviations would still be collected. This would exclude observation of most of the direct collisions. The only collisions in which they would suffer large apparent deviations would be ones in which excitation transfer occurred, the struck atoms carrying off the excitation in a direction making a large angle with that of the incident metastable atom. The cross-section was found to be about 2×10^{-16} cm.²

7. Collisions in which electron transitions occur—Quenching of radiation

7.1. Introduction

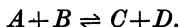
We now consider inelastic collisions in which electron transitions occur. As we are confining ourselves to gas-kinetic conditions the energy of relative motion is never more than a fraction of an electron volt. Unless the energy change in the electronic levels is also of the order of a fraction of an electron volt, the only cases involving collisions between atoms in which electron transitions can take place will be of the superelastic type, in which energy of electron excitation is transferred to energy of relative motion. The removal of an atom from a metastable state by collision with a second atom may take place by deactivation in this way or by further excitation. Thus we have, for example,



Numerous other examples will be discussed below, including cases in which a change of the electronic states of both atoms occurs.

When one, or both, of the colliding partners is a molecule changes in the vibrational and rotational states of the molecules may also take place on collision. These may or may not be associated with electronic transitions. In this section we shall confine the discussion to cases in which the latter transitions do occur. The following sections will be devoted to cases where they do not.

It may readily be shown by arguments based on statistical balancing that the cross-section for a given superelastic process is related to that for the corresponding inverse process (see also Chap. II, § 5.3, and Chap. III, § 3.76). Consider a reaction



Let p_{AB} be the momentum of the relative motion of the systems A and B , p_{CD} of the systems C and D . Then we have, if Q_{AB} is the effective cross-section for the forward process, Q_{CD} for the inverse,

$$g_A g_B p_{AB}^2 Q_{AB} = g_C g_D p_{CD}^2 Q_{CD}, \quad (65)$$

g_A, g_B, g_C, g_D are the respective statistical weights of the internal states of the systems A, B, C , and D . If the forward process is of superelastic type $p_{CD}^2 > p_{AB}^2$ so that, in general, the cross-section for the superelastic process is greater than for the corresponding inverse process.

We now proceed to discuss the experiments which give information about these cross-sections.

7.2. Quenching of radiation

Suppose that, by some exciting agency of constant strength, a number R of atoms A is raised per second to an excited state so that at any instant there are n'_A excited atoms present. If τ is the lifetime of these atoms towards emission of radiation, then the intensity of radiation emitted per second will be proportional to n'_A/τ .

We suppose now that the conditions are such that this radiation does not suffer absorption before emergence from the gas to an observation chamber. This requires that the atoms A are present at a sufficiently low pressure. Otherwise they will absorb much of the radiation by a resonance process and re-emit it one or more times so that imprisonment of the radiation occurs and the emergent intensity is not proportional simply to n'_A/τ .

If the excited atoms lose their excitation solely by radiation then, in equilibrium,

$$n'_A/\tau = R. \quad (66)$$

On the other hand, if a foreign gas of molecules B , which are capable of removing the electronic excitation of an atom A in a collision at a gas-kinetic velocity, is present, a number $n''_A Z$ of excited atoms will be deactivated per second by these collisions. Z is the number of deactivating collisions made per second by an excited atom A and is given in terms of the effective collision cross-section for the deactivation by the usual gas-kinetic formula

$$Z = 2n_B Q \{2\kappa T(M_A + M_B)/\pi M_A M_B\}^{\frac{1}{2}}, \quad (67)$$

where n_B is the number of molecules B /c.c., T is the absolute temperature, and M_A , M_B are the respective masses of the atoms A and molecules B .

We now have, for equilibrium,

$$R = n''_A(Z + 1/\tau), \quad (68)$$

provided the strength of the exciting agency is unchanged, and the addition of the foreign gas does not alter its effectiveness in producing excited atoms, i.e. by producing line broadening.† Comparing (68) and (66) it will be seen that the foreign gas decreases the intensity of emitted radiation in the ratio $n''_A/n'_A = 1/(1 + \tau Z)$. Measurement of this quantity therefore gives $Z\tau$. The radiative lifetime τ may be measured by suitable experiments‡ so that Z and hence Q may be derived.

The smallness of the effective cross-section Q for the deactivation of

† See, for example, Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge, 1934, Chap. IV.

‡ Ibid., Chap. III.

excited atoms A by the molecules B may impose a limitation on the method, for it may be that, to avoid broadening, the foreign gas pressure has to be so low that quenching is also negligible. Fortunately, in many cases, this is not so.

Two sources of excited atoms have been used for quantitative experiments on quenching—absorption of resonance radiation and optical dissociation of molecules.

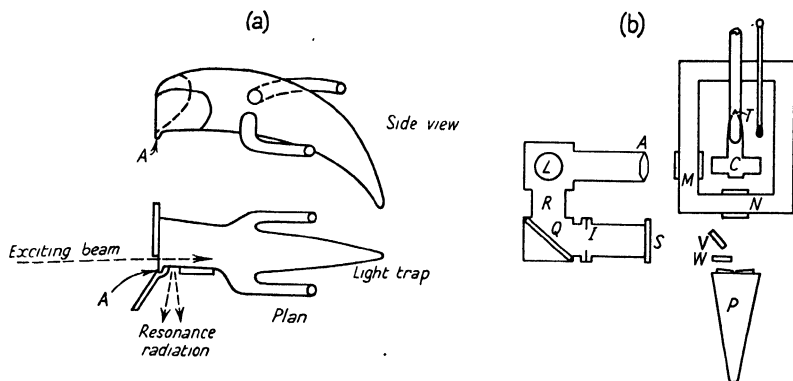


FIG. 186. (a) Illustrating the design of a resonance lamp. (b) Apparatus used by Norrish and Smith for studying the quenching of sodium resonance radiation.

7.21. Quenching experiments with resonance radiation. In principle these experiments consist in exciting the atoms of a vapour such as mercury by a beam of radiation from a suitable source in which the same vapour is excited. The emission from this source will include radiation arising from transitions from the first excited state (which combines optically with the ground state) to the ground state of the atoms concerned. If radiation of this wave-length is selected to illuminate the vapour, atoms will be raised to the first excited state by resonance absorption.

A typical resonance lamp for quenching experiments has the form shown in Fig. 186(a). The light trap is arranged to prevent internal reflections and so to reduce the amount of stray light present. To reduce the path, through the gas, of the emergent radiation, which is observed at 90° to the exciting beam, the entrance window has a slight projection, A , so there is no large thickness of unexcited gas between the exciting beam and the window from which the resonance radiation emerges. In this way imprisonment of the resonance radiation is avoided. Although it is possible to make allowance for imprisonment in terms of

a theory such as that of Milne,[†] it renders the interpretation of the experiments very much more difficult and uncertain.

In order to satisfy the condition that the addition of foreign gas should not change the effectiveness of the exciting agency for producing excited atoms it is necessary that the foreign gas should not produce appreciable Lorentz broadening of the absorption lines of the main gas atoms. This limits the pressure of the foreign gas which may be used and makes it difficult to obtain anything more than qualitative information about the quenching cross-sections when they are small. If they are comparable with the gas-kinetic values, then the quenching can be observed at foreign gas pressures for which Lorentz broadening is unimportant.

The quenching of resonance fluorescence has been studied quantitatively in mercury,[‡] cadmium,[§] and sodium.|| Fig. 186 (*b*) illustrates the apparatus used in the most recent experiments, those of Norrish and Smith on sodium. *C* is the quenching cell with light trap *T*. The exciting radiation, emitted from the sodium lamp *L*, passed through the lens *A* and the two glass windows *M* into the cell *C*. The resonance radiation emitted from the cell through the glass windows *N* was observed in the photometer *P*. To avoid errors due to variation in the intensity of the source *L* the intensity of the resonance radiation entering the photometer was compared always with that entering directly from the source *L* via the tube *R*, mirror *Q*, iris diaphragm *I*, opalescent screen *S* mirror *V*, and adjustable wedge *W*.

The resonance cell was enclosed in hot air at a thermostatically controlled temperature and contained specially purified sodium. Special precautions were also taken to ensure that the foreign gases introduced were very pure.

To check that imprisonment of resonance radiation was not important it was verified that, at a temperature 20° above that (130° C.) of the cell in the actual observations, the resonance radiation was emitted only from the path of the exciting beam.

It was found that foreign gases could be divided into two categories, which quench strongly and weakly respectively. For the former the quenching cross-sections are greater than 10⁻¹⁵ cm.² and it is only necessary to employ pressures of a few mm. Hg to make satisfactory

[†] *J. Lond. Math. Soc.* **1** (1926), 1; a further discussion has been given by Holstein, *Phys. Rev.* **72** (1947), 1212.

[‡] Zemansky, *ibid.* **36** (1930), 919; Bates, *J.A.C.S.* **52** (1930), 3825 and **54** (1932), 569; Duffendaack and Owens, *Phys. Rev.* **46** (1934), 417; Evans, *J. Chem. Phys.* **2** (1934), 445; Olsen, *Phys. Rev.* **60** (1941), 739; Olsen and Kerr, *ibid.* **72** (1947), 115.

[§] Lifson and Mitchell, *ibid.* **48** (1935), 625.

|| Norrish and Smith (W. M.), *Proc. Roy. Soc. A*, **176** (1940), 295.

measurements. Thus in Fig. 187 the observed ratio of $n'/n'' = 1 + \tau Z$ is plotted against the foreign gas pressure of hydrogen, nitrogen, and benzene respectively. It is clear that a linear relation is found as it should be and the effects of Lorentz broadening are likely to be unimportant. This is further confirmed by reference to the measurements by Schutz† of Lorentz broadening of the sodium absorption line by helium.

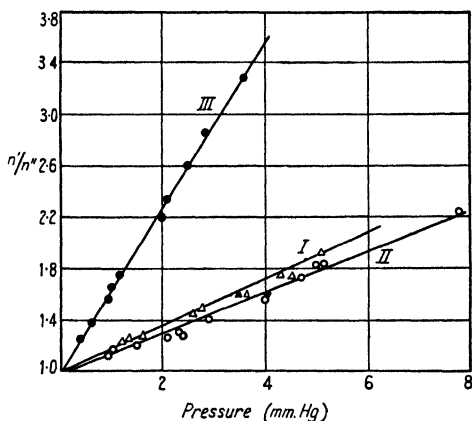


FIG. 187. Observed reciprocal n'/n'' of the quenching ratio as a function of pressure for the quenching of Na resonance radiation by I, H₂; II, N₂; III, C₆H₆.

At the temperature of the quenching experiments and a pressure of 5 mm. the Lorentz breadth, which does not depend markedly on the nature of the foreign gas, was found to be less than 3 per cent. of the Doppler breadth.

For the strongly quenching gases measurements could therefore be made with a quenching ratio between 0.50 and 0.67 without risk of complication by Lorentz broadening. On the other hand, for the weakly quenching gases, the quenching at a pressure of 5 mm. Hg was only barely measurable and the cross-sections had to be estimated from quenching ratios of 0.97. To obtain much stronger effects it was necessary to raise the foreign gas pressure so much that Lorentz broadening became very serious. Thus it was found, for helium, that the intensity of the resonance radiation actually increased when pressures of 30–50 mm. Hg of the gas were added. The values given for the quenching cross-sections for these weakly quenching gases can therefore only be regarded as rough estimates.

† *Zeits. f. Phys.* **45** (1927), 30; **71** (1931), 301.

The results obtained in these and other experiments are given in Table XII.†

7.22. Excited atoms produced by optical dissociation. Certain molecules such as NaI dissociate on absorption of a quantum with frequency lying in a certain range, to produce an excited and a normal atom, viz.:

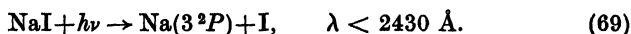


TABLE XII

Observed Cross-sections (in 10^{-16} cm^2) for Quenching of Resonance Radiation by Foreign Gases

Excited atom	Na	Hg	Cd	Tl(3S_1)
<i>Foreign gas</i>				
He	$\sim 0^{(1)}$	$\sim 0^{(5,7)}$	..	..
Ne	..	$\sim 0^{(8)}, 1.0^{(7)}$	..	..
A	..	$\sim 0^{(8)}, 0.7^{(7)}$	..	$(2.6^{(10)})$
Kr	..	$\sim 0^{(8)}, \sim 0^{(7)}$	..	..
H ₂	$23.2^{(1)} (19^{(2)})$	$18.8^{(11)}$	$2.10^{(9)}$	$(\sim 0^{(10)})$
D ₂	..	$26.6^{(11)}$	$0.60^{(9)}$	..
N ₂	$45.5^{(1)}$ $(91^{(3)}, 28^{(2,4)})$	$6.0^{(8)}$	$0.066^{(9)}$	$(11.0^{(10)})$
O ₂	..	$62^{(6)}, 70^{(8)}$	..	$(23-86^{(10)})$
NO	..	$105^{(6)}$	..	..
CO	$87.9^{(1)} (12^{(4)})$	$183^{(6)}$	$0.44^{(9)}$	$(10.8^{(10)})$
H ₂ O	..	$3.1^{(11)}$	..	$(10^{(10)})$
CO ₂	$(53^{(4)})$	$11.1^{(6)}$	..	$(30^{(10)})$
NH ₃	..	$10.4^{(11)}$	$0.13^{(9)}$	..
CH ₄	$0.3^{(1)}$	$0.18^{(5)}, 0.26^{(6)}$	$0.038^{(9)}$	..
C ₂ H ₆	$0.5^{(1)}$	$1.32^{(5)}, 18.6^{(6)}$	..	..
C ₂ H ₄	$138^{(1)}$	..	..	..
C ₃ H ₈	$0.6^{(1)}$	$5.0^{(5)}, 7.2^{(6)}$	..	..
C ₃ H ₆	$163^{(1)}$	..	..	..
C ₆ H ₆	$235^{(1)}$	$132^{(6)}, 188^{(6)}$	..	..
C ₆ H ₁₂	$1.25^{(1)}$	..	..	..

The bracketed values were obtained with excited atoms produced by optical dissociation, the others, with excited atoms produced by resonance radiation.

References

1. Norrish and Smith (W.), *Proc. Roy. Soc. A*, **176** (1940), 295.
2. Winans, *Zeits. f. Phys.* **60** (1931), 631.
3. von Harnos, *ibid.* **74** (1932), 379.
4. Kisilbasch, Kronratjew, and Leipunsky, *Phys. Zeits. Sowjetunion*, **2** (1932), 201.
5. Bates, *J.A.C.S.* **54** (1932), 569.
6. Zemansky, *Phys. Rev.* **36** (1930), 219.
7. Olsen, *ibid.* **60** (1941), 739.
8. Olsen and Kerr, *ibid.* **72** (1947), 115.
9. Lifson and Mitchell, *ibid.* **48** (1935), 625.
10. Prileschaweja, *Acta Physicochim.* **2** (1935), 647.
11. Evans, *J. Chem. Phys.* **2** (1934), 445.

† It has been common to give quenching cross-section in terms of the square R^2 of the effective quenching radius instead of as πR^2 . In Table XII the latter more usual cross-section is given.

This process may be used as a source of excited atoms for quenching experiments. It has the advantage that the concentration of sodium atoms is always very small. Absorption of the emitted radiation, the *D* lines of sodium, therefore occurs to a negligible extent in the vapour so that there is no risk of radiation imprisonment. Foreign gases may

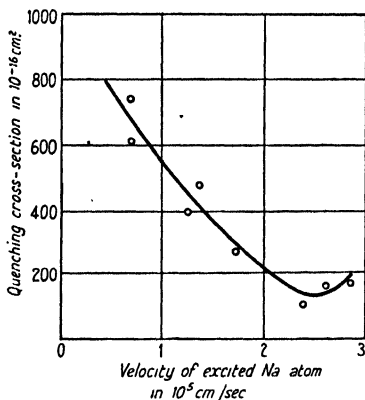


FIG. 188. Observed variation of the cross-section for quenching of excited Na atoms by I_2 with velocity of the sodium atoms. (Note that the ordinates refer to true cross-sections and not the squares of the quenching radii sometimes given in the literature.)

be used even though they react chemically with sodium. It is also possible in this type of experiment to obtain some information about the variation with relative velocity of the effective cross-section for the quenching process. This is because, by varying the frequency of the dissociating radiation, the velocity of the excited atoms produced may be varied.

This method has been applied to sodium produced from $\text{NaI}^\dagger$ and $\text{NaBr}^\ddagger$ and to thallium produced from $\text{TlI}^\S$. Some of the results obtained are given in Table XII. The most thorough study of the variation of a quenching cross-section with relative velocity of the colliding systems has been carried out by Terenin and Prileschawaja[†] for the quenching of sodium radiation by I_2 . By using successively as exciting sources the resonance radiation from Fe, Tl, Sb, Ni, Cd, Zn, Mg, and Al lamps they were able to measure the quenching cross-section for velocities of the sodium atom ranging from 0.7 to 2.8×10^5 cm./sec. Their results are illustrated in Fig. 188.

[†] *Zeits. f. phys. Chem. B*, **13** (1931), 72.

[‡] Winans, *Zeits. f. Phys.* **60** (1930), 631.

[§] Prileschawaja, *Acta Physicochim.* **2** (1935), 647.

7.23. Observed deactivation cross-sections. Table XII gives the observed cross-sections for deactivation of Hg, Cd, Na, and Tl by various foreign gases. The method used in each case is indicated. The data are discussed in § 11.

8. Collisions in which electronic transitions occur—Sensitized fluorescence

The effect of the admission of foreign gas in quenching resonance fluorescence has been discussed in § 7.21. In certain circumstances, however, excitation may be transferred in collision to the foreign gas molecules. Radiation from these excited molecules will then occur, giving rise to sensitized fluorescence. In many cases the transfer process will involve increase of kinetic energy so that the excited molecules will have a kinetic energy considerably in excess of the gas-kinetic value. This will appear in a Doppler effect of the emitted lines.

Observation of the intensity distribution in the spectrum of the sensitized fluorescence gives valuable information about the relative magnitudes of the cross-sections for transfer of excitation. It is difficult, however, to obtain the absolute magnitudes in this way.

The first experiments which established the existence of the effect were made by Cario and Franck,[†] who observed the sensitized fluorescence of thallium by mercury excited to the 6^3P_1 level by resonance absorption of the 2537 mercury line. This level lies 4.9 eV above the ground state, but Cario and Franck found that thallium lines requiring up to 5.6 eV for excitation were excited. The additional energy presumably came from relative kinetic energy. Similar effects were observed with cadmium in place of thallium.

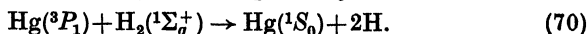
Sensitized fluorescence may occur due to transfer of excitation from metastable atoms (see also § 9). This may be used to determine what transition is responsible for the quenching of mercury resonance radiation by a particular foreign gas. Donat[‡] and Loria[§] made a study of the effect of argon, nitrogen, and hydrogen on the mercury-sensitized fluorescence of thallium. Whereas hydrogen produced a quenching effect on both the mercury and thallium emission, argon and nitrogen increased the thallium emission while decreasing that from mercury. This may be explained by supposing that the argon and nitrogen quench the mercury atoms by producing transitions to the metastable 6^3P_0 level and not to the ground state. These atoms, which have a much longer lifetime towards radiation than the 6^3P_1 , are likely to be as

[†] *Zeits. f. Phys.* **17** (1923), 202.

[‡] *Ibid.* **29** (1924), 345.

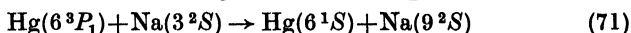
[§] *Phys. Rev.* **26** (1925), 573.

effective per collision in transferring excitation to the thallium atoms. Because of their longer radiative life they will have much more chance to do so before radiating, so increasing the thallium fluorescence. Hydrogen, on the other hand, presumably quenches by some process which does not lead to the production of metastable atoms. The nature of this process is discussed in § 11. It is probably



8.1. Energy resonance

One of the most detailed studies of the relative effectiveness of energy transfer from a given excited atom to different states of a second atom has been carried out by Beutler and Josephy.[†] They studied the mercury-sensitized fluorescence of the diffuse series of sodium (3^2P-n^2S). A mixture of mercury and sodium vapour at partial pressures of 8×10^{-3} and 0.015 mm. Hg respectively was irradiated with mercury resonance radiation ($\lambda 2537$). The relative intensity I of the diffuse series lines of sodium which were excited through such collision processes as



was measured with a Zeiss microphotometer. The fraction of sodium atoms in a given excited state will be proportional to $I/f/\nu f_1$, where ν is the frequency of the line, f_1 the transition probability from the excited state to the final state concerned, and f that to all final states. In Beutler and Josephy's experiments f/f_1 was not determined, but the variation of I/ν with the initial state gives quite convincing results, as may be seen by reference to Fig. 189. This diagram includes lines originating from D as well as S states. To make these comparable it is necessary to divide I/ν by the statistical weight g of the initial state, and this has been done in Fig. 189.

It will be seen that a sharp maximum of $I/\nu g$ occurs for the $7S$ level, the excitation energy of which is only 0.020 eV higher than that of the 6^3P_1 state of Hg. A weaker maximum seems also to be apparent for the $5S$ level which is closest to energy resonance with the metastable 6^3P_0 state of Hg. An appreciable proportion of mercury atoms will be present in this state.

Thus the experiments indicate that the probability of transfer is greatest when the change in relative kinetic energy is least, i.e. when the difference in the excitation energy of initial and final states is least.

Resonance effects of this kind are also observed in the enhancement of spark lines excited in a discharge by admixture of a suitable foreign gas.

[†] *Zeits. f. Phys.* **53** (1929), 747.

Thus a discharge through neon in which metal vapour such as silver, gold, aluminium, copper, or lead is present provides a strong source of the spark lines of the particular metal atom. The process responsible involves transfer of charge as well as excitation:

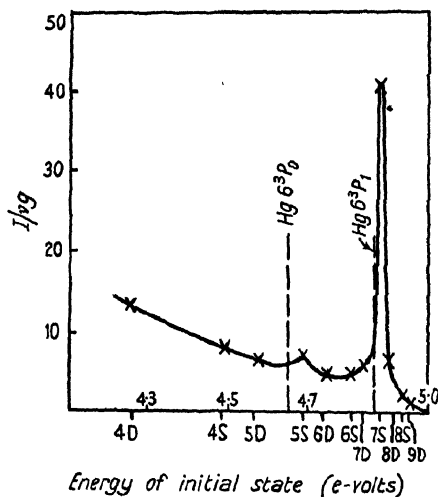
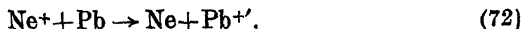


FIG. 189. Excitation probabilities of various sodium lines produced in collisions of the second kind with excited mercury atoms. The abscissae show the energy of the initial states of the Na lines. The broken lines indicate the energies of the 6^3P_0 and 6^3P_1 states of mercury.

The most detailed study of these processes has been made by Duffendack and Gran.† They studied the enhancement of the spark lines of lead by neon, the enhancement of any level of Pb^+ being defined as the ratio of the intensity of a line originating in that level when excited mainly by neon ions to that when excited mainly by electron impact. The discharge tube was a low-voltage arc in neon in the presence of lead vapour. The lead was vaporized in a quartz crucible enclosed in a nickel cylinder. A special filament placed near the mouth of the crucible was the hot cathode, while a nickel hood, completely enclosing the filament and crucible, served as anode. The discharge was observed through a side tube in the anode.

Measurements were made of the intensities of various lead spark lines at a number of neon pressures from 5.5 to 1.6 mm. Hg, the intensity for a given arc current being independent of the pressure as would be expected. These were compared with the corresponding intensities when the excitation was by electron impact only. This required a discharge potential of 450 volts. There was little doubt that at the neon pressures employed the spark-line excitation was due to processes of

† *Phys. Rev.* 51 (1937), 804.

the type (72). With the neon present the lines were prominent even when the discharge was operated at a potential as low as 24 volts, but when the pressure was reduced to 0.05 mm. they did not appear even at 150 volts. All intensities were measured in terms of those of certain standard lines which were assumed to be unaffected by the neon. These were chosen among lines whose initial levels were 1.6 eV below the ground level of Ne^+ .

Fig. 190 illustrates the observed enhancements for the s , p , d , and f series of Pb^+ levels as a function of the energy discrepancy ΔE , the energy difference between the Pb^+ level and that of the ground level of Ne^+ . The resonance character of the results for each series is clear, although for the s and f series at least the maximum enhancement appears at a small positive energy discrepancy. It is also clear that the enhancement is not determined wholly by the value of ΔE , for it is markedly different for the different series at the same ΔE .

Similar results were obtained in less extensive experiments by Duffendaek and Thomson† on the enhancement of the copper and aluminium spark lines by neon.

An attempt was made by Gran and Duffendaek‡ to obtain an estimate of the absolute value of the transfer cross-section, but, as this depends on various uncertain assumptions concerning the discharge conditions, the very large value they find must be regarded as very doubtful.

8.2. Wigner's spin conservation rule

Considerable attention has been devoted to the study of the effect of electron spin changes on the probability of transfer collisions. Owing to the very small coupling between the spin and electron orbital motion it would be expected that no change of total spin would occur in the collision. If s_1 and s_2 are initial spin quantum numbers of the electronic states of the colliding systems, the resultant spin quantum number S of the two systems taken together will have one of the values

$$s_1 + s_2, \quad \dots, \quad |s_1 - s_2|.$$

Then we should expect that the only transfer reactions which would be

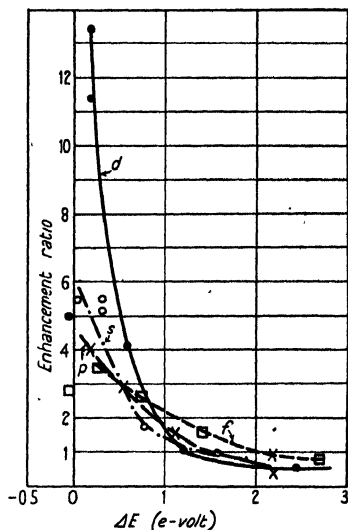


FIG. 190. Illustrating the enhancement of the spark lines of Pb in the presence of Ne. The observed enhancement ratio is shown as a function of ΔE , the difference in energy between the excitation potential of the Pb I line concerned, and the ionization potential of Ne. The curves refer to the s , p , d , and f series lines. $\circ$ — $\circ$ — $\circ$ — $\circ$ s ; $\times$ — $\times$ — $\times$ — $\times$ p ; $\bullet$ — $\bullet$ — $\bullet$ — $\bullet$ d ; $\square$ — $\square$ — $\square$ — $\square$ f .

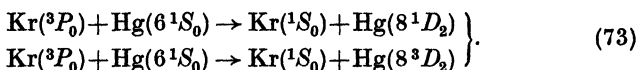
† Ibid. 43 (1933), 106.

‡ Loc. cit.

important would be such that if s_3 and s_4 are the spin quantum numbers of the final states, one of the numbers $s_3 + s_4, \dots, |s_3 - s_4|$, must be included in the set $s_1 + s_2, \dots, |s_1 - s_2|$. This rule was first enunciated by Wigner† and is known as the conservation of total spin.

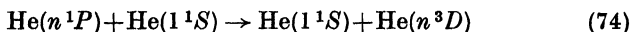
As an example suppose that $s_1 = 1$, $s_2 = 0$ so that one atom is in a triplet, the other in a singlet state. The total spin quantum number must be 1 so that, according to Wigner's rule, either $s_3 = 1$, $s_4 = 0$ or $s_3 = 0$, $s_4 = 1$. The chance of transfer when both the final states are singlets, giving $S = 0$, should be very much smaller.

Beutler and Eisenschimmel‡ tested this rule for the reactions



The first of these disobeys Wigner's rule while the second does not. The energy discrepancy in both cases is very small. The effect of adding krypton to a discharge in a mixture of mercury and helium was found to enhance the lines emanating from the triplet level much more than those from the singlet state, in accordance with the rule.

On the other hand, strong evidence was brought forward by Lees and Skinner§ that the cross-sections for such reactions as



are quite comparable with the gas kinetic. In their experiments on the excitation of helium lines by an electron beam (see Chap. II, §§ 4.2, 4.31) they observed that, while most of the lines were emitted from the region of the beam, lines of the series 2^1S-n^1P and 2^3P-n^3D arose from a wider region. It was verified that, while the intensity of the 'spread' lines remained proportional to the beam current, it was not proportional to the gas pressure. The possibility that it arose from recombination to ions drifting out of the beam was excluded by showing that a powerful electrostatic field applied at right angles to the beam had no effect on the relative intensity of the spreading.

There is no difficulty in providing an explanation of the spreading of the 2^1S-n^1P lines consistent with these results. The upper levels must be populated by resonance absorption of 1^1S-n^1P radiation emitted from the beam, a conclusion confirmed by an analysis of the intensity expected and its variation with pressure. No such possibility exists for the spreading of the 2^3P-n^3D lines. The similarity in the intensity pressure relation for these and for the 2^1S-n^1P lines suggests that they

† *Gött. Nachr.* (1927), 375.

‡ *Zeits. f. phys. Chem. B*, **10** (1930), 89.

§ *Proc. Roy. Soc. A*, **137** (1932), 186.

arise from the population of n^1P atoms outside the beam by a collision process such as (74). The strongest evidence in favour of this, which was provided by Skinner and Lees, was the form of the excitation functions observed for these lines. These are illustrated in Fig. 191. While the

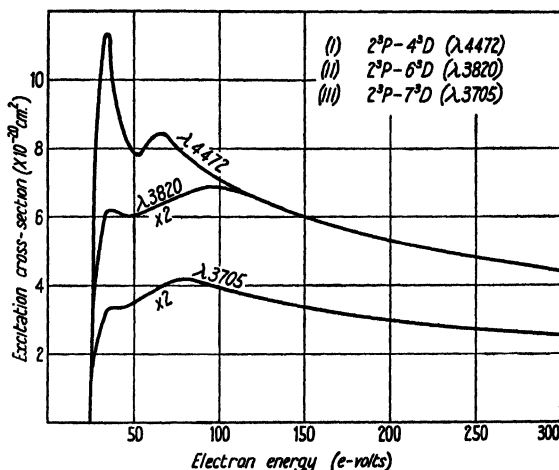


FIG. 191. Observed excitation functions for the 'spread' λ 4472 (2^3P-4^3D), λ 3820 (2^3P-6^3D), λ 3705 (2^3P-7^3D) lines of He excited by electron impact.

sharp maximum at low electron energies is expected for excitation to a triplet state, the second flat maximum is entirely uncharacteristic and closely resembles the excitation functions for lines originating from 1P levels (see Chap. II, Fig. 24). For the explanation to be valid, however, the process must occur with high probability in a gas-kinetic collision.

A detailed investigation, which confirms and extends the conclusions of Skinner and Lees, has been made by Maurer and Wolf.† The general principle of their apparatus is illustrated in Fig. 192. An electron beam from the oxide-coated cathode K , confined to a narrow pencil by a longitudinal magnetic field, H , of 1,000 gauss, excited helium gas in the region beneath the slit S . The light resulting directly from this excitation was observed through the quartz window B . The light passing through the slit S into the upper chamber C produced a faint green fluorescence in the helium gas within that chamber. This fluorescence was observed at right angles to the plane of the paper. The helium purity was maintained by continual circulation of the gas throughout the experimental

† *Zeits. f. Phys.* **92** (1934), 100 and **115** (1940), 410.

chambers. The purity was continually checked by spectroscopic observation. A light trap was fitted to the chamber *C* so as to remove effects from scattered radiation.

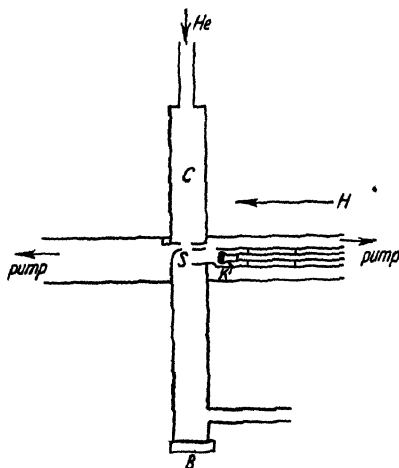


FIG. 192. Apparatus used by Maurer and Wolf for the study of spin-reversal effects in collisions of the second kind between helium atoms.

The spectrum of the fluorescent light showed the presence not only of lines of the principal singlet series (2^1S-n^1P) but also 'unexpected' lines such as 2^3P-4^3D , 2^1P-4^1D , whose initial levels are 3D and 1D terms. Maurer and Wolf showed that the only possible way in which these terms could have been excited was by collisions of the second kind such as (74).

The possible exciting agencies and the evidence against their effectiveness may be summarized as follows:

(a) Direct excitation of normal helium atoms by fast electrons. This is unlikely in any case because of the strong confining effect of the magnetic field, but is completely excluded by showing that a transverse electric field had no effect on the fluorescent beam.

(b) Excitation of metastable atoms by slow electrons. This was excluded by the linear variation of the intensity of the 'unexpected' lines with the beam current, for both the concentration of metastable atoms and of slow electrons should be proportional to this current.

(c) Fluorescent excitation of excited helium atoms. Diffusion of excited atoms, which were not metastable, from the chamber *A* to *C* would be most unlikely owing to their small radiative lifetime.

(d) Excitation by scattered light. This was excluded by examining the effect of introducing a quartz plate in the chamber *C* which absorbed the principal series lines. The fluorescence disappeared at the same time.

(e) Excitation by a recombination continuum. In the chamber below S , light could be produced by recombination of helium atoms and electrons. The ultra-violet continuum produced in this way could then ionize helium atoms in the chamber C . In that case the unexpected lines might have arisen from population of the D levels by recombination. This is excluded because of the absence of influence of the transverse electric field and the failure to observe any continuum in the direct radiation from around S .

There remain the transfer reactions such as (74). Positive evidence in favour of this explanation was obtained as follows:

(f) The quartz plate experiment described in (d) above shows that the excitation of the unexpected lines was associated with the fluorescent excitation of the principal series. The lines could not have been excited by direct fluorescence from normal atoms because transitions from the ground state to the D levels are optically forbidden, both in emission and in absorption.

(g) The ratio of the intensities of the unexpected lines to those of the principal series increased linearly with the pressure at small helium pressures. In most cases the increase with pressure became slower at pressures above 0.04 mm. Hg. The departures from linearity can be understood in detail in terms of the occurrence of the reverse transfer reactions when account is taken of the lifetimes of the different states.

(h) The explanation is in agreement with the observed constancy of the intensity ratio as the electron beam current varied.

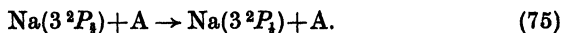
From the observed intensity ratios at a pressure so low that the variation with pressure is linear, and from the known lifetimes of the 1P states, the effective cross-sections for different transfer processes could be determined. The results are given in Table XIII.

TABLE XIII
Effective Cross-sections for Transfer Reactions in Helium

Reaction	Resonance discrepancy (eV)	Cross-section in 10^{-15} cm. ²
$3^1P \rightarrow 3^3P$	0.079	2.1
$3^1P \rightarrow 3^3D$	0.013	11.9
$4^1P \rightarrow 4^1D$	0.006	67
$\rightarrow 4^3D$	0.006	15
$4^1P \rightarrow 4^1S$	0.068	3
$\rightarrow 4^3S$	0.148	1.5
$5^1P \rightarrow 5^1D$	0.003	51
$\rightarrow 5^3D$	0.003	27
$5^1P \rightarrow 5^1S$	0.034	1.5
$\rightarrow 5^3S$	0.071	0.9

It will be seen that the resonance effect is still apparent, but the Wigner rule is obeyed in a very weak sense only. For a given D level the singlet cross-section is greater than the triplet, but not by a large factor. In the two cases given, the ratio of the cross-sections decreases with increase of the principal quantum number.

An remarkable example involving interaction of angular momenta was first observed by Wood.† He found that if sodium vapour mixed with argon is irradiated by one of the D lines the other D line also shows up in the fluorescence. This must be ascribed to collisions with argon atoms in which a sodium atom excited to one D level undergoes a transition to the other, i.e.



In experiments by Lochte-Holtgreven‡ the ratio of the fluorescent intensity of the two D lines when one only was used for excitation was measured as a function of the argon pressure. From his results the cross-section for the process (75) can be estimated as $1.2 \times 10^{-14} \text{ cm.}^2$ and for the inverse process about $\frac{1}{2}$ as large. It is very surprising that such a large cross-section should exist for a process in which the total angular momentum changes without any change of that due to spin.

9. Collisions in which electronic transitions occur—Experiments involving metastable atoms

We have already had occasion to refer to collisions in which metastable atoms are involved. In § 6.7 the possibility of directly measuring the coefficient of diffusion of the metastable rare gas atoms through different gases was mentioned, while the part played by metastable mercury atoms in certain processes of sensitized fluorescence has been described in § 8. We discuss here some further techniques by which information about the collision cross-sections for processes involving metastable atoms can be obtained.

The first concerns the rate at which a concentration of metastable atoms, present in a container of simple geometrical boundaries, disappears when the existing source which produces the metastable atoms is cut off. This rate may be measured by observing the variation in the absorption of radiation of suitable wave-length which is selectively absorbed by the metastable atoms, a method which has been described in Chap. II, § 4.41. In this way the relaxation time $1/\alpha$ may be obtained, during which the concentration falls by a factor e . There are two ways in which the metastable atoms are disposed of. They may either diffuse, at a rate inversely proportional to the gas pressure p , to the walls of the containing vessel where they give up their excitation, or they may be destroyed by collision in the gas phase before reaching the walls. The contribution from this effect will be proportional to p , so that α may be written

$$\alpha = ap + b/p. \quad (76)$$

† *Phil. Mag.* **27** (1914), 1018; Wood and Mohler, *Phys. Rev.* **11** (1918), 70.

‡ *Zeits. f. Phys.* **47** (1928), 362.

Their radiative lifetime is so long that the chance that they are deactivated by radiation is negligibly small.

By observing the pressure variation of α , a and b may be determined and hence, if the geometrical conditions are chosen so that the details of the diffusion may be calculated, the diffusion coefficient D and the cross-section for destruction of the metastable atoms in the gas phase may be derived. This method is simple in principle, but suffers from the difficulty of ensuring that no atoms enter metastable states after the excitation has been cut off. The usual source, a glow discharge, produces atoms in various excited states so that after the discharge is cut off transitions from higher states to the metastable state may occur either by radiation or on collision.

If the containing vessel is a circular cylinder of length l and radius a , with plane ends, the problem is as follows. Let Z be the number of impacts per second per metastable atom which lead to a transition from the metastable state. Then the number n of such atoms per c.c. at time t , after the excitation is cut off, satisfies

$$\frac{\partial n}{\partial t} + Zn = D \left(\frac{\partial^2 n}{\partial r^2} + \frac{1}{r} \frac{\partial n}{\partial r} + \frac{\partial^2 n}{\partial z^2} \right), \quad (77)$$

where z is measured along the axis of the tube and r radially outwards from the axis. This equation must be solved subject to the boundary conditions

$$\begin{aligned} n &= f(r, z), & t &= 0, \\ n &= 0, & \begin{cases} r = a \\ z = \pm \frac{1}{2}l, \end{cases} & t > 0, \end{aligned} \quad (78)$$

to obtain at time t the average number $\bar{n}$ of metastable atoms in the path of the light beam. This beam may be chosen to occupy a circular cylinder of radius b coaxial with the containing vessel. It may then be shown that†

$$\bar{n} = n_0 e^{-\alpha t}, \quad (79)$$

where

$$\alpha = \left(\frac{5.81}{a^2} + \frac{\pi^2}{l^2} \right) D + Z. \quad (80)$$

D is given in terms of the pressure and diffusion cross-section by (7), (8) of § 3.1 and Z in terms of the cross-section for destruction of the metastable atoms by (67).

This method has been applied to metastable helium,‡ neon,§ and argon|| in the corresponding pure rare gas, the experimental technique used being essentially that used by Meissner and Graffunder§ in their first work, that with neon. The gas in a tube was excited electrically and the exciting field was then cut off. After a short interval, a beam of light, capable of selective absorption by the metastable atoms, was sent through the tube and the absorption measured photographically. By

† Zemansky, *Phys. Rev.* **34** (1929), 213.

‡ Ebbinghaus, *Ann. der Physik*, **7** (1930), 267.

§ Meissner and Graffunder, *ibid.* **84** (1927), 1009.

|| Anderson, *Can. Journ. Res.* **2** (1930), 13.

operating the emitting lamp and the electrical excitation with A.C. of the same frequency but with adjustable phase difference, the interval between cessation of excitation and emission of the absorbable beam could be varied at will. Fig. 193 illustrates the variation of αp with p^2 as found for neon, showing the relation to be as expected from (76).

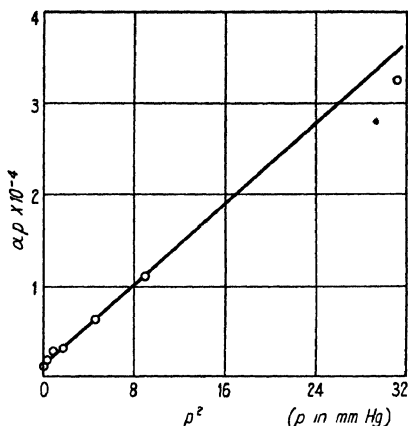


FIG. 193. Observed linear relation between αp and p^2 in the experiments of Meissner and Graffunder on the destruction of metastable neon atoms in collisions with normal neon atoms.

The results obtained for the diffusion and destruction cross-sections are given in Table XIV. In all these cases destruction almost certainly occurs by excitation to the nearest upper state, the transitions concerned and the energies ΔE required being given in Table XIV. The destruction

TABLE XIV

Cross-sections for Diffusion and for Destruction of Metastable Rare Gas Atoms by Inelastic Collisions

Metastable atoms	Conditions	Q_d ($\times 10^{16}$ cm. ²)	γQ ($\times 10^{16}$ cm. ²)	Nearest final state	$\Delta E_{\min}$ eV	γ (approx.)
Ne ($^3P_{3,1,0}$)	..	7.66	0.0042	1P_1	0.15	7×10^{-3}
A ($^3P_{2,1}$)	$T = 300^\circ \text{K}$	33.9	0.00065	1P_1	0.21	10^{-3}
A (3P_3)	$T = 80^\circ \text{K}$	50.0	0.00048	1P_1	0.28	8×10^{-5}
He (2^3S_1)	$a = 1.65$ cm.	54.4	0.00018	2^1S_0	0.78	3×10^{-13}
He (2^3S_1)	$a = 3.0$ cm.	34.8	0.00018	..	..	..

Q_d = diffusion cross-section.

Q = cross-section for excitation of metastable atoms to state of high energy.

γ = fraction of all collisions in which relative kinetic energy is greater than ΔE .

a = thickness of absorption tube.

cross-section is given in the form γQ , where γ is the fraction of collisions in which the relative kinetic energy is greater than ΔE . The order of magnitude of γ is given in the table. It will be seen that, while the diffusion cross-sections are not unreasonable, the destruction cross-sections are more suspect, particularly for helium in which the value given is far too large. The main defect of the method, noted above, is that no allowance is made for production of metastable atoms by downward transitions after the electrical excitation is cut off.

A method depending essentially on the same principle has been employed by Webb and Messenger† and by Samson,‡ to study the collisions of metastable mercury atoms with nitrogen molecules. The metastable mercury atoms in the 6^3P_0 state were produced by irradiation of the mercury–nitrogen mixture with the mercury 2537 line which produced resonance excitation of the 6^3P_1 mercury level. Collisions of these atoms with nitrogen molecules resulted in the production of 6^3P_0 metastable mercury atoms by the usual quenching process (see § 7.2). After the excitation is cut off some radiation from 6^3P_1 mercury atoms persists because some of the atoms return to the 6^3P_1 state in super-elastic collisions. The intensity of the radiation produced in this way was used as an indicator of the concentration of metastable atoms. To analyse the data Samson assumed that both 6^3P_0 and 6^3P_1 atoms possess the same diffusion cross-section, allowed for the imprisonment of the 2537 radiation in the mercury vapour and took account, not only of collisions in which transitions between the 6^3P_0 and 6^3P_1 states occurred, but also of those in which the transition was from either to the 6^1S_0 state. From the pressure variation of the coefficient α separate values were found for all these cross-sections and are given in Table XV. The value for the quenching cross-section agrees quite well with that found by Zemansky (see Table XII).

A further variant of the same method was introduced by Webb.§ He made use of the fact that when a metastable atom strikes a metal plate there is a high probability that the atom will be deactivated and an electron emitted (see Chap. IX, § 6.1), as in the experiments of Dorrestein and Smit|| (§ 6.7). The most thorough experiments on these lines have been carried out by Coulliette†† for metastable mercury atoms in mercury vapour. His apparatus (illustrated in Fig. 194) contained mercury vapour, the pressure of which could be varied by changing the

† *Phys. Rev.* **40** (1932), 466.

§ *Ibid.* **24** (1924), 113.

†† *Phys. Rev.* **32** (1928), 636.

‡ *Ibid.* 940.

|| *K. Wet. Amst.* **41** (1938), 725.

TABLE XV

Cross-sections for Diffusion and Destruction of Metastable Mercury Atoms in Collisions of the Second Kind in Nitrogen

Process	Conditions	Cross-section ($\times 10^{18}$ cm. ²)	ΔE eV
Diffusion {	$T = 301^\circ \text{K}$	48.7	..
	$T = 374^\circ \text{K}$	56.5	..
	$T = 486^\circ \text{K}$	57.8	..
	..	0.21	+0.20
$6^3P_0 \rightarrow 6^3P_1$	..	0.97, 0.86†	-0.20
$6^3P_1 \rightarrow 6^3P_0$	..	$\leq 0.069^*$	-4.86
$6^3P_1 \rightarrow 6^1S_0$	..	$\leq 0.0, 22$	-4.66
$6^3P_0 \rightarrow 6^1S_0$	..		

All values except that marked † are given by Samson, *Phys. Rev.* **40** (1932), 940.

† Zemansky, *Phys. Rev.* **36** (1930), 919.

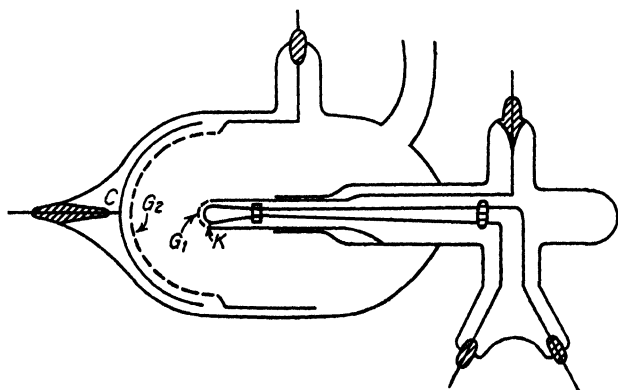


FIG. 194. Coulliette's apparatus for studying the diffusion of mercury metastable atoms in mercury.

temperature of the glass walls. Electrons from the cathode K were accelerated to the grid by a potential difference of 4.9 eV, just too small to produce metastable mercury atoms. At intervals of about 10^{-3} sec. rectangular voltage pulses applied an additional potential difference of 0.7 volts between G_1 and K and metastable mercury atoms were produced near G_1 . These diffused in the space between G_1 and the concentric hemispherical collecting electrode C . Their arrival at C was detected by the ejection of electrons, these being collected by the concentric hemispherical grid G_2 . Normally the potential difference between G_2 and C was such that there was no flow of current. At regular intervals after the application of the pulse between G_1 and K , however, another rectangular pulse could be applied between C and G_2 to attract secondary

electrons to G_2 and thus to give a measure of the rate of arrival of metastable atoms at that instant. The experiment was carried out with variable time-intervals t (up to about 2×10^{-3} sec.) between the $G_1 K$ pulse and the $G_2 C$ pulse. In this way the variation with t of the rate of arrival of metastable atoms at C could be determined. For very small values of t (less than 3×10^{-5} sec.) effects could be observed due to direct photoelectric emission from C , but these had become entirely negligible by the time the metastable atoms started to arrive.

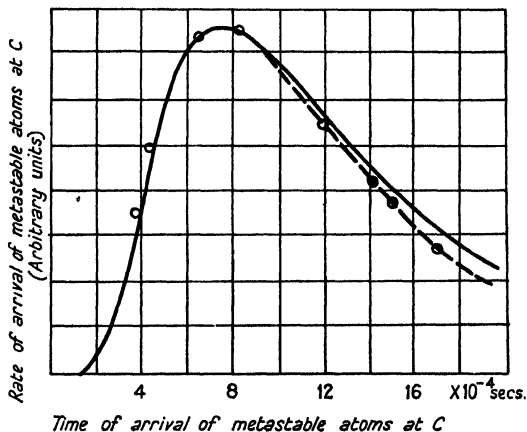


FIG. 195. Rate of arrival of metastable Hg atoms at the collector in Coulliette's apparatus at various time-intervals after their production has ceased. —○—○— observed rate of arrival; ——— curve calculated for a diffusion coefficient of 1,700.

Owing to the spherical symmetry of the arrangement the diffusion equation could be solved explicitly, giving for the rate of arrival of metastable atoms at C at a time t after their production at G_1 ,

$$i = A \sum_{n=0}^{\infty} \frac{(-1)^n}{n} \left\{ \sin \frac{n\pi a}{b} - \frac{n\pi a}{b} \cos \frac{n\pi a}{b} \right\} e^{-(n^2 \pi D t / b^2)}, \quad (81)$$

where a , b are the radii of the hemispherical grid G_1 and collector C respectively. In Coulliette's apparatus these radii were respectively 0.63 cm. and 3.80 cm. D is the diffusion coefficient for the mercury metastable atoms in mercury vapour, and is related to Q_d according to equations (7) and (8) of § 2.

Fig. 195 shows a typical curve obtained by Coulliette for a temperature of the tube of 65°C . corresponding to a concentration of mercury atoms of 1.05×10^{15} atoms per c.c. The figure also shows the curve computed

from equation (81) for a value of D of 1,700 which gives the best fit with the experimental data. The corresponding value of Q_d is 4.8×10^{-15} cm.²†

A second method, applicable to metastable atoms whose radiative lifetime is not so long that forbidden lines arising from them are never observed, has been applied by Kvitte and Vegard‡ to study the collisions of metastable oxygen atoms in the 1S level. This level is the upper state of the green line (λ 5577) which is such a prominent feature of the auroral night-sky emission from the earth's upper atmosphere.§ Although the transition involved ($^1S \rightarrow ^3P$) is forbidden and the radiative lifetime of the 1S state is about 0.5 sec., it is possible to observe the line in discharges through pure oxygen and through mixtures with rare gases. Kvitte and Vegard investigated the intensities of the green line and of the allowed line λ 5555 emitted from a discharge through an oxygen-neon mixture contained in a cylindrical tube, as functions of the discharge-tube current, pressure, fractional neon concentration, and tube radius, when steady conditions had been set up.

If it is assumed that the number N of oxygen atoms excited to a given stationary state per c.c. per second is the same at all points of the tube cross-section, then the radial distribution of the emitted atoms will be determined by the equation (77) in which $\partial n / \partial t$ is replaced by N . Also, except near the ends of the tube, $\partial^2 n / \partial z^2$ may be ignored.

Solving the equation with the boundary condition that $n = 0$ at the bounding wall $r = a$ gives

$$n = \frac{N}{Z} \left[1 - \frac{I_0\{r(Z/D)^{\frac{1}{2}}\}}{I_0\{a(Z/D)^{\frac{1}{2}}\}} \right], \quad (82)$$

where I_0 is the Bessel function defined by Whittaker and Watson, *Modern Analysis*, Chap. XVII.

The mean value $\bar{n}$ over a section is then given by

$$\bar{n} \simeq \left(\frac{Na^2}{8D} \right) / (1 + \frac{1}{8}a^2Z/D), \quad (83)$$

under the experimental conditions. For metastable atoms Za^2/D is small and the concentration is nearly proportional to the square of the tube radius. But for other excited atoms, indicated by the suffix r ,

† Under these conditions the value of γQ , where Q is the cross-section for destruction of the mercury metastable atoms by raising them from the 3P_0 to the 3P_1 state, was estimated by Coulliette as 0.05×10^{-16} cm.² γ is here as defined in connexion with Table XIV.

‡ *Geofys. Publ. Oslo*, 17 (1947), 1.

§ See Bates, Massey, and Pearse, *Report on the Emission Spectra of the Night Sky and Aurorae*, Physical Society (1948), 97.

the most important term in Z arises from radiative transitions and Z/D is large, giving

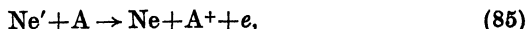
$$\bar{n}_r \simeq N_r/Z_r. \quad (84)$$

To use these formulae to determine D and Z for a given mixture the pressure variation of the line intensities must be studied. To overcome the difficulty of determining the pressure variation of the rate of production N , the variation of n_r with pressure was observed at such pressures that the only important term in Z was due to radiative transitions. It was then assumed that the same variation held for metastable atom production, a partial but by no means complete justification for this being the similarity in the intensity variation of forbidden and allowed lines with current density. By studying the pressure variation for different mixtures the ratio of the cross-sections for destruction by collisions of 1S atoms with oxygen molecules and neon atoms respectively to the diffusion cross-section could then be obtained.

The values found were 3.6×10^{-6} and 2.9×10^{-7} of the gas-kinetic cross-section for deactivation by oxygen and neon respectively. These very low cross-sections are not surprising in view of the large energy interchange required to bring about deactivation, particularly in neon. On the other hand, it was also possible to obtain information on the cross-sections for quenching the allowed λ 5555 radiation of atomic oxygen by studying the variation of Z_r with pressure. For quenching by oxygen the cross-section was found to be of the order of the gas-kinetic, whereas neon was about 100 times less effective. The energy interchange necessary in these cases is smaller than for the deactivation of metastable 1S_0 atoms, so the larger cross-sections are to be expected.

Although the method of Kvifte and Vegard involves many assumptions which are difficult to justify, it provides at least semi-quantitative information about reactions of considerable interest in applications to upper atmospheric physics. It might well be studied in greater detail and applied to other cases.

Kruithof and Druyvestyn† have obtained information concerning the effectiveness of such reactions as



in which Ne' represents a metastable neon atom, in the following way. The ionization coefficient η for a swarm of electrons drifting through a gas at pressure p under a uniform electric field F has been defined in Chap. II, § 4.54. It is a function of F/p . For a pure atomic gas such as

† *Physica*, 4 (1937), 450; Kruithof and Penning, *ibid.* 430.

neon it is determined by the ionization cross-section of the atoms and the velocity distribution function for the electrons. Fig. 196 illustrates the observed† variation of η with F/p for highly purified neon. The effect of a small admixture of argon is very marked, particularly for small F/p , as may be seen from the observed results of Fig. 196. This may be interpreted in terms of the reaction (85).

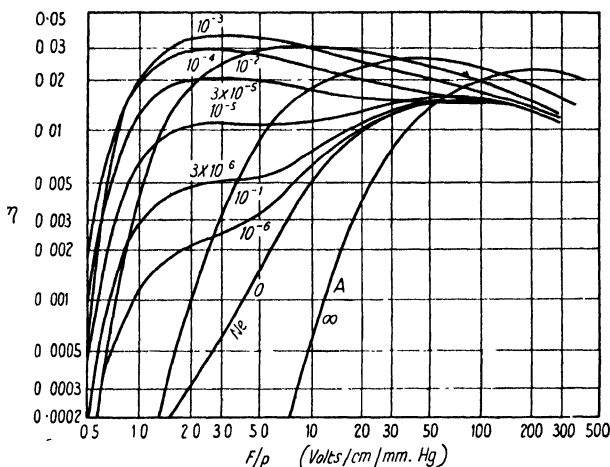


FIG. 196. Observed ionization coefficient η as a function of F/p for various mixtures of Ne and A. The numbers on each curve give the ratio of the argon pressure to the total pressure of the mixture.

Because of this, energy which would be used in producing excitation and emission of radiation is made available for ionization. From a study of the variation of η with argon admixture it is possible to obtain values for the chance q that an excited neon atom passes into a metastable state and the ratio of the probability of destruction of a metastable Ne atom by collision with a Ne and an A atom respectively. The latter ratio comes out to be 2.4×10^{-5} . Since the probability of destruction in a Ne collision is of the order 10^{-5} (see Table XIV above), it follows that the chance of the reaction (85) occurring is of the order unity per collision. This represents a reaction which may be regarded as one of exact resonance as far as the relative translational energy of the heavy particles is concerned, the electron taking up the energy excess (16.53 eV excitation energy of Ne (3P_2)—15.76 eV ionization energy of A). It is not surprising that the probability should be high.

† Kruithof and Penning, loc. cit.; Glotov, *Phys. Zeits. Sowjetunion*, **12** (1937), 256.

10. Collisions in which electronic transitions occur. Discussion and theoretical interpretation of results. Collisions between atoms only

10.1. *The resonance effect—near-adiabatic conditions*

The most outstanding feature of the results which have been described in §§ 7–9 is the existence of an energy resonance effect. The effective cross-section for a collision between two atoms in which electronic transitions occur is very small unless the change ΔE of internal energy is very small. Furthermore, for comparable transitions, the variation with ΔE generally follows a resonance curve (see Figs. 189, 190 and Table XIII). Rare gas atoms are very ineffective in quenching resonance radiation because of the high value of ΔE involved. Metastable neon atoms have very little chance of deactivation in impact with a normal neon atom but readily transfer their energy to an argon atom to ionize it, and so on.

A correspondence principle argument may be given to show that, under gas-kinetic conditions, the cross-section will be small unless ΔE is very small. This is because of the gradual character of the collision, the atoms approaching each other with a velocity very small compared with that of the atomic electrons. The latter have therefore plenty of time to readjust themselves to the slowly changing conditions without a transition taking place—the impact will be nearly adiabatic. Classically we may represent this by considering the amplitude of vibration which will be set up by applying a disturbing force to an oscillator of natural frequency ν . This disturbance will vary with the time t according to some function $F(t)$. To determine the effect on the oscillator we expand $F(t)$ in a Fourier integral. It is only the components of this expansion which have frequencies between ν and $\nu + d\nu$ which will produce any appreciable forced oscillation. In order that these components of $F(t)$ should be strong it is necessary that the time τ of collision should not be large compared with a natural period of the oscillator. Excitation will be weak if $\tau\nu \gg 1$. As τ is of the order a/v , where a is the range of interaction between the atoms and v their relative velocity, the condition for weak excitation becomes

$$av/v \gg 1. \quad (86)$$

To transfer this classical picture over to the quantum theory it is only necessary to replace the frequency ν by $\Delta E/h$, where ΔE is the internal energy change involved in the electronic transition. We have, then, that the chance of the transition occurring per impact will be small if

$$a \Delta E/hv \gg 1. \quad (87)$$

For helium atoms at room temperature, taking a as 2×10^{-8} cm., the condition becomes

$$32 \Delta V \gg 1, \quad (88)$$

where ΔV is the value of ΔE in electron volts. Even for this case, in which very light and hence relatively fast atoms are concerned, the cross-section is likely to be small under gas-kinetic conditions unless the internal energy change is much less than 0.1 eV. For the heavier rare gas atoms v will be smaller and a larger than for helium, so that the conditions will be even more nearly adiabatic.

For a given value of ΔE we may expect the cross-section to be an increasing function of the relative kinetic energy of impact, at least until the condition (87) is no longer satisfied. This is justified by a more detailed analysis as described below (see Fig. 199).

This argument gives no indication of the size of the maximum cross-section to be expected either as a function of ΔE for fixed v and a or as a function of v for fixed ΔE and a . The special case of exact resonance in which $\Delta E = 0$ can be discussed without difficulty by a straightforward extension of the method of partial cross-sections for the calculation of elastic scattering by a centre of force. It provides a good indication of the maximum cross-section for fixed v and a as this is likely to occur when ΔE is nearly zero. Accordingly we first discuss the case of exact resonance.

10.2. *The case of exact resonance—maximum cross-sections*

We have already had occasion to discuss cases of charge or excitation transfer in which exact resonance prevails, namely in the mobility of He^+ ions in He and the diffusion of metastable He atoms in He. In these cases a collision in which charge or excitation transfer occurs is not distinguishable from a direct elastic collision but it is possible to make the distinction theoretically. Thus it is found in a thorough theoretical analysis that the relative angular distribution is of the general shape indicated in Fig. 197. It has a large maximum at zero angle and falls rapidly to a very small value. This is maintained up to an angle near 180° , after which the distribution increases to a second maximum at 180° . The first maximum can be regarded as due to direct elastic scattering, the second to collisions in which resonance charge or excitation transfer or both has occurred. The two processes are only probable at angles near 0° and 180° respectively, so that they interfere very little and a classical separation is possible (for experimental applications see Chap. VIII, § 5.1). In this way it is possible to assign a separate cross-section

for the transfer collision, although in calculations of diffusion or mobility the effective cross-section to be taken must include both direct elastic scattering and resonance transfer (see §§ 6.52, 6.7).

As explained in § 2 and § 6.7, a normal and an excited atom of the same kind can interact in two distinct ways† so that the interaction energy is either

$$V_0(r) \pm U(r). \quad (89)$$

The existence of the term $U(r)$ is essentially due to the fact that resonance transfer of excitation may occur, i.e. the energy of the system $A + A'$ is the same as that of $A' + A$. It may be shown that the cross-section for transfer, defined as above, is given by

$$Q_t = \frac{\pi}{k^2} \sum (2l+1) \sin^2(\eta_l^+ - \eta_l^-), \quad (90)$$

where $k\hbar$ is the momentum of relative motion. η_l^+ , η_l^- are the phase shifts for motion with relative angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$ produced by the respective interactions $V_0 \pm U$. According to this formula the chance of transfer vanishes with U , as it should.

It is now possible to determine the conditions under which Q_t is likely to be much larger than the usual gas-kinetic cross-section.

For this purpose we must consider the effectiveness of U as a scattering potential. If its range is much greater than that of V_0 , Q_t is likely to exceed substantially the gas-kinetic value as this is given by a scattering potential very similar to V_0 . It has been pointed out in § 2 that if the excited state concerned in the transfer is one from which a transition to the ground state is associated with an electric moment of order p , then U falls off for large separations r as $r^{-(2p+1)}$. Thus if the excited state is one which combines optically with the ground state so that p is 1, U decreases as slowly as r^{-3} . This is so slow that the differential cross-section $I(\theta) d\omega$ for scattering by such a field becomes logarithmically infinite at $\theta = 0$. The total cross-section, although finite, is likely therefore to be large unless the interaction, although of long range, is very weak. Actually in these cases

$$U(r) \sim -\mu^2 r^{-3}, \quad (91)$$

† It is assumed as usual that the normal atom possesses a complete outer shell of electrons.

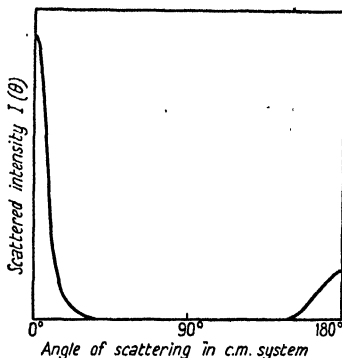


FIG. 197. Angular distribution in the scattering of ions by atoms in the exact resonance case showing the effect of charge exchange.

where μ is the dipole moment associated with the optical transition which occurs in either atom. Q_t will be of the same order as the elastic cross-section for scattering by the field (91). Referring to § 3.32 we have approximately

$$Q_t = 12\pi^2\mu^2/vh,\dagger$$

where v is the velocity of relative motion. Taking μ to be of the order 10^{-18} e.s.u. we find that Q_t has the large value 5×10^{-14} cm.² Although this is a very rough estimate it shows that, under the conditions we have assumed of exact resonance and optically allowed transitions in each atom, the transfer cross-section may greatly exceed the gas-kinetic. It must be emphasized, however, that this does not arise because of the wave aspect of the collision but because the possibility of the resonance transfer introduces a long-range interaction which would otherwise not occur. Apart from this the collision is essentially classical in character, the wave-length of relative motion being very short compared with the range of a strong interaction.

If the transfer involves a transition in each atom associated with a quadrupole moment, then $U(r) \sim (\nu^2/\epsilon^2)r^{-5}$, where ν is of the same order as μ^2 in (91). In this case the formula (32) of § 3.32 shows that the transfer cross-section is of order 10^{-15} cm.², not much greater than the gas-kinetic. For transitions involving higher-order moments the cross-section can be expected to exceed the gas-kinetic to an even smaller extent. In particular, if the transfer process is one involving charge exchange, $U(r)$ falls off exponentially and cross-sections greatly exceeding the gas-kinetic are not to be expected. On the other hand, even in this case $U(r)$ falls off somewhat less rapidly than the repulsive part of V_0 in (89), so that some increase above the gas-kinetic value still occurs (see § 6.52).

As far as the variation of the cross-section with relative velocity is concerned, the transfer cross-section, in the case of exact resonance, falls off monotonically as the velocity increases, approximately as $v^{-2/s-1}$ when $U(r) \sim Cr^{-s}$.

So far we have assumed that the two colliding systems are identical, apart from the presence of excitation or an additional electron in one of them. The same conclusions follow, however, if they are not identical provided the change of internal energy is zero. $U(r)$ then has the asymptotic form Cr^{-s} , where $s = p + q + 1$. p is the order of the electric moment associated with the transition in the first atom, q in the second. If electron exchange or an s - s transition is involved, $U(r)$ falls off exponentially.

† A more accurate calculation gives $Q_t = 2\pi^2\mu^2/vh$.

10.3. Case of imperfect resonance

We must now turn to consider transfer collisions in which the resonance is imperfect so that ΔE is finite. No such simple discussion as was available for the case of exact resonance is now possible. It is true that we may identify a function corresponding to $U(r)$ above, the magnitude of which is important in determining the transfer cross-section and which

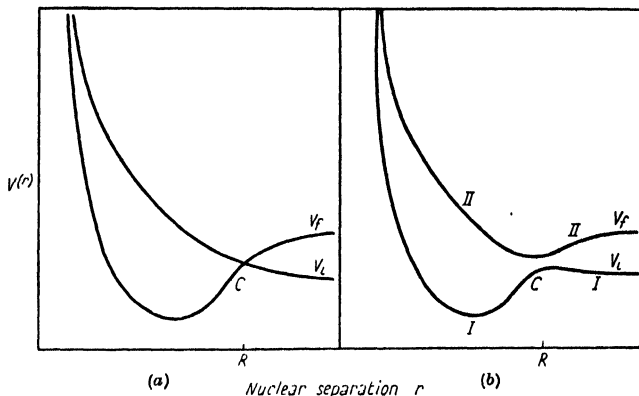


FIG. 198. Illustrating the crossing of potential energy curves. In the absence of interaction between the curves they follow V_i , V_f with a crossing-point at C . Interaction separates them to the curves I , II which approach closely but do not cross at C .

has the same properties as for the case of exact resonance. However, the interaction between the two atoms in their initial states may no longer be described by a function of the form (89). Instead, only one interaction is possible when the atoms are in their initial states and one when in their final states. Whereas, when $\Delta E = 0$, $U(r)$ acts fully as a scattering potential which determines the transfer cross-section, when $\Delta E \neq 0$ its effect is reduced by the interference between the waves, representing the initial and final states of relative motion, which are no longer of the same wave-length. This is one way in which the decrease of transfer cross-section with increase of ΔE may be understood.

Consider a transfer reaction in which the resonance is imperfect, viz. $A' + B \rightarrow A + B'$. Let V_i , V_f be respectively the interaction between the atoms in the initial and final states, ignoring any modifications due to the possibility of transfer. Fig. 198(a) shows the corresponding potential energy curves V_i , V_f , including the internal energy of excitation. If at some separation R , $V_i \sim V_f = \Delta E$, the curves V_i and V_f of Fig. 198(a) cross. Two cases can thus be distinguished, according to whether or not a crossing point occurs.

10.31. The crossing-point case. Crossing only occurs because the possibility of transfer has been ignored. When this is included the two interactions are replaced by

$$V'_i + V'_j \pm \{(V'_i - V'_j)^2 + \frac{1}{4}U^2\}^{\frac{1}{2}}, \quad (92)$$

and may be represented by the curves I and II in Fig. 198 (b). The curves no longer cross and the point C , where $r = R$, is one in which the separation is a minimum and of order $|U(R)|$. If the collision is now allowed to take place infinitely slowly the interaction will be of the form of curve I, Fig. 198 (b), throughout, the atoms will approach and separate again in the same state as initially. This is no longer the only possibility if the collision takes place at a finite rate. As the atoms approach along curve I of Fig. 198 (b) there is a chance that a jump will take place to curve II. This chance will have a strong maximum at the point C and may be regarded as only finite there. After passing C the chance that the interaction will still be following curve I is $1 - P$, there being a chance P that it will follow curve II instead. Eventually the atoms will reach the distance of closest approach and then begin to separate again. There will again be a probability P of a transition at the crossing-point C . The chance that, after separating finally beyond C the atoms will be found to be following interaction II, will therefore be $(1 - P)P + P(1 - P)$. The first arises from the chance of a jump at C occurring on the way back along curve I, the second from the chance of no jump at C on the way back following curve II. The chance of a transition is therefore $2P(1 - P)$.

To convert this argument into a means of determining the cross-section we note first that the probability P depends on the relative angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$ of the impinging atoms. Associated with this angular momentum is a classical cross-section $(2l+1)\pi/k^2$, where $k\hbar$ is the relative linear momentum of the two atoms (see Chap. III, § 2.21). The transfer cross-section is therefore

$$Q_l = \frac{\pi}{k^2} \sum (2l+1)2P_l(1-P_l). \quad (93)$$

P_l has been calculated by several authors.† It is given by

$$P_l = e^{-2\delta_l},$$

$$\delta_l = (2\pi)^{\frac{1}{2}} U^2(R)\hbar \left/ \left\{ \left| \frac{dV'_i}{dr} - \frac{dV'_j}{dr} \right|_R v_l \right\} \right., \quad (94)$$

v being the relative velocity of the two atoms, with relative angular momentum $\{l(l+1)\}^{\frac{1}{2}}\hbar$ at the crossing-point. This formula is valid provided v_l , which is given by

† Landau, *Phys. Zeits. Sowjetunion*, **2** (1932), 46; Zener, *Proc. Roy. Soc. A*, **137** (1932), 696; Stueckelberg, *Helv. Phys. Acta*, **5** (1932), 370.

$(\hbar/M)\{k^2 - (8\pi^2 M V_i'/\hbar^2) - l(l+1)/R^2\}^{1/2}$, is real. If it is not, then P_i is negligible. The value l_0 of l for which v_l vanishes will be large for all gas-kinetic encounters, so that

$$Q_i \simeq \frac{4\pi}{k^2} \int_0^{l_0} l e^{-2\delta_l} (1 - e^{-2\delta_l}) dl. \quad (95)$$

It is of interest to note that $P(1-P)$ is small, not only when the potential $U(R)$ is small but also in the opposite extreme of large $U(R)$, small v_l , or small difference in slope of the functions V_i' and V_f' . The first is the case of weak interaction, the second of nearly adiabatic conditions.

10.32. The case of no crossing-point. If no crossing-point exists there may nevertheless be a separation R at which $V_i' \sim V_f' + |\Delta E| \simeq |U(R)|$. Such a point is a critical region in which transitions may take place just as near a crossing-point. In both cases the separation between the curves is of order $|U(R)|$. It would be expected then that a formula similar to (94) would hold in this case with $\left| \frac{dV_i'}{dr} - \frac{dV_f'}{dr} \right|_R$ replaced by $(dv/dr)_R$. Although this has not been proved in general Stueckelberg† has shown that, when $U(r)$ has the form C/r^s , and V_i' and V_f' are negligible,

$$P_i = e^{-2\delta_i}, \quad \delta_i = 2\pi \{U(R)\}^2 M_s / \hbar (dU/dr)_R v_i, \quad (96)$$

where M_s , which depends on s , is of order unity, and v_i is real. This will be so for $l < l_0 (= kR)$. However, in this case it is not possible to ignore the contribution from relative angular momenta greater than $\{l_0(l_0+1)\}^{1/2} \hbar$ and Stueckelberg gives an approximate expression p_l for such cases also. We then have

$$Q_i \simeq \frac{4\pi}{k^2} \int_0^{l_0} l e^{-2\delta_l} (1 - e^{-2\delta_l}) dl + \frac{2\pi}{k^2} \int_{l_0}^{\infty} l p_l dl. \quad (97)$$

If neither a crossing-point R nor a critical region in the sense described above exists, then the transition can only take place with appreciable probability in two stages provided there is a third potential energy curve which crosses or possesses a critical region with respect to both curves. Even in this case the overall probability is likely to be greatly reduced because of the need for two transitions.

10.33. Application of the formulae. The case in which a critical region exists rather than a crossing-point is of most importance for the discussion of the transfer of excitation. With $U(r) \sim -C/r^s$ Stueckelberg finds from (97) that

$$Q_i = \pi (C/|\Delta E|)^{2/s} f(\Delta E^{s-1/s} C^{1/s} / \hbar v), \quad (98)$$

† Loc. cit.

where

$$\begin{aligned} f(x) &= 8M_s x/s, & x \ll 1, \\ &= 32N_s x^{s-1} e^{-2x}, & x \gg 1, \end{aligned}$$

N_s being a quantity of order unity depending on s . $f(x)$ is illustrated for $s = 3$ in Fig. 199 (a).

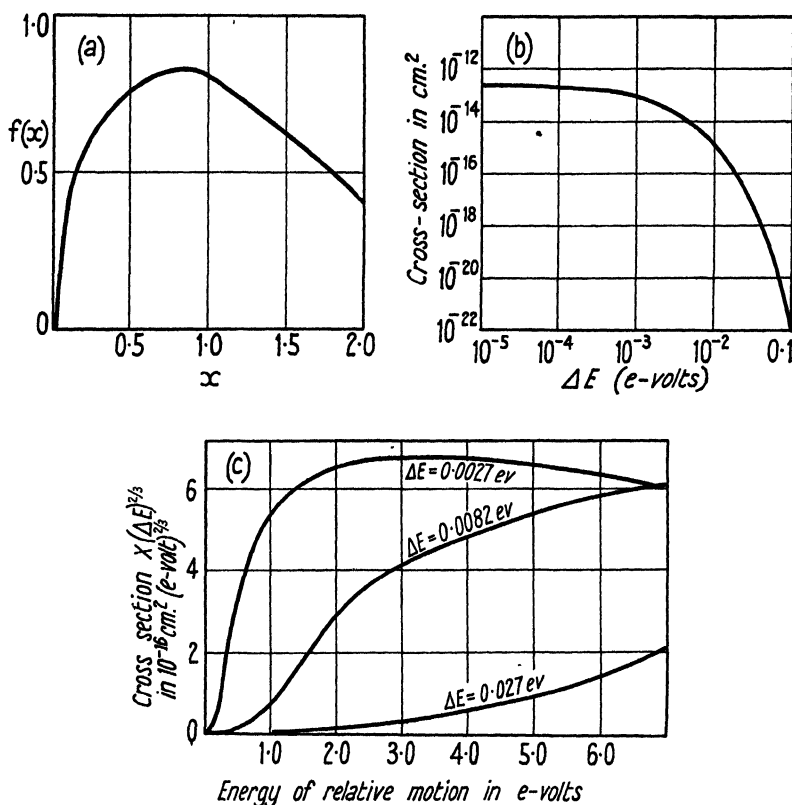


FIG. 199 (a) The function $f(x)$ occurring in Stueckelberg's formula for the excitation transfer cross-section.

(b) and (c) Theoretical variation of the transfer cross-section Q_s with the energy discrepancy ΔE and relative velocity of impact v .

(b) Variation with ΔE , v being constant ($= 1.25 \sqrt{\text{volts}}$ for atoms of mass 40).

(c) Variation with v for three values of ΔE . The energy scale in (c) is appropriate to the case of two helium atoms ($M = 40$).

For $s = 3$ and exact resonance ($\Delta E = 0$) we obtain the same result as in (32) of § 3.3. When

$$\Delta E^{\frac{1}{2}} C^{\frac{1}{2}} / \hbar v \gg 1, \quad (99)$$

which corresponds to nearly adiabatic conditions (see (87)), the transfer cross-section Q_i , for constant v , falls off as $\Delta E^{\frac{1}{2}} \exp\{-2\Delta E^{\frac{1}{2}} C^{\frac{1}{2}}/\hbar v\}$. Fig. 199 (b) illustrates the variation of Q_i with ΔE for a case in which $C = e^2 a_0^2$, and a velocity corresponding to argon atoms with 1.6 eV energy. The sharpness of the resonance is obvious.

The variation of Q_i with velocity for a fixed ΔE is of the form $v^2 e^{-a/v}$, where $a = 2\Delta E^{\frac{1}{2}} C^{\frac{1}{2}}/\hbar$, reaching a maximum of order $\pi(C/\Delta E)^{\frac{1}{2}}$ for a velocity of order $(C\Delta E^2)^{\frac{1}{2}}/\hbar$ and falling off as v^{-1} at higher velocities. Fig. 199 (c) illustrates some typical examples. They exhibit the general features predicted in § 10.1. Thus the rate of rise to the maximum increases with decrease of ΔE .

Similar results are obtained for other values of s except that, according to (98), Q_i vanishes in the case of exact resonance, reaching a maximum at a small value of ΔE and then decreasing. The zero value for $\Delta E = 0$ cannot be correct, as is clear from the discussion in § 3.32, so the approximations made in obtaining (98) must fail in these cases for small ΔE . The variation of Q_i with ΔE probably follows a resonance curve similar to that for $s = 3$.

In many collisions involving electron exchange a crossing-point exists. Thus, in collision between an ion and an atom, the interaction V_i will fall off as $\alpha e^2/r^4$, where α is the polarizability of the atom. There will therefore be a crossing-point at $R = \{(\alpha_1 - \alpha_2)e^2/\Delta E\}^{\frac{1}{2}}$, where α_1, α_2 are the polarizabilities of the neutral atoms before and after charge transfer. R will be very large if ΔE is small, but the cross-section for charge transfer will then be much less than πR^2 . This is because in such cases $U(r)$ falls off exponentially with r and will be so small at large separations that P_i in (94) will be very small. The variation of Q_i with ΔE , using (95), is much the same as for transfer of excitation with $s > 3$, although the rate of decrease for large ΔE is much slower. The approximations break down again very close to exact resonance, but there is little doubt of the resonance character of the charge transfer process.

Further experimental evidence concerning near-adiabatic collisions between atoms will be described and discussed in Chap. VIII, § 6, in connexion with excitation and ionization by homogeneous beams of ions and neutral atoms as well as with charge transfer. In Chap. X, § 2.3, collisions involving mutual neutralization of a positive and a negative ion by charge transfer between them are discussed in terms of the crossing-point theory.

The Wigner rule (§ 8.2) follows because of the small value of the function $U(r)$ if the transitions concerned violate the spin selection rules.

It is still far from clear why such transfer reactions as (74) occur with high probability. Although $U(r)$ will not exactly vanish for such cases due to the presence of spin-orbit coupling, which leads to some admixture of triplet character in a singlet state and vice versa, such effects are very small in a light atom such as helium.

10.4. Summary

We may summarize the conclusions which are obtained from the experimental results, amplified by the theoretical discussion, as follows:

(a) The cross-section for a collision between two atoms with initial relative velocity v , in which a change ΔE of internal energy occurs, will be small compared with the gas-kinetic if

$$a|\Delta E|/\hbar v \gg 1,$$

a being of the order of the gas-kinetic radius.

(b) The cross-sections for a particular process of charge or excitation transfer, for a fixed initial relative velocity, fall off rapidly, for similar systems, as $|\Delta E|$ increases, exhibiting a maximum at or near exact energy resonance.

(c) The maximum cross-sections will not greatly exceed the gas-kinetic except for collisions in which a transfer of excitation occurs involving an optically allowed transition in each colliding atom.

(d) For a fixed ΔE and a the cross-section increases rapidly with relative velocity until $a|\Delta E|/\hbar v$ is of order unity, after which it decreases very slowly. In the case of exact resonance the cross-section decreases slowly as v increases from zero.

11. Collisions in which electronic transitions occur. Discussion of results—Collisions involving molecules

In dealing with collisions in which more than two atoms are involved the course of the reaction can no longer be traced out completely by following the relative motion in relation to a single set of potential energy curves. The potential energy for a given state of the polyatomic system will depend on more than one coordinate defining the configuration of the system. Even in the simplest case of three atoms, as, for example, in discussing the quenching of excited atoms by diatomic molecules, three such coordinates are required and, instead of a potential energy curve for a given electronic state, it is necessary to consider a three-dimensional potential energy hypersurface.

The course of a reaction may be represented by the path of a representative point on the hypersurface,[†] starting from given initial conditions. On tracing out such paths the chance of a jump occurring to another hypersurface corresponding to a different electronic state may be ignored except where two such surfaces intersect. To examine the consequence of a jump the Franck-Condon principle may be assumed—the configuration coordinates and velocities remain unchanged during the electronic transition. The chance of the jump taking place depends on the same formula as (94), the relevant slope of the functions V_i and V_j and component of velocity v being taken along the tangent to the path of the representative point at the hypersurface intersection concerned. Although it is usually out of the question to attempt to trace out the possible reaction paths in detail, in all but the simplest cases, there are two general features, distinguishing the polyatomic from the diatomic case, which emerge, both due to the extra degrees of freedom.

In the diatomic case the probability of a reaction may be small due to the absence of any crossing or critical point between the corresponding potential energy curves and of a third curve which interacts with both. The chance of a small probability in the polyatomic case from this cause is much less because of the greater number of degrees of freedom open to the representative point.

The second effect, which also tends to increase the probability of reaction, is that the chance of an electronic transition being reversed on the outward path is much reduced. So many paths are available that the chance that the path of the representative point will pass twice through an intersection between two hypersurfaces is usually very small. The chance of an electronic transition persisting to the conclusion of the collision is then no longer given, in the notation of (93), by $2P(1-P)$ but by P . This is of order unity when the crossing-point occurs with the atoms not too far apart, and there are no selection rules (such as forbidden change of multiplicity) operating. In the diatomic case the factor $1-P$, allowing for reversal of the process on the return path, very much reduces the chance of the transition persisting. For the polyatomic case the chance will remain high.

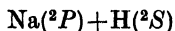
The chance of reversal may nevertheless be appreciable even in the polyatomic case if the separation of the interacting hypersurfaces is small over a wide region. Thus the chance of a transition involving a considerable change of electronic energy may be greater than that when a small

[†] See Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941, Chap. III.

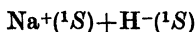
change only is involved. This is in sharp contrast to the diatomic case where a resonance effect occurs as far as the change of electronic energy is concerned. It is not correct to suppose, however, that in the polyatomic case a large amount of electronic energy is transferred to energy of relative translation. Instead it will, in general, be taken up as energy of molecular vibration. A change of curvature of the path of the representative point corresponds to excitation of vibrational degrees of freedom and is almost certain to occur when a jump takes place to a different potential energy hypersurface.

Summarizing these conclusions we should expect that molecules would be much more effective than atoms in producing quenching of excited atoms and that the biggest cross-sections are likely to be associated with large changes in electronic excitation. If the change is too large, however, the cross-section may be small even in the polyatomic case because of the absence of an intersection between the respective hypersurfaces or of a hypersurface intersecting both.† The excess energy released by the quenching will be mainly taken up as molecular vibration.

These conclusions are in general agreement with the data on quenching. Laidler,‡ extending earlier work by Magee and Ri,§ has considered in some detail the quenching of sodium by hydrogen and halogen molecules. To simplify the problem he supposed that the course of events for a collision in which the three atoms remained collinear was sufficiently representative of the average case. The configurational coordinates are then limited to two which may be taken as the respective distances of one of the molecular atoms from the other and from the sodium atom. Contrasting the effectiveness of atomic and molecular hydrogen in quenching, Laidler showed first that no crossing-point exists between any potential curve, of the same multiplicity, derived from the respective interaction of a normal hydrogen atom with a sodium atom in the normal 2S and excited 2P states. A curve derived from the interaction of $\text{Na}+(^1S)+\text{H}-(^1S)$ does intersect the lowest curve derived from



but does not have a deep enough maximum to intersect the curve derived from $\text{Na}(^2S)+\text{H}(^2S)$. Quenching by atomic hydrogen would therefore be very ineffective. On the other hand, with molecular hydrogen it is found that the potential energy surface which arises from the



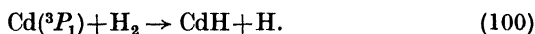
† This must be the reason for the low deactivation cross-section of $\text{O}(^1S)$ by O_2 in the measurements of Kvitte and Vegard (§ 9).

‡ *J. Chem. Phys.* **10** (1942), 34.

§ *Ibid.* **9** (1941), 638.

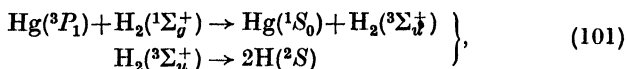
curve for infinite separation of the second hydrogen atom does intersect *both* the surfaces arising from the $\text{Na}(^2S) + \text{H}(^2S)$ and $\text{Na}(^3P) + \text{H}(^2S)$ curves at H-H separations somewhat larger than the equilibrium value for H_2 . Molecular hydrogen is thus an effective quencher, the cross-section being of the order πR^2 , where R is the Na-H separation at the innermost crossing-point. Laidler's estimate of R is of the correct order of magnitude (see Table XII). A similar state of affairs prevails for the halogens. In these cases the cross-section is larger as the crossing-points occur at a greater sodium-halogen atom separation.

A similar analysis has been applied by Laidler† to discuss the quenching of excited mercury and cadmium. In § 8 evidence was given which indicated that, whereas nitrogen quenches by producing a transition to the nearby metastable state, hydrogen produces transitions to the ground state. With mercury the hydrogen is dissociated, but with cadmium the process involves the production of cadmium hydride, viz.:



According to the general arguments presented above, hydrogen should be more effective than nitrogen as it quenches by producing a much larger change of electronic energy. This is in agreement with the observed data.‡ Presumably with nitrogen there are no common interactions which would make a transition to the ground state possible.

Tracing the probable course of the representative point in the hydrogen quenching, Laidler found that the process with mercury can be regarded as a transfer of electronic excitation of the form



in which the hydrogen molecule is excited to the unstable state (see Chap. IV, § 5.1). In this case the initial state of the combined system is a triplet. A surface corresponding to a polar state of the same multiplicity intersects this surface and also one which connects the curves for the $\text{HgH}(^2\Sigma^+)$ and $\text{H}_2(^3\Sigma_u^+)$ states of the corresponding diatomic molecules in the respective limits of large H and Hg atom distance. The minimum of this latter surface, which occurs at large H atom distance, represents an HgH molecule, but the conversion of surplus energy into vibration within this molecule is likely to be so effective that it is excited above dissociation, leading essentially to the above reaction. The dissociation

† Ibid. 10 (1942), 43.

‡ Some contribution to the small observed cross-section may be due to repopulation of the 3P_1 level from the metastable state by collision, thus reducing the quenching.

of hydrogen by metastable xenon† presumably occurs in a similar way. With cadmium, on the other hand, the CdH molecule formed is stable, there being insufficient surplus energy available to dissociate it.

Laidler‡ has also considered the quenching efficiency of hydrocarbons, but the discussion of these questions would take us too far into the field of photochemistry.

One further question arises. It has often been assumed that, in considering the efficiency of inelastic collisions involving molecules, vibrational energy should be treated on the same footing as electronic energy and a resonance criterion applied as in § 10.1. The above discussion does not take any account of the quantization of vibration and it is probable that this is of no great importance except perhaps when a small change of electronic energy, comparable with the energy separation of the lowest molecular vibrational levels, is concerned. Zemansky§ derived evidence of a resonance effect in the quenching of mercury resonance radiation by different molecules on the assumption that a transition to the metastable state occurred accompanied by excitation of molecular vibration. Many of the molecules which he included have since been shown to quench by a chemical mechanism and insufficient data remain to establish the case for or against a resonance effect.

12. Collisions involving vibrational and rotational energy changes

12.1. *Introductory remarks concerning the probability of vibrational and rotational transitions in gas-kinetic collisions*

We have discussed a number of collision reactions in which electronic energy is transformed into energy of molecular vibration as well as energy of relative translation. In the present section we now consider collisions in which changes in molecular vibration or rotation occur, unaccompanied by electronic transitions. It is convenient to defer the discussion of the transformation of energy into, or out of, energy of rotation until we have considered vibrational energy changes.

The considerations of § 10.1 may be applied to examine the conditions under which a collision will be nearly adiabatic with respect to vibrational energy changes. Thus the condition (87) shows that the probability of vibrational excitation in a collision will be small if

$$\frac{av}{v} \gg 1. \quad (102)$$

† *J. Chem. Phys.* **10** (1942), 43.

‡ *Phys. Rev.* **36** (1930), 919. See also Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge (1934).

§ Calvert, *Zeits. f. Phys.* **78** (1932), 479.

In this expression $h\nu$ is the energy of the vibrational quantum excited and a/v is the time of collision. a may be taken as of the order of gas-kinetic radii and v as the relative velocity of the colliding systems when widely separated, unless a strong attractive force exists between them as, for example, when there is a chemical affinity between atoms in the colliding systems. If such a force exists the relative motion may be so strongly accelerated during the collision that the correct value to take for v may be much larger.

The condition (102) may be recast in a slightly different form which is sometimes useful. If d is the amplitude of vibration and M the reduced mass associated with it, then

$$d \simeq (\hbar/\pi\nu M)^{\frac{1}{2}},$$

so that (102) becomes
$$\frac{a}{d} \left(\frac{\hbar\nu}{\pi M v^2} \right)^{\frac{1}{2}} \gg 1.$$

Under gas-kinetic conditions we may write

$$v^2 \simeq \kappa T/M_1,$$

where M_1 is the mass of the lighter molecule concerned in the collision and T the absolute temperature. We thus have, finally, the condition

$$\frac{a}{d} \left(\frac{\hbar\nu M_1}{\pi\kappa T M} \right)^{\frac{1}{2}} \gg 1 \quad (103)$$

as that which must be satisfied in order that the chance of excitation of a vibrational quantum $h\nu$ should be small.

For most molecules $h\nu$ will be greater than κT only for transitions between the deepest vibrational levels for which $a \gg d$. The chance of vibrational deactivation under these conditions will certainly be small. On the other hand, if $h\nu < \kappa T$, the condition may still be satisfied because $a \gg d$, but when $h\nu/\kappa T$ is sufficiently small the probability of excitation or deactivation per collision will be comparable with unity.

As we shall see in §§ 12.2–12.4, these features are exhibited by the experimental data. The dispersion of sound is due to the slowness of vibrational deactivation when (103) is satisfied but $h\nu < \kappa T$. On the other hand, the study of sensitized band fluorescence reveals cases in which $h\nu/\kappa T$ is so small that (103) is not satisfied and exchange of vibrational and translational energy occurs freely. A more detailed discussion of these questions will be given in § 12.6 after the nature of the experimental evidence has been described.

Turning to the excitation of rotational energy, we may obtain the condition for it to occur readily on collision by substituting for ΔE in (87)

$$\Delta E = \frac{1}{2} I \omega^2,$$

where the angular momentum $I\omega$ is of order $\hbar$. The condition becomes

$$\frac{a\hbar}{4\pi Iv} \gg 1.$$

Substituting further

$$I = MR^2,$$

where M is the reduced mass for the internal molecular motion and R is of the order of the interatomic separation, gives the condition as

$$\frac{a}{8\pi^2 R^2} \frac{\hbar}{Mv} \gg 1. \quad (104)$$

In all cases, except for the lightest molecules at very low temperatures, the wave-length $\hbar/Mv$ is very small compared with either a or R , which are of the same order of magnitude, so that the condition is not satisfied. Accordingly, it is to be expected that excitation or deactivation of molecular rotation will take place very readily in gas-kinetic collisions. This is generally confirmed by the experimental evidence discussed in § 12.7 below.

12.2. *The dispersion and absorption of high-frequency sound*

The well-known Laplace formula for the velocity v of sound in a gas at pressure p and density ρ ,

$$v = (p\gamma/\rho)^{\frac{1}{2}}, \quad (105)$$

where γ is the ratio of the specific heats of the gas, includes no dependence on the frequency of the sound. If account is taken of viscosity and of heat conduction and radiation, an absorption coefficient α/λ where

$$\alpha = \frac{4\pi^2}{v\rho\lambda} \left(\frac{4}{3}\mu + \frac{\gamma-1}{c_p} K \right), \quad (106)$$

where μ is the viscosity, K the heat conductivity, λ the wave length, and c_p the molar specific heat at constant pressure, is found and also a slight dependence of velocity on frequency. This is far too small to explain the observed dispersion of high-frequency sound. The observed absorption in the same frequency range is also much greater than that given by the formula (106) and depends on the frequency. It is only in monatomic gases that the classical formulae (105) and (106) are found to hold.

The explanation of these anomalies was first given by Herzfeld and Rice,[†] after which the theory was developed in detail by a number of authors.[‡] The Laplace formula (105) supposes that the thermal changes

[†] *Phys. Rev.* **31** (1928), 691.

[‡] See, for example, Bourgin, *Nature*, **122** (1928), 133; *Phys. Rev.* **50** (1936), 355; *J. Acous. Soc. America*, **5** (1934), 57; Kneser, *Ann. der Physik*, **11** (1931), 761; Rutgers, *ibid.* **16** (1933), 350.

which take place as the sound wave travels through the gas occur so slowly that the changes in the excitation of all the degrees of freedom which contribute appreciably to the specific heat can follow with very little time lag. If this is not true, then the effective specific heat, and hence the velocity of propagation, will depend on the frequency. Furthermore, there will be a phase difference between the pressure and density fluctuations giving rise to an absorption.

We now put this in more definite terms and see how, from measurements of dispersion and absorption, the rate of vibrational excitation and deactivation by collision can be determined. We shall consider the simplest case in which the effect arises from the slowness of transitions between the ground and first excited vibrational levels.

We may still start from the formula (105) with the ratio γ written in the form $1 + R/c_v$, where c_v is the molar specific heat at constant volume and R the gas constant. The only modification is that we must regard c_v as a complex function c_ω of frequency $\omega/2\pi$, the imaginary part corresponding to the phase difference between the pressure and density fluctuations. Writing the complex velocity v as $V(1 + i\alpha/4\pi)$, say, the absorption coefficient is then given approximately by α/λ as in (106).

We write c_ω for the effective specific heat at frequency ω so that c_∞ is the limit for infinitely high frequencies. At these frequencies a vibrational degree of freedom can no longer play any part in the specific heat, whereas at a lower frequency it can do so. Hence, if $h\nu$ is the energy difference between the ground state and the first excited state,

$$c_\omega - c_\infty = h\nu \Delta n_1 / \Delta T,$$

where n_1 is the number per mole of vibrationally excited molecules.

The time rate of change of n_1 will be given by

$$\frac{\partial n_1}{\partial t} = -k_1 n_1 + k_0 n_0.$$

k_1 is the number of deactivating collisions made by an excited molecule per second, k_0 the corresponding number of exciting collisions made per second by a normal molecule. They will be related by

$$k_0/k_1 = g \exp(-h\nu/\kappa T),$$

where g is the ratio of the statistical weights of the ground and excited vibrational states.

With a periodic disturbance of frequency $\omega/2\pi$ we may replace $\partial/\partial t$ by $i\omega$, so that

$$i\omega n_1 = -k_1 n_1 + k_0 n_0,$$

and, as $n_0 + n_1$ is constant,

$$\Delta n_1 = (n_0 \Delta k_0 - n_1 \Delta k_1) / (i\omega + k_0 + k_1).$$

We then have

$$\Delta n_1 / (\Delta n_1)_{\omega=0} = (k_0 + k_1) / (i\omega + k_0 + k_1),$$

so that

$$\hbar\nu \frac{\Delta n_1}{\Delta T} = \hbar\nu \left(\frac{\Delta n_1}{\Delta T} \right)_{\omega=0} \frac{k_0 + k_1}{(i\omega + k_0 + k_1)}.$$

Hence

$$c_\omega - c_\infty = \frac{k_0 + k_1}{i\omega + k_0 + k_1} (c_0 - c_\infty),$$

where c_0 is the specific heat at very low frequencies. This gives

$$v^2 = \frac{p}{\rho} \left\{ 1 + R \frac{1 + i\omega\beta}{c_0 + i\omega\beta c_\infty} \right\}, \quad (107)$$

where $k_0 + k_1 = 1/\beta$.

As in all cases of practical importance the imaginary part of v is small we obtain, to a good approximation,

$$V^2 = (V_0^2 \omega_i^2 + V_\infty^2 \omega^2) / (\omega_i^2 + \omega^2), \quad (108)$$

$$\alpha = 2\pi(V_\infty^2 - V_0^2)\omega_i \omega / (V_0^2 \omega_i^2 + V_\infty^2 \omega^2). \quad (109)$$

V_0 and V_∞ are the velocities of propagation in the limiting cases of very low and very high frequencies respectively and

$$\omega_i = c_0 / c_\infty \beta.$$

The variation of these expressions with $\log \omega$ is illustrated in Fig. 200. V^2 has a point of inflexion at $\omega = \omega_i$ and α a maximum at $\omega = \omega_m = \omega_i V_0 / V_\infty$.

Both V^2 and α may be measured as functions of frequency. From such measurements ω_i may be obtained. Thus, from (108),

$$\omega_i^2 = \omega^2 (V_\infty^2 - V^2) / (V^2 - V_0^2), \quad (110)$$

and the velocities V_∞ and V_0 may be calculated from the known specific heats and vibrational constants of the molecules concerned.

Once β is known the collision cross-section for deactivation, Q_v , is given from the relation

$$\begin{aligned} \beta^{-1} &= k_1 \\ &= n_0 Q_v (2\pi\kappa T/M)^{\frac{1}{2}}, \end{aligned} \quad (111)$$

where M is the mass of a gas molecule. It is customary to express Q_v

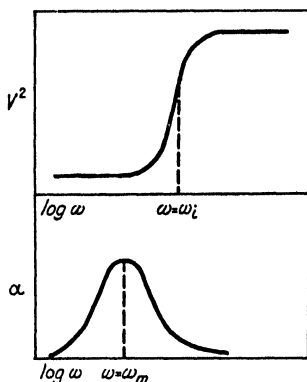


FIG. 200. Illustrating the variation with frequency $\omega/2\pi$ of the velocity V and the quantity α (absorption coefficient $= \alpha/\lambda$), for high-frequency sound in a dispersive gas.

as a fraction of the gas-kinetic cross-section of the molecule determined from the viscosity of the gas concerned (see § 4).

The formulae may easily be generalized to cases in which more than one vibrational mode contributes. In (106), $c_0 - c_\infty$ is the contribution to the equilibrium specific heat due to the particular vibrational mode concerned. When there are a number of contributing modes $A, B, \dots$, whose contributions to the equilibrium specific heats are $c_A, c_B, \dots$, respectively and whose relaxation times are $\beta_A, \beta_B, \dots$, then (106) is replaced by

$$c_\omega - c_\infty = \sum c_A / (1 + i\omega\beta_A). \quad (112)$$

With the values of β all different this gives rise to a step-like dispersion curve involving a number of different dispersive regions. In many cases, however, the effective relaxation times are so nearly equal that separate regions cannot be distinguished. This is probably because excitation is transferred between the modes without difficulty.

12.21. Variation of dispersion and absorption with pressure, temperature, and impurity content. According to the theory outlined above, the relaxation time must vary inversely as the gas pressure so that the dispersive region should shift to higher frequencies as the pressure increases. This provides a test of the essential validity of the theory. It must be remembered, however, that in some cases the rate of vibrational deactivation by collision is so slow that the possibility of radiation may not be negligible. This would include in β a term independent of pressure. At the other extreme, at high pressures, three-body collisions may have some influence, introducing a quadratic pressure variation.

Study of the effect of temperature on the dispersion and absorption gives information about the variation of the deactivation cross-section Q_v with relative kinetic energy of the colliding molecules.

If the deactivation cross-section is very sensitive to the detailed properties of the colliding molecules it is to be expected that small admixtures of impurities might have a profound influence on dispersion and absorption. There can only be such an effect if the molecules of the impurity are much more effective in deactivating the excited molecules of the main gas than are normal molecules of the same gas. An impurity must therefore either shift the dispersive region to higher frequencies or have no effect. Study of the effect of impurities leads to valuable information about the deactivation cross-sections when the colliding molecules are unlike.

12.22. The evidence from measurements of dispersion and absorption of ultrasonic waves. The first measurements which revealed a dispersion

effect in the propagation of sound waves were made by Pierce,† in 1925, in carbon dioxide. Since then the propagation in this gas has been studied very extensively, while the behaviour of a number of other gases has also been investigated. For a summary of the methods used reference may be made to the article by W. T. Richards, 'Supersonic Phenomena' in *Rev. Mod. Phys.* 11, 36 (1939).

In general the results are in complete agreement with the predictions of the theory outlined in § 8.21. The pressure variation is consistent with the collision theory and in all cases impurities either have no effect or shift the dispersion to higher frequencies.

We are particularly interested here in the evidence provided about the cross-sections for vibrational deactivation.

TABLE XVI

Mean Number of Collisions before Vibrational Deactivation occurs at Ordinary Temperatures

Main gas	CO ₂ ‡	Cl ₂ §	N ₂ O	O ₂ ††
<i>Impurity</i>				
CO ₂	50,000 (90,000)	..	..	..
Cl ₂	..	34,000	..	..
N ₂ O	..	..	7,500	..
O ₂	..	..	..	160,000
N ₂	1,200	43,000	..	100,000
A	47,000	32,000	3,000	..
He	2,600	900	1,000	160,000
H ₂	300	780	650	20,000
D ₂	..	..	440	..
CO	230	230	3,600	7,000
CH ₄	2,400	190	840	..
NH ₃	..	..	450	390
HCl	130	120	..	..
H ₂ O	105	..	105	420

‡ Eucken and Becker, *Zeits. f. phys. Chem.* B, 20 (1933), 467; 27 (1943), 219; Wallmann, *Ann. der Physik*, 21 (1934), 671; Metter, *Phys. Zeits. Sowjetunion*, 12 (1937), 233. More recent measurements by van Itterbeek, de Bruyne, and Mariëns, *Physica*, 6 (1939), 511 give the somewhat greater collision numbers which are indicated by brackets. They attribute this to greater purity of their gas (see § 8.21).

§ Eucken and Becker, loc. cit.

|| Eucken and Jaachs, *Zeits. f. phys. Chem.* B, 30 (1935), 85.

†† Knudsen, *J. Acous. Soc. America*, 5 (1933), 112; 6 (1935), 199. Kneser and Knudsen, *Ann. der Physik*, 21 (1935), 682. Sinness and Roseveare, *J. Chem. Phys.* 4 (1936), 427.

Table XVI summarizes the results obtained from typical measurements of the dispersion of sound in CO₂, Cl₂, N₂O, and O₂.

No dispersion is observed in nitrogen up to frequencies of 500 kc. or

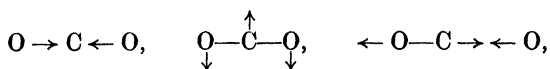
† *Proc. Am. Acad. Arts and Sciences*, 60 (1925), 271.

hydrogen up to frequencies of 1,000 kc. and it has been checked that none occurs in helium. Dispersion, and sometimes absorption, has been observed also in NH_3 ,[†] CS_2 ,[‡] CO ,[§] C_2H_4 ,^{||} SO_2 ,[‡] and N_2O_4 .^{††}

The striking features of this result are the very low probabilities of deactivation in collision between like molecules and the highly specific character of the dependence on the nature of the colliding molecules. Thus, in chlorine, carbon monoxide is 200 times as effective in producing deactivation as is nitrogen, a remarkable result in view of the general similarity of N_2 and CO in most respects.

A very interesting study of the variation of the deactivation probability with temperature has been carried out by Eucken and his collaborators.^{‡‡} They studied the dispersion of CO_2 and N_2O , both pure and with various admixed impurities, in the temperature range from 20° to 400° C. They found that, with the pure gases, the deactivation probability per collision increased steadily and rapidly with the temperature, but this was by no means a general feature for impure gases. Some typical results are illustrated in Fig. 201. A suggestive correlation is that the temperature coefficient of the probability is high and positive when the probability is very small but is much smaller and may be negative when the probability is larger. Further details are given in § 12.6 in connexion with the theoretical discussion.

A point which is not yet completely clarified concerns the identification of separate dispersive regions due to the existence of normal modes of vibration with different relaxation times. Thus in CO_2 the three fundamental modes of vibration



have frequencies 4.16 , 2.00 , and $7.05 \times 10^{13} \text{ sec.}^{-1}$ respectively, the second being doubly degenerate. Only a single dispersive region is observed, even though the first harmonic of the lowest frequency mode is in approximate resonance with the ground vibration of the first mode. The same absence of distinct contributions from different normal modes is a general feature of the observations. It is probably due to rapid redistribution of excitation among the different modes.

[†] Steil, *Zeits. f. phys. Chem. B*, **31** (1936), 343.

[‡] Richards and Reid, *J. Chem. Phys.* **2** (1934), 193, 206.

[§] van Itterbeek and Mariëns, *Physica*, **4** (1937), 207, 609.

^{||} Richards and Reid, loc. cit.; Richards, *J. Chem. Phys.* **4** (1936), 561.

^{††} Richards and Reid, *ibid.* **1** (1932), 114, 737; *J.A.C.S.* **54** (1932), 3014.

^{‡‡} *J. Chem. Phys.* **10** (1942), 145; **14** (1946), 150.

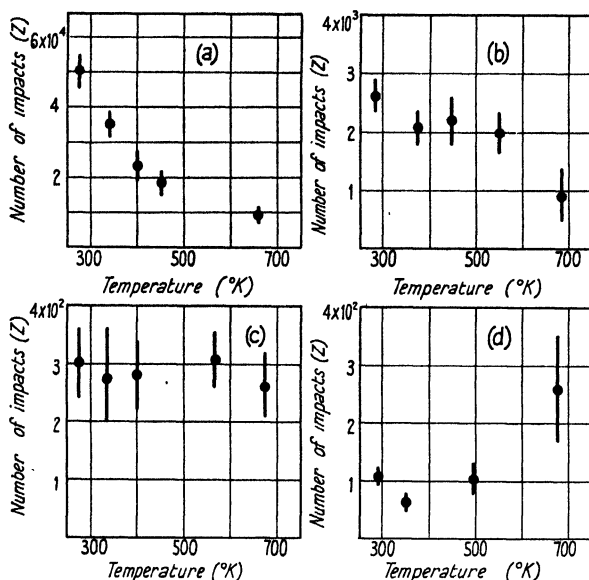


FIG. 201. Effect of impurities on the vibrational deactivation probability of CO_2 and its variation with temperature. The figure shows the mean number (Z) of impacts before vibrational deactivation occurs as a function of temperature. (a) Pure CO_2 ; (b) $\text{CO}_2 + \text{He}$; (c) $\text{CO}_2 + \text{H}_2$; (d) $\text{CO}_2 + \text{H}_2\text{O}$.

12.3. The effect of persistence of vibration in gas dynamics

In the flow of compressible fluids about obstacles, compressions and rarefactions occur which are accompanied by temperature changes. The rate of change of temperature is determined by the velocity of flow and the scale of the obstacles. If the rates of change are faster than or comparable with the rate of vibrational deactivation, the vibrational degrees of freedom will not come to thermodynamical equilibrium with the other degrees of freedom. The transfer of energy between the vibrational and the other degrees of freedom will therefore take place by an irreversible process leading to an increase of entropy.

Such effects may lead to additional loss in high-speed turbines at high temperatures, which may be comparable with that due to skin friction. In wind-tunnel and similar tests it is often convenient to substitute for the working gas another one which may be used more conveniently at a given Mach or Reynolds number. Care must be taken in adopting such a procedure because the substitute gas may exhibit a substantially different vibrational heat lag from that of the actual gas, resulting in a different behaviour under the flow conditions.

A detailed investigation of these effects has been carried out by Kantrowitz.[†]

The experimental method introduced by Kantrowitz utilizes the arrangement illustrated in principle in Fig. 202. Gas enters the chamber

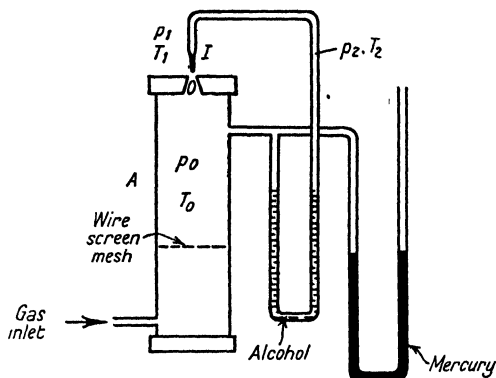


FIG. 202. Illustrating the principle of the apparatus used by Kantrowitz to study the lag in vibrational deactivation in a flowing gas.

A in which it settles at pressure p_0 and temperature T_0 . It expands adiabatically to pressure p_1 and temperature T_1 through a faired orifice *O* of suitable design. Gas which is flowing along the axial stream line of an impact tube *I* is brought to rest at the nose during which its pressure rises to p_2 and temperature to T_2 . If this process is also sufficiently slow to be adiabatic, the molar entropy and energy of the gas which has reached equilibrium at the nose of the impact tube will be the same as the corresponding quantities in the chamber *A*. Hence $p_2 = p_0$ and the reading of the alcohol manometer will be zero. We now consider circumstances in which the expansion through the faired orifice *O* is still so slow that it may be followed by all degrees of freedom, but the compression at the nose of the impact tube is so fast that the vibrational degrees of freedom do not contribute to the heat changes.

Let c_p be the specific heat per unit mass of gas at constant pressure, c'_p that due to all but the vibrational degrees of freedom. Then, if u is the velocity of flow, we must have for the slow expansion

$$c_p T + \frac{1}{2} u^2 = \text{constant}, \quad (113)$$

so

$$c_p T_0 = c_p T_1 + \frac{1}{2} u_1^2,$$

[†] *J. Chem. Phys.* **10** (1942), 145; **14** (1946), 150.

where u_1 is the velocity on leaving the faired orifice. For the compression at the nose we have, on the other hand,

$$c_p' T + \frac{1}{2} u^2 = \text{constant}, \quad (114)$$

so

$$c_p' T_2 = c_p' T_1 + \frac{1}{2} u_1^2.$$

Hence

$$c_p(T_0 - T_1) = c_p'(T_2 - T_1).$$

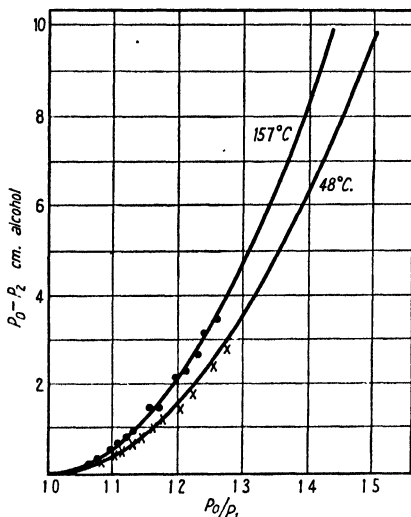


FIG. 203. Comparison of calculated pressures with those observed by Kantrowitz in CO_2 using the apparatus illustrated in Fig. 202.

× experimental points (48°C.); • experimental points (157°C.); ——— calculated.

Also, for the separate adiabatic processes we have

$$\left(\frac{p_2}{p_1}\right)^{R/c_p'} = \frac{T_2}{T_1}, \quad \left(\frac{p_0}{p_1}\right)^{R/c_p} = \frac{T_0}{T_1},$$

where R is the gas constant. Eliminating T_2 we find

$$\frac{p_0}{p_2} = \left[\frac{c_p'}{c_p - (c_p - c_p')T_1/T_0} \right]^{c_p'/R} \left(\frac{T_0}{T_1} \right)^{(c_p - c_p')/R}. \quad (115)$$

This relation was checked in CO_2 by choosing the dimensions of orifice and impact tube so that the time of expansion was of order 10^{-4} sec. and that of compression about 100 times shorter. (The orifice was a hole in a $\frac{1}{2}$ in. plate, the glass impact tube of 0.005 in. diameter, and the chamber pressure such that the gas velocity at the orifice was between 300 and 600 ft./sec.) As the relaxation time for CO_2 is about 6×10^{-6} sec.

the conditions assumed in the equations (113) and (114) are both well satisfied. Fig. 203 illustrates the comparison between the observed values of $p_0 - p_2$ for different values of p_0/p_1 at two temperatures T_0 , 48°C . and 157°C . The agreement is very satisfactory. It was also checked that no pressure difference occurred when the CO_2 was replaced by nitrogen.

To extend these considerations to determine relaxation times by choosing comparable compression times it is necessary to develop a more general theory of the entropy increase which accompanies flow.

Let $u(x, y, z)$ be the speed at some point of the fluid in a state of steady flow and ϵ the energy per unit mass in the vibrational degrees of freedom in excess of that for equilibrium partition at the translational temperature T . We wish to calculate the entropy increase ΔS in proceeding along a stream line with a given element of fluid from a point at time t_0 to another at time t .

The rate of heat flow per unit mass from the vibrational excitation will be proportional to ϵ , so that the rate of entropy change due to this flow will be given by

$$\frac{dS}{dt} = k\epsilon \left(\frac{1}{T} - \frac{1}{T_{\text{vib}}} \right), \quad (116)$$

where T_{vib} , the temperature of the vibration, is given by

$$\epsilon = c_{\text{vib}}(T_{\text{vib}} - T), \quad (117)$$

c_{vib} being the molar vibrational specific heat $c_p - c_p'$. We now have, eliminating T_{vib} ,

$$\frac{dS}{dt} = k\epsilon \left(\frac{1}{T} - \frac{1}{T + T_1} \right), \quad (118)$$

where

$$T_1 = \epsilon / c_{\text{vib}}.$$

Hence

$$\Delta S = \int_{t_0}^t k\epsilon \left(\frac{1}{T} - \frac{1}{T + T_1} \right) dt. \quad (119)$$

If the flow is such that p and T are nearly equal to their ambient values, k is practically constant throughout and

$$\Delta S \simeq \frac{k}{c_{\text{vib}} \bar{T}^2} \int_{t_0}^t \epsilon^2 dt, \quad (120)$$

$\bar{T}$ being the mean temperature. It remains to identify k and determine ϵ^2 in terms of the flow pattern.

Since along a stream line $c_p T + \frac{1}{2} u^2 + \epsilon$ will be constant we have

$$\frac{d\epsilon}{dt} + c_p \frac{dT}{dt} = -\frac{1}{2} \frac{du^2}{dt}. \quad (121)$$

To eliminate dT/dt we note that, if q_{vib} is the heat content of the vibration,

$$\frac{dq_{\text{vib}}}{dt} = -k\epsilon \quad \text{and} \quad \epsilon = q_{\text{vib}} - c_{\text{vib}} T,$$

so

$$c_{\text{vib}} \frac{dT}{dt} = -\frac{d\epsilon}{dt} - k\epsilon. \quad (122)$$

H h

This gives for ϵ the first-order differential equation

$$\frac{c_p'}{c_{vib}} \frac{d\epsilon}{dt} + \frac{kc_p}{c_{vib}} \epsilon = \frac{1}{2} \frac{du^2}{dt}, \quad (123)$$

from which ϵ may be determined, provided we assume that the disturbance of the flow pattern by the vibrational heat lag is small so that u is given from the appropriate standard hydrodynamical solution.

k may be related to the relaxation time τ by noting that, if there were no flow, we would have, from (123),

$$\frac{d\epsilon}{dt} = -k\epsilon c_p/c_p'.$$

This shows that kc_p/c_p' is to be taken as $1/\tau$ or, in terms of the notation of § 12.2, $kc_p/c_p' = \beta$.

Kantrowitz has applied this analysis to the flow through a faired orifice and to the compression at an impact tube to obtain the entropy change ΔS when the time of compression is comparable with the relaxation time. Knowing ΔS the pressure change may be calculated from the relation

$$\Delta S = R \log(p_0/p_2).$$

From a series of measurements of p_0/p_2 in CO_2 Kantrowitz obtained a relaxation time corresponding to a probability of vibrational deactivation of about 1/30,000 per collision at a temperature of 306° K. This agrees well with the values derived from ultrasonic dispersion and absorption measurements (see Fig. 204). The reality of the effect in gas dynamics is thus established and an alternative method of obtaining vibrational deactivation probabilities becomes available.

12.4. Spectroscopic evidence on vibrational deactivation

The effect of collisions on the nature of the band spectrum emitted by excited molecules can be observed. In most instances the conditions differ from those prevailing in the dispersion of sound because the molecules will usually be in excited electronic states with highly excited vibration. The spacing of the vibrational levels at these excitations will normally be very small compared with κT so that deactivation can take place in very small steps, and the conditions are classical. Corresponding to these very different circumstances it is found that vibrational deactivation takes place with ease, in contrast to the strong persistence of vibration observed from the dispersion of sound. On the other hand, Dwyer† has been able to confirm the persistence of large vibrational quanta by a band fluorescence experiment.

The first quantitative study was made by Roessler.‡ He investigated the effect of the rare gases on the sensitized band fluorescence of iodine

† *J. Chem. Phys.* **7** (1939), 40.

‡ *Zeits. f. Phys.* **96** (1935), 251.

excited by the green mercury line 5461 Å. Absorption of this line produces exclusive excitation of an electronic state in which the vibrational quantum number v is 26, so that the excited level is one in which the molecule possesses vibrational excitation equal to $\frac{3}{5}$ of the dissociation energy of the particular electronic state.

The effect of foreign gas is not only to produce quenching so that the total intensity of the fluorescent radiation is reduced but also is apparent in the appearance of new bands. These are due to the collision excitation of new vibrational levels. The change of vibrational quantum number in the collision is never greater than ± 2 . In addition a broadening of the lines indicated that rotation was also being excited by collision. This aspect will be discussed further in § 12.7.

To obtain quantitative information about the cross-sections for collisions in which the vibration is changed, Roessler measured the following intensity ratios:

- (a) the ratio R_1 of the total fluorescent intensity before and after the introduction of the foreign gas at pressure p ;
- (b) the ratio R_2 of the intensity of the lines beginning on the level with $v = 26$ before and after introduction of the foreign gas at pressure p ;
- (c) the ratio R_3 of the intensity of the lines beginning on levels other than that with $v = 26$ to those beginning on that level, when foreign gas is present at pressure p .

To obtain the cross-sections for quenching and for vibrational transitions an extension of the analysis of § 7.21 may be adopted.

Let N_0 be the number of exciting quanta absorbed per c.c./sec., n_p the equilibrium concentration of molecules excited to the level with $v = 26$, and n_i the concentration of molecules in another vibrational level to which the molecule may be transferred on collision. Then, in equilibrium,

$$N_0 = n_p \left(\frac{1}{\tau} + p\delta + p \sum \epsilon_i \right) - p \sum n_i \epsilon_i. \quad (124)$$

On the right-hand side n_p/τ represents the loss per c.c./sec. due to radiation, $pn_p\delta$ that due to quenching, and $pn_p \sum \epsilon_i$ that due to collision-induced vibrational changes. The term $p \sum n_i \epsilon_i$ represents the rate of repopulation per c.c./sec. due to collision-induced transitions back from other vibrational levels.

In the same way we may write the equilibrium relations for the gain and loss of molecules from other vibrational states:

$$pn_p \epsilon_i = n_i \left(\frac{1}{\tau} + p\delta + p\epsilon_i A \right).$$

The factor A has been introduced to allow for transitions to states other than that with $v = 26$.

We now have, writing $\epsilon = \sum \epsilon_i$,

$$R_2 = n_0/n_p = 1 + p\tau\delta + p\tau\epsilon - p^2\tau^2 \sum \epsilon_i^2 / (1 + p\tau\delta + p\tau A\epsilon) \quad (125)$$

and

$$R_3 = n_i/n_p = p\tau\epsilon_i / (1 + p\tau\delta + p\tau A\epsilon). \quad (126)$$

If it is assumed that ϵ_i is independent of the level concerned, so that we may write

$$\epsilon = \sum \epsilon_i = z\epsilon_i,$$

where z is the number of occupied levels, we may eliminate A to give

$$R_2 - 1 - p\tau\delta = p\tau\epsilon(1 - R_3). \quad (127)$$

To correct for the variation of ϵ_i with the particular vibrational level, Roessler replaced $1 - R_3$ by $1 - BR_3$, where B is a correcting factor to be determined. By comparison with an exact treatment with helium as foreign gas a value 0.85 was found for B , practically independent of the relative importance of transitions involving changes ± 1 , ± 2 , in the quantum number v . It was therefore taken as 0.85 for all other gases.

Having measured R_2 and R_3 and taking for the radiative lifetime $\tau = 10^{-8}$ sec. the relation (127), with the correcting factor B , gives ϵ in terms of δ . The measurement of R_1 gives δ directly (see the discussion of quenching in § 7.21), so ϵ may be derived.

From δ and ϵ the respective cross-sections may be obtained in the usual way. The absolute values are not likely to be very accurate, but there is no doubt that the cross-sections for collisions involving vibrational transfer are in all cases comparable with the gas-kinetic. In fact the actual values found are from 5 to 10 times larger. This is in sharp contrast to the results obtained from the dispersion and absorption of sound in which large vibrational quanta were involved.

A similar investigation was carried out by Durand,[†] who studied the effect of the rare gases on the fluorescence of sulphur excited by a magnesium spark line to the vibrational level $v = 8$ in the first excited electronic state. In this level of the S_2 molecule the energy of vibration is about $\frac{1}{4}$ of the dissociation energy. Collisions leading to transitions to the level $v = 10$ produced quenching by pre-dissociation which could be separately distinguished in the spectrograms from transitions to $v = 7$ or 9 which led to new bands. The results agree qualitatively with those of Roessler, though the cross-sections are somewhat smaller. This may be because the vibrational quanta concerned are rather larger but the quantitative accuracy of the method may not be high enough for the difference to be significant.

Dwyer[‡] was able to obtain evidence of the persistence of large vibrational quanta by studying the band absorption of iodine in the visible region. Under normal conditions, at ordinary temperatures, the strongest transitions in these bands are from the ground vibrational state. When the iodine is excited by electron impact the proportion of molecules in the first vibrational state is considerably increased. This is because downward transitions from electronically excited molecules often end in this level rather than in the ground level. Observations of the band absorption during the discharge revealed this effect clearly.

[†] *J. Chem. Phys.* **8** (1940), 46.

[‡] *Loc. cit.*

When the discharge was cut off it was found to persist for at least 1/30th of a second, showing that the excited vibration was able to survive over 7,000 collisions. This is in general agreement with the evidence from the dispersion of sound since in Dwyer's experiments large quanta are concerned.

12.5. Evidence from unimolecular reactions

A unimolecular reaction is one in which the concentration n of reacting molecules satisfies the equation

$$\frac{dn}{dt} = -kn,$$

where k is a constant.

The mechanism of these reactions is now understood.† Two processes are actually involved. In the first a molecule A receives energy on collision with a second molecule B which is more than sufficient to produce dissociation if it concentrates in a certain degree of freedom of internal motion. There will be an appreciable time θ which must elapse between the excitation and the concentration in the appropriate mode. If in a time θ the chance of a second collision is small, then the dissociation of the molecules A will be a bimolecular reaction, occurring at a rate proportional to the pressure of molecules B . In the other extreme, in which θ is great compared with the times between collisions, excited molecules A will be effectively in thermal equilibrium with the normal molecules A and B . Their concentration will then be independent of the collision rate and so also will be the rate of reaction. The process will then be effectively unimolecular.

The critical pressure range at which the reaction changes from bimolecular to unimolecular will be such that the time between activating collisions is of the order θ . If these initial pressures are determined for a given molecule A with different molecules B , a measure of the relative efficiency of the latter molecules in exciting internal vibration of the molecule A becomes available. The absolute value of the cross-section for activation cannot be obtained with any certainty from the measured values of θ and of the critical pressure because there is uncertainty in any particular case about the number of degrees of freedom involved.

In these collisions the degree of vibrational excitation will vary greatly from one mode of internal motion to another. It is clear, however, that when concentrated in one mode it represents a degree of excitation up to dissociation. The average cross-sections, determined in principle from unimolecular reactions, should therefore correspond to conditions intermediate between those prevailing in the dispersion of sound and in the band fluorescence experiments of § 12.4.

Table XVII summarizes measurements of the relative cross-sections for activation of F_2O , N_2O , and azomethane respectively by different foreign gases.

12.6. Theoretical discussion of experimental evidence on the probability of vibrational excitation on impact

In § 12.1 we have already discussed in general terms the conditions under which the probability of occurrence of vibrational changes on impact will be small. The condition (103) is satisfied in the collisions

† See, for example, Fowler and Guggenheim, *Statistical Thermodynamics*, C.U.P., 1939, p. 526.

TABLE XVII

Relative Efficiencies of Different Gases in activating F₂O, N₂O, and Azomethane

Added gas	F ₂ O (250° K.)	N ₂ O (635° K.)	Azomethane (310° K.)
He	0.40	0.66	0.07
Ne	..	0.47	..
A	0.52	0.20	..
Kr	..	0.18	..
Xe	..	0.16	..
O ₂	1.13	0.23	..
N ₂	1.01	0.24	0.21
F ₂	1.13	..	..
CO	..	..	0.13
D ₂	..	..	0.37
H ₂ O	..	1.50	0.46
N ₂ O	..	1.00	..
CO ₂	..	1.32	0.25
F ₂ O	1.00	..	..
HF ₄	..	..	0.20
SiF ₄	0.88	..	..
Azomethane	..	..	1.00

which determine the vibrational heat lag phenomena if it is assumed that the time of collision is not reduced much by the presence of a strong attractive force between the colliding systems. In this way one can account in general terms for the very low probability of vibrational deactivation per collision found for various gases. A more detailed theory was first attempted by Zener† and it has been extended particularly by Jackson and Mott,‡ Landau and Teller,§ and Devonshire.||

Jackson and Mott considered the head-on collisions between an atom *A* and a molecule *BC*. If the interaction energy between *A* and *B* can be represented by a pure repulsion

$$V = Ce^{-r/a}, \quad (128)$$

where *r* is the distance between *A* and *B*, then the interaction between *A* and the molecule *BC* can be written

$$V = Ce^{-(R+\lambda\rho)/a}, \quad (129)$$

where *R* is the distance of the nucleus of atom *A* from the centre of mass of *BC*, *ρ* is the distance between *B* and *C*, and $\lambda = M_C/(M_B + M_C)$, *M_B* and *M_C* being the masses of the atoms *B* and *C* respectively. In obtaining (129) the unimportant interaction between *A* and *C* is neglected.

† *Phys. Rev.* **37** (1931), 556; *Proc. Cambridge Phil. Soc.* **29** (1933), 136.

‡ *Proc. Roy. Soc. A*, **137** (1932), 703.

§ *Phys. Zeits. Sowjetunion*, **10** (1936), 34.

|| *Proc. Roy. Soc. A*, **158** (1937), 269.

Assuming the vibrations of the atoms in the molecule BC to be strictly harmonic, Mott and Jackson used the form (129) to calculate the probability p_{nm} of a transition occurring from the n th to the m th vibrational state of the molecule on impact. They employed a modified form of Born's approximation known as the method of distorted waves.† In this the plane waves representing the relative motion of the colliding systems before and after impact are replaced by waves distorted by the average interaction energy between the two systems in the initial and final states respectively. Since the mean interaction is a strong repulsion, the inclusion of the distortion allows for the fact that the two systems cannot approach closer than a distance of the order of the gas-kinetic radius.

In this way they obtained

$$p_{nm} = \frac{32\pi^4 a^2}{h} \frac{M_C(M_B + M_C)M_A^2}{M_B(M_A + M_B + M_C)^2} (n + \frac{1}{2} \pm \frac{1}{2})^\nu \frac{\sinh \pi q_n \sinh \pi q_m}{(\cosh \pi q_n - \cosh \pi q_m)^2} \\ (m = n \pm 1), \\ = 0 \quad (m \neq n \pm 1), \quad (130)$$

where $q_n = 2M^*v_n a/\hbar$, $q_m = 2M^*v_m a/\hbar$,

and $M^* = M_A(M_B + M_C)/(M_A + M_B + M_C)$.

ν is the natural frequency of the vibrator, and v_n, v_m are the velocities of relative motion of A and BC before and after impact respectively.

We have further, since

$$\frac{1}{2}M^*(v_n^2 - v_m^2) = h\nu, \\ q_n - q_m = (q_n^2 - q_m^2)/(q_n + q_m) \\ = 4\pi a\nu/\bar{v}, \quad (131)$$

where $\bar{v}$ is the mean relative velocity $\frac{1}{2}(v_n + v_m)$. In gas-kinetic collisions q_n and q_m are both large so that, if $4\pi a\nu/\bar{v}$ is $\gg 1$,

$$\frac{\sinh \pi q_n \sinh \pi q_m}{(\cosh \pi q_n - \cosh \pi q_m)^2} = \exp(-4\pi^2 a\nu/\bar{v}). \quad (132)$$

The formula may now be immediately related to the condition (102).

Zener‡ has derived the same formula by a method in which the relative motion of the colliding systems is treated classically, and Landau and Teller§ have also obtained the same form of variation with $a\nu/v$ by a completely classical treatment on the same lines as the correspondence principle argument given in § 10.1.

† See Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. VIII, § 5.

‡ *Proc. Cambridge Phil. Soc.* 29 (1933), 136.

§ Loc. cit.

The temperature variation of the relaxation time in ultrasonic dispersion can now be predicted from the expression (130) for p_{nm} using the approximation (132). The probability of deactivation by impacts of relative velocity v will be proportional to

$$f(v)\exp(-4\pi^2av/v), \quad (133)$$

where $f(v)$, the fraction of collisions in which the relative velocity is

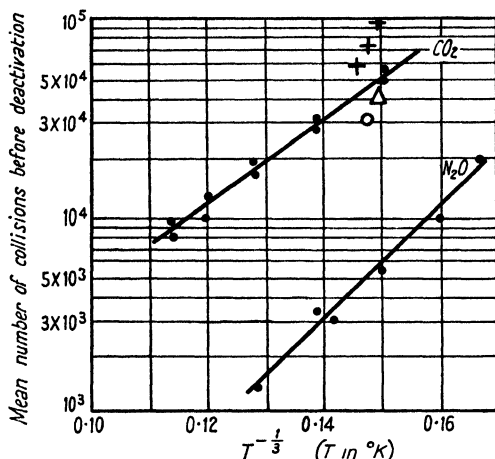


FIG. 204. Observed variation of the average number of collisions which occur before vibrational deactivation in pure CO_2 and N_2O with absolute temperature. The full lines are calculated from eq. (135) using values of a of 0.22×10^{-8} cm. for CO_2 and 0.36×10^{-8} cm. for N_2O .

- Observations of Eucken *et al.* (see references, p. 460).
- + Observations of van Itterbeek and Mariens (CO_2) (see p. 461).
- Δ Observations of Richards and Reid (CO_2) (see references, p. 461).
- $\circ$ Observations of Kantrowitz (CO_2) (see references, p. 463).

between v and $v+dv$, is approximately equal to $\exp(-\frac{1}{2}M^*v^2/\kappa T)$. The probability will be a maximum for those collisions in which

$$4\pi^2a(v/v) + \frac{1}{2}M^*v^2/\kappa T$$

is a minimum, i.e. for which

$$v = (4\pi^2a\kappa T/M^*)^{\frac{1}{2}}. \quad (134)$$

The temperature variation of the deactivation probability, averaged over the molecular velocity distribution, should therefore be given by

$$\exp\left[-\left(\frac{27}{2} \frac{\pi^2 a^2 v^2}{\kappa T}\right)^{\frac{1}{2}}\right]. \quad (135)$$

This does represent the data for CO_2 and N_2O quite well, as may be seen

from Fig. 204, with the reasonable respective values 0.22×10^{-8} cm. and 0.36×10^{-8} cm. for a .

The theory thus seems to be adequate for dealing with cases in which the probability of deactivation is low and it is not inconsistent with a high probability when the vibrational quantum $h\nu$ is so small that $\pi a\nu/\nu < 1$. It is incapable, however, of interpreting those cases in which, while $h\nu$ is not small, the probability is not very low (e.g. the effectiveness of H_2O and CO in deactivating CO_2 , Table XVI). This is presumably because it neglects attractive forces which may lead to a gross error if the attractions are of a chemical nature. It is noteworthy that chemical reactivity between molecules is often associated with a comparatively high probability of vibrational deactivation.

No attempt has been made to allow for chemical attractions, but Zener† and Devonshire‡ have obtained a modified form of (130) which allows for an attraction of van der Waals type. They replaced the interaction (128) by one of the form

$$V = -D[2\exp\{-(r-b)/2a\} - \exp\{-(r-b)/a\}] \quad (136)$$

which has the shape illustrated in Fig. 205. The corresponding modified form of (129) is then obtained by replacing r by $R + \lambda\rho$. Zener using his semi-classical method obtained in this case

$$p_{nm} = \frac{32\pi^4 a^3}{h} \frac{M_C(M_B + M_C)M_A^2}{M_B(M_A + M_B + M_C)^2} \times \\ \times (n + \frac{1}{2} \pm \frac{1}{2}) \nu \frac{\cosh^2(q_n - q_m)(\eta - \pi)}{\sinh^2 \pi(q_n - q_m)}, \quad (137)$$

where

$$\cos \eta = (1 + E^*/D)^{-1/2}, \quad E^* = \frac{1}{2} M^* \bar{v}^2.$$

This reduces to (130) in the limit $D \rightarrow 0$, provided q_n and $q_m \gg 1$ as they always are in practice. Devonshire, using the same method as Mott and Jackson, obtained the formula (130) with an additional factor

$$\frac{A_{q_n}(d) + A_{q_m}(d)}{A_{q_n}(0) + A_{q_m}(0)} \frac{A_{q_n}(0)A_{q_m}(0)}{A_{q_n}(d)A_{q_m}(d)},$$

where

$$A_{q_n}(d) = |\Gamma(-d + iq_n + \frac{1}{2})|^2, \quad d^2 = M^* D a / h^2.$$

If q_n , q_m , and d are large compared with unity and with $q_n - q_m$, the factor becomes approximately

$$(\bar{q}^2 + d^2)^d \exp\{\pi\mu - 2d - 2\mu \arctan(\mu/d)\},$$

where $\bar{q} = \frac{1}{2}(q_n + q_m)$.

No use has yet been made of these formulae in discussing collisions in the gas phase.

† *Proc. Cambridge Phil. Soc.* **29** (1933), 1936.

‡ *Loc. cit.*

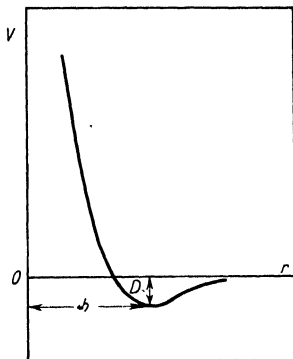


FIG. 205. Illustrating the function $V = -D(2e^{-r/2a} - e^{-r/a})$ used to represent the general shape of the interaction between atoms including van der Waals attraction (cf. Fig. 171).

In Chap. IX, § 10.3, the related question of the transfer of energy from an atom to a solid surface will be discussed.

It is of interest to note that Zener† has applied his method to discuss the probability of *transfer* of vibration from one molecule to another on impact. He finds that, if strong attractions are ignored, this probability is very low even for exact resonance. Thus the probability of transfer of vibrational energy from a nitrogen molecule in its first excited state to a normal nitrogen molecule, in a collision at room temperature, is only of order 10^{-5} .

Summarizing, we may say that the qualitative interpretation of the probabilities of vibrational transitions on collision, in terms of the closeness of approach to adiabatic conditions (§ 12.1), is reinforced by the more detailed theory except under conditions in which a strong attraction (probably chemical) exists between the colliding systems. Thus the very low probabilities of deactivation revealed by vibrational heat lag are a consequence of the discriminating quantity $\pi a v / v$ being large, while the high probabilities of vibrational transitions when a molecule is already highly excited are due to this quantity being no longer large. The specific character of the vibrational heat lag effects does not fit into the picture unless we regard v as sometimes abnormally large due to the presence of a strong attraction.

12.7. Collisions involving change of molecular rotation

The experimental information concerning the probability of rotational energy changes occurring in a collision between an atom and a molecule or between two molecules is neither so extensive nor so definite as for change of vibration. Nevertheless, taken as a whole it does support the general expectation of easy exchange between rotational and translational energy.

Most of the evidence comes from spectroscopic studies. In the experiments of Roessler and of Durand, described in § 12.4, it was noted that the addition of foreign gas produced a broadening of the fluorescent lines due to the excitation of a wider range of rotational levels. Rough estimates indicated that the cross-section for excitation of a quantum of rotation by a foreign gas is of the same order as the gas-kinetic. Haber‡ also observed a similar effect in the bands of AlH produced in a hollow cathode discharge when rare gases were added.

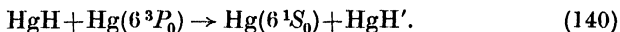
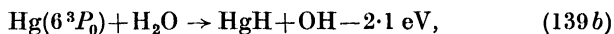
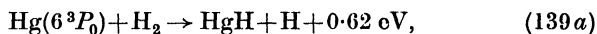
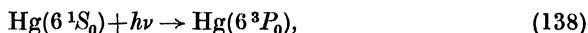
Certain band spectra exhibit the phenomenon of 'abnormal rotation'. In these, the rotational temperature derived from the intensity distribution in the band is much greater than the temperature of the excited gas.

† *Phys. Rev.* **37** (1931), 556.

‡ *Phys. Zeits.* **40** (1939), 541.

It occurs, for example, in the bands of OH, HgH, and CO⁺ excited in certain ways. Considerable attention has been devoted to the study of this phenomenon and the way it is influenced by excitation conditions and the presence of foreign gases. Thus Oldenburg† investigated the abnormal rotation in the OH bands excited by an electric discharge in water vapour. He found that the abnormal rotation disappeared quite quickly when helium or argon were added to the discharge. The position is not quite clear for, in the most recent observations of Oldenburg and Rieke,‡ a semi-quantitative estimate indicated that the high rotational excitation persists through some 500 or more collisions.

Abnormal rotation is exhibited by the HgH bands produced by irradiating a mixture, consisting of mercury vapour (at about 0.001 mm. Hg pressure), a few thousandths of a mm. pressure of hydrogen, and a few cm. pressure of nitrogen, with mercury resonance radiation.§ If the hydrogen and nitrogen are replaced by a few mm. pressure of water vapour, the bands are again produced by sensitized fluorescence but without abnormal rotation. The reactions responsible in the two cases are



It was suggested by Beutler and Rabinowitsch§ that the abnormal rotation is produced in the reactions (139) and then only by (139a), in which there is surplus energy available. If this were correct the abnormal rotation would have to persist through some thousands of collisions with nitrogen molecules before a collision with an excited Hg(6³P₀) atom leading to the process (140) would occur. An alternative explanation due to Oldenburg has been largely confirmed by Rieke.|| This supposes the excitation of abnormal rotation to take place in process (140) and in collision processes taking place during the lifetime of the HgH'. In support of this viewpoint Rieke found that the band intensity distribution, as measured by the ratio *R* of the intensity of the tail to the head of the band, depended strongly on the nitrogen pressure. This showed that the nitrogen played a positive role in the process. He further

† *Phys. Rev.* **37** (1931), 1550.

‡ *J. Chem. Phys.* **6** (1938), 439.

§ Beutler and Rabinowitsch, *Zeits. f. phys. Chem. B*, **8** (1930), 231, 403.

|| *J. Chem. Phys.* **4** (1936), 513; see also *ibid.* **5** (1937), 831.

investigated the variation of the ratio R with the partial pressures $p(\text{N}_2)$, $p(\text{H}_2\text{O})$ of nitrogen and water vapour respectively when the sensitized fluorescence took place in a mixture of these gases with mercury. He found that:

- (a) for any mixture, R is less than for pure N_2 with a trace of hydrogen and greater than that for pure water vapour;
- (b) for $p(\text{H}_2\text{O})$ fixed, R increases with $p(\text{N}_2)$;
- (c) for $p(\text{N}_2)$ fixed, R decreases with $p(\text{H}_2\text{O})$.

These results are consistent with the supposition that the effective process with nitrogen consists in a transfer of vibrational excitation in the HgH molecule into high rotation. The relatively heavy nitrogen molecule is not likely to be very effective in removing internal energy of motion of the light H atom in the HgH molecule, but it may readily transform vibrational energy of that atom into energy of rotation. On the other hand, the presence of hydrogen atoms in the water molecule leads to the possibility of easy transfer of internal energy from the HgH molecule. This would distribute energy readily between different degrees of freedom and reduce the rotational temperature to normal.

A further example of redistribution of energy between vibrational and rotational degrees of freedom on impact is provided by the appearance of abnormal rotation in the band spectrum of H_2 .† The initial excitation by electron impact leads to high vibrational excitation but normal rotation. On collision with other molecules redistribution takes place, leading to the abnormal rotation. Addition of helium removes the excess rotation, but quantitative estimates of the chance of deactivation per collision are not available.

The only gases in which persistence of rotation could be detected by ultrasonic dispersion or absorption are H_2 and D_2 for which the rotational quanta are not too small. Although some early experiments which indicated that dispersion did occur in these gases have since been disproved, van Itterbeek and Mariens‡ have recently reported measurements of sound absorption in H_2 and D_2 which are explicable in terms of persistence of rotation. The absorption they found indicated a relaxation time of the order 10^{-8} sec. at room temperature and atmospheric pressure which was inversely proportional to the pressure. This is not inconsistent with an estimate made by Roy and Rose,§ using the method of distorted waves (see § 8.6), of the cross-section for excitation of rotation on impact

† Roy, *Proc. Nat. Acad. Sci.* **19** (1933), 441; Smith, *Phys. Rev.* **49** (1936), 345.

‡ *Physica*, **7** (1940), 938.

§ *Proc. Roy. Soc. A*, **149** (1935), 511.

of two hydrogen molecules, which would correspond to a relaxation time of the same order as that observed. The cross-section is smaller than gas-kinetic not because the conditions are nearly adiabatic but because the collision takes place so quickly that there is not sufficient time for any excitation to take place, the condition (104) not being satisfied.

VIII

THE PASSAGE OF HOMOGENEOUS BEAMS OF POSITIVE IONS OR NEUTRAL ATOMS THROUGH GASES

In the preceding chapter we discussed phenomena associated with the impact of atoms, charged or uncharged, under gas-kinetic conditions, i.e. in which the relative energy involved is only a fraction of an electron volt and is not definite but spread over the Maxwellian distribution at the appropriate temperature. It is possible, however, to study the collisions between particles of atomic mass by a technique employing a beam of ions or atoms of homogeneous energy, provided that this energy is greater than a few electron volts. Experiments on slower ion beams are very difficult because of effects of space charge, contact potentials, and stray fields. In this chapter we shall discuss this technique and the results obtained with its use, which are largely complementary to those derived from gas-kinetic studies.

1. The effects to be expected on passage of a homogeneous ion beam through a gas

In Chapter I we discussed the types of collision which could occur between gas atoms and an electron beam—elastic scattering, excitation, ionization, and radiation. The same possibilities arise with an ion beam as well as an additional possibility, that of charge transfer which results in neutralization of an incident ion and ionization of the struck atom. On the other hand, the behaviour of the cross-sections for the different processes is very different, particularly as regards the distribution of scattering with angle and the variation of the total cross-sections with relative velocity. Unless these differences are realized at the outset a false interpretation of experiments using apparatus similar to that employed to study the behaviour of electron beams may easily be made.

The essential differences between the behaviour of electron and of ion beams of comparable energy may be summarized as follows:

(a) The wave-length of the ions is very much shorter than that of the electrons and is much smaller than atomic dimensions. Thus the wave-length of a helium ion of 1,000 eV energy is 4.52×10^{-11} cm. as compared with 3.86×10^{-9} cm. for a 1,000 eV electron. Two important consequences follow.

(b) Diffraction effects will not occur in the elastic scattering. Indeed, over the major part of the angular range the elastic scattering will be as given by the classical theory. It will only be at very small angles that the quantum theory gives different results.

(c) Most of the elastic scattering is confined to very small angles—the angular distribution falls off very steeply with increasing angle (see § 4.3). This effect is already of importance for collisions between atoms of gas-kinetic velocity (see Chap. VII, § 5) in requiring high angular resolving power in measurements of total elastic cross-sections. Much higher resolution still is necessary in order to measure these cross-sections for encounters with gas atoms of positive ion or neutral atom beams of many electron volts energy.

(d) The cross-sections for ionization and excitation rise steadily with increase of energy of the ion beam up to a flat maximum at energies of the order of thousands of electron volts, whereas for electrons the maximum occurs at a few times the onset energy (see § 6.41). For inelastic collisions the considerations of Chap. VII, § 10.1 apply and the cross-section is small when

$$a \Delta E / h v \gg 1, \quad (1)$$

ΔE being the excitation or ionization energy, a the effective collision radius, of the order of the gas-kinetic diameter, and v the velocity of the ions. Thus for ionization of hydrogen by protons the condition is satisfied unless the proton energy is greater than 10,000 eV (a being taken as of order 10^{-8} cm.).

The greater the value of ΔE the greater the energy at which the maximum cross-section occurs. As a rough rule the maximum cross-sections for different inelastic collisions are of the same order of magnitude, so the larger the excitation energy the smaller the cross-section for a given value of v satisfying (1).

(e) Charge exchange is normally the most important inelastic collision process. This is because of the relatively small value of ΔE . In fact, for ions passing through a gas of the same kind $\Delta E = 0$. Although elastic scattering produces only very small deviations from the incident direction of the beam, an appreciable current of ions will be observed at large angles of scattering. These are essentially atoms projected mainly at 90° to the beam in a collision in which the relative velocity vector is turned through a very small angle. Owing to charge transfer, certain of these atoms will have transferred an electron and will be observed as ions. Just as directly scattered ions are concentrated mainly around the incident direction, the ions resulting from charge exchange are to be

found moving in directions making an angle of nearly 90° with the beam. The two groups overlap to a negligible extent (see Fig. 197, Chap. VII). A direct experimental verification of this description is provided by Ramsauer and Kollath's experiments on the angular distribution of scattered protons (see § 4.3).

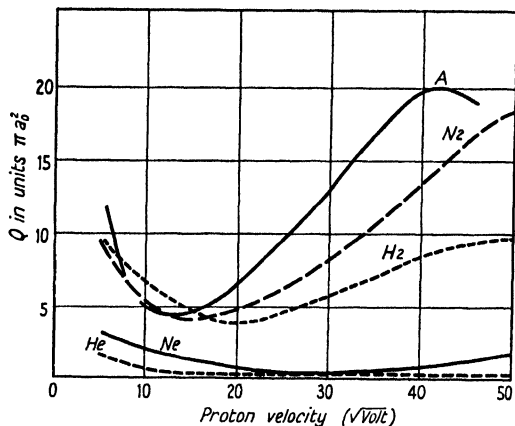


FIG. 206. Apparent 'total collision cross-section' for protons in He, Ne, A, H₂, N₂ observed by Ramsauer, Kollath, and Lilienthal.

1.1. Interpretation of experiments on ion cross-sections obtained by the Ramsauer method

To illustrate the effect of the differences listed above it is of interest to analyse the results obtained for the total collision cross-sections of protons in different gases using an apparatus of very similar type to that employed so successfully for electrons (see Chap. I, § 3). Fig. 206 illustrates the apparent total collision cross-sections found by Ramsauer, Kollath, and Lilienthal† for protons in the rare gases using an apparatus of the same design and comparable dimensions to that illustrated in Chap. I, Fig. 1. The proton source used is described in § 2.2.

The most obvious feature of these results is the apparent existence of a Ramsauer-Townsend effect for argon (compare with Fig. 2 of Chap. I). This would be most unlikely in view of (b) above and an alternative explanation may readily be given. With the apparatus used a fraction only of the total elastic cross-section can be observed. Moreover, this fraction will decrease as the proton energy increases because

† *Ann. der Physik*, 8 (1930), 709.

the angular distribution of elastic scattering becomes steeper. The net result is that the contribution to the apparent total cross-section due to elastic scattering decreases with increasing energy. On the other hand, all inelastic collisions will be correctly included in the apparent cross-section. The only important one of these will be charge exchange for which the cross-section will be rising steadily with proton energy. It will be very small for low-energy protons so, in this region, the contribution from elastic scattering dominates, but at higher energies is exceeded by that from charge exchange. The combination of the two gives rise to the observed cross-section with a minimum.

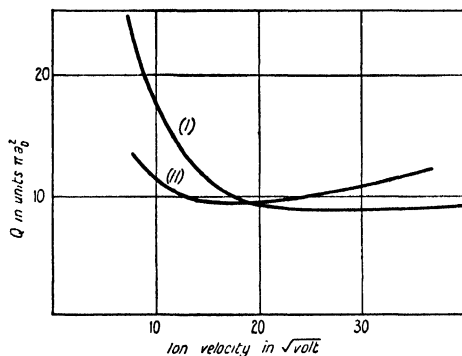


FIG. 207. Illustrating the effect of slit width on the observed apparent 'total cross-section' for H_2^+ ions in argon. Curves I and II were obtained with different defining slits (see text).

This interpretation is in agreement with the observed behaviour for helium. The large value of ΔE in this case, even for charge exchange, leads to a small inelastic cross-section which, combined with a very small contribution from elastic scattering—especially concentrated at small angles for a light atom (see § 4.1)—gives the observed very small apparent cross-section.

The importance of slit width in measurement of total collision cross-sections was directly confirmed by Wolf.[†] He measured the apparent total cross-section for H_2^+ ions in A, using two different openings in front of the collector. The results are shown in Fig. 207. Curve I refers to measurements made with a circular hole 4.5 mm. diameter and such that ions deflected by more than a mean angle of 3.5° could not enter the collector. Curve II was taken with a rectangular slit of dimensions

[†] Ibid. 25 (1936), 737.

14 × 6 mm. in front of the collector, and this had the effect of excluding ions scattered through an angle of more than 5°. It is a little difficult to understand why curve II falls above curve I at high energies.

It appears from the above considerations that the total collision cross-section is a very difficult quantity to measure, since the resolving power of the apparatus has to be made very large. Fortunately, much interesting information may be obtained by excluding the elastic scattering from effective contribution altogether by working with comparatively wide slits. In this way the total inelastic cross-section—in most cases mainly the charge exchange cross-section—will be measured. Methods along these lines have indeed been used and will be described in § 5.

1.2. *Further introductory remarks—relative and laboratory coordinates*

It is possible to make separate measurements of the cross-sections for excitation, ionization, and charge transfer as well as to study the angular distribution of elastically scattered ions. We shall discuss these methods and results in §§ 5 and 6, after first describing in §§ 2 and 3 the sources available for preparation of ion and neutral atom beams and the methods of detection of ions and fast atoms which may be employed.

As mentioned in Chap. VII, § 3, the collision of two massive particles may be discussed in terms of their relative motion, the motion of the centre of mass having been separated out. For theoretical purposes it is convenient to describe the collision in this way, the angle of scattering θ being the angle the direction of relative motion is turned through by the collision. When using ion beams it is natural to work in terms of the angle of deviation ϑ from the initial direction of motion of the beam—the ‘laboratory’ system of coordinates in which the struck particle is initially at rest. We now give certain formulae relating θ and ϑ , which are readily obtained from the conditions of energy and momentum conservation.

Let E_1 be the energy of the incident particle in the laboratory system and M, M' the respective masses of the incident and target particles. The energy of motion of the centre of mass of the system is then $ME_1/(M + M')$ and that of the relative motion, which is alone available for transfer to internal energy, is $M'E_1/(M + M')$.

If the energy transferred in the collision from relative translation to internal motion is ϵ , then the angles of scattering θ and ϑ in the relative (or centre of mass) and laboratory system respectively are given by

$$\left\{ E_2 + \left(\frac{M}{M' + M} \right)^2 E_1 - \frac{2M}{M' + M} (E_1 E_2)^{\frac{1}{2}} \cos \vartheta \right\} \sin^2 \theta = E_2 \sin^2 \vartheta, \quad (2)$$

where E_2 , the energy of the incident particle after the scattering, is given by

$$\cos \vartheta = \frac{1}{2} \left\{ \left(\frac{E_2}{E_1} \right)^{\frac{1}{2}} \left(1 + \frac{M'}{M} \right) + \left(\frac{E_1}{E_2} \right)^{\frac{1}{2}} \left(1 - \frac{M'}{M} \right) + \frac{\epsilon}{(E_1 E_2)^{\frac{1}{2}}} \frac{M'}{M} \right\}. \quad (3)$$

The angle ϑ' of recoil of the struck particle, in the laboratory system, is given by

$$\cos \vartheta' = \frac{1}{2} \left[\left(\frac{M}{M'} \right)^{\frac{1}{2}} + \left(\frac{M'}{M} \right)^{\frac{1}{2}} \right] \left(\frac{E_2'}{E_1} \right)^{\frac{1}{2}} + \left(\frac{M}{M'} \right)^{\frac{1}{2}} \frac{\epsilon}{(E_1 E_2')^{\frac{1}{2}}}, \quad (4)$$

where E_2' , the energy of the recoiling particle, is equal to $E_1 - E_2 - \epsilon$. Also

$$\left\{ E_2' + \frac{MM'E_1}{(M+M')^2} - \frac{2(MM')^{\frac{1}{2}}}{M+M'} (E_1 E_2')^{\frac{1}{2}} \cos \vartheta' \right\} \sin^2 \theta = E_2' \sin^2 \vartheta'. \quad (5)$$

2. Sources of homogeneous ionic and atomic beams

2.1. Arc sources

The earliest type of source of positive ions employed the canal rays from an ordinary glow discharge. Ions from such a source, however, are not homogeneous in energy, since, depending on their place of origin in the discharge, they may possess energies ranging from a small value up to the energy of the full cathode fall. For this reason more recent work has usually employed a low-voltage arc as an ion source.

In the conventional arrangement a potential of the order of 100 volts pulls electrons out from a hot filament to an anode, ionizing the gas in between. A perforated cathode placed in the discharge plasma so produced attracts positive ions, some of which pass through the hole and are available for acceleration. The operating pressure of a low-voltage arc is usually of the order of 10^{-2} mm. Hg—considerably lower than a glow discharge—and the cathode potential is of the order of a few hundred volts. In view of this low cathode potential, and the high ion density of the arc plasma (usually several orders of magnitude greater than the ion density of a glow discharge plasma), the cathode sheath, across which practically the entire cathode drop occurs, is generally very small (a fraction of a millimetre)—much smaller than the mean free path of the electrons in the gas—so that very few positive ions are produced in the sheath. Practically all the ions that pass through the hole in the cathode therefore have energy corresponding to the full cathode fall of potential and so can be used to produce homogeneous ion beams of any desired energy.

Special types of low-voltage arc sources have been developed to produce high ion currents. These have usually been developed for use as ion sources for nuclear disintegration, but such sources have also been used for the study of atomic and ionic collisions.

2.11. Arc sources employing longitudinal magnetic field. One type of arc source useful for collision experiments makes use of a longitudinal magnetic field to collimate the electron beam.† A useful variant of this

† Nier, *Phys. Rev.* **50** (1936), 1041.

idea, due to Finkelstein,[†] which has been used for collision experiments by Berry,[‡] is shown diagrammatically in Fig. 208. Electrons from the filament F are accelerated through the hole in electrode 1 and enter the chamber C which contains the gas whose ions are required. A magnetic field of strength a few hundred gauss is applied along the axis.

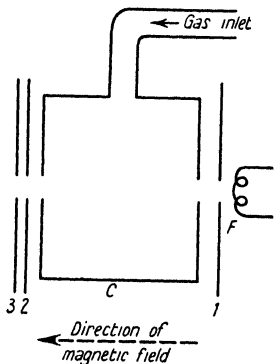


FIG. 208. Finkelstein's positive ion source.

A negative potential is applied to the electrode 2 which has the effect of pulling out ions from the arc. These electrodes also have the effect, however, of reflecting back the beam of electrons from the filament. Owing to the effects of the ion space charge and the magnetic field, the electrons move back and forth between the electrode 2 and the filament, spiralling around the lines of force of the magnetic field, until they lose their

energy in inelastic collisions and are finally collected by the electrode 1, or the walls of chamber C . The Finkelstein source differs from the older Nier source in the use of electrons that traverse the gas chamber several times, thus increasing the ion density produced by a given electron current.

Owing to the high efficiency of utilization of the electron beam in this type of source, the working pressures (from 2 to 6×10^{-4} mm. Hg in the case of a hydrogen arc) are considerably lower than those used in more conventional arcs.[§]

2.12. Capillary arc source. The capillary arc provides a convenient source for the production of intense positive ion beams. One type of capillary arc, due to Tuve and others,^{||} which has been used by Trittelvitz^{††} for experiments (§ 5.23) on optical excitation by means of positive ions, is shown diagrammatically in Fig. 209.

The capillary C consists of a hole a few mm. in diameter and a few cm. long drilled in a metal block. At either end of the capillary, the hole is opened out to a few cm. in diameter to accommodate a hot filament F and an anode A . Electrons drawn from the filament towards the anode ionize the gas in the capillary and an arc is struck, the ion density within

[†] *Rev. Sci. Inst.* **11** (1940), 94.

[‡] See, for example, *Phys. Rev.* **75** (1949), 913.

[§] A somewhat similar principle has been used by von Ardenne (*Phys. Zeits.* **43** (1942), 91) and Heil, *Zeits. f. Phys.* **120** (1944), 212.

^{||} Tuve, Dahl, and Hafstad, *Phys. Rev.* **48** (1935), 241.

^{††} *Ann. der Physik*, **40** (1941), 131.

the capillary being particularly high. The pressure in the capillary is of the order of 0.1 mm. Hg.

The arc body *B* is usually allowed to float at some potential intermediate between that of the filament and the anode. Ions produced in the capillary are drawn out through the hole *H* by a negative potential applied to electrode *E* and can then be focused into a beam by means of electrode *G*.

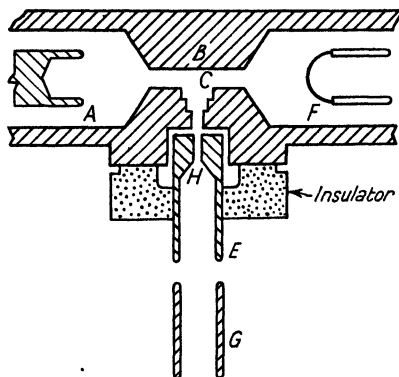


FIG. 209. Capillary arc positive ion source.

2.13. Arc sources used for producing a very high percentage of atomic ions. In cases where a very high intensity of atomic ions is desirable a source developed by Lamar and Luhr† has been used for atomic and ionic collision experiments. This arc source has been used, for example, by Simons and his collaborators (§ 4.21) and by Amdur and Pearlman (§ 4.22).

The arc, which appears conventional enough in construction, is illustrated diagrammatically in Fig. 210. A low-voltage arc is struck between the filament *F* and the anode *A* by the application of a potential difference of from 50 to 75 volts. Positive ions are drawn to the cathode *C* which encloses the arc and which is maintained at a potential of a few hundred volts negative to it. Some of these ions are pulled through the hemispherical grid *E* by the ion gun *F*.

In order to produce a high concentration of atomic hydrogen ions it is necessary to cool the cathode *C*. It is believed that the presence of an adsorbed H_2 layer at the walls of the cathode hinders the recombination of atomic hydrogen there (see Chap. IV, § 5.5). If this layer is destroyed,

† *Phys. Rev.* **46** (1934), 87.

as when the cathode temperature is too high, or the cathode potential too great, the atomic hydrogen concentration falls markedly. The pressure used within the Lamar-Luhr type of arc is high—0.23 mm. Hg—and this is a disadvantage of this type of source.

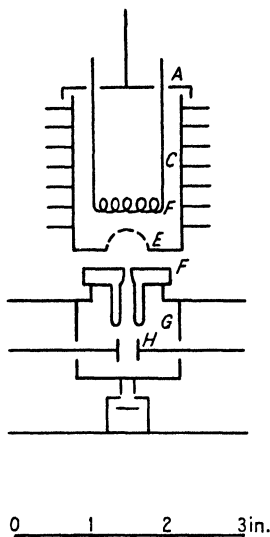


FIG. 210. Lamar-Luhr positive ion source as used in apparatus for studying the scattering of atomic beams.

2.2. The electrodeless discharge

The importance of conditions at the walls in influencing the proton content in a discharge in hydrogen has been pointed out earlier (Chap. IV, § 5.5). It was stated there that the highest relative proton concentrations had been obtained using an electrodeless discharge in hydrogen, run in a glass tube. With such an arrangement the amount of metal in contact with the plasma can be reduced to a minimum and relative proton concentrations up to 70 per cent. with a total ion density of 10^{12} ions/c.c have been obtained.†

Although this type of source has not so far been applied to experiments of the type discussed in this chapter, it is potentially a very powerful tool for such work.

2.3. Hydroxide type of proton source

A piece of lithium metal when exposed to air usually becomes covered with a thin layer of lithium hydroxide. When such a surface is bombarded with electrons positive ions are liberated which, on analysis, are found to be very largely protons. This method was used by Dempster to give a source of protons and was later used in the series of measurements by Ramsauer, Kollath, and Lilienthal discussed in § 1.1. The proton currents obtained from sources of this type are very small.

2.4. Filament type sources

Many of the earlier experiments on positive ions were carried out using a hot filament, usually of platinum, as an emitter. Positive ions of alkali metals were found to be emitted from such a filament. The technique of using this type of source to produce positive ions of a desired variety of alkali or alkaline earth metal was put on a sound basis by Kunsman.‡

† See Thonemann, *Nature*, **158** (1946), 61; Rutherglen and Cole, *ibid.* **160** (1947), 545.

‡ *Science*, **62** (1925), 269.

He coated his filaments with a mixture of iron oxide and about 1 per cent. of the required alkali or alkali earth metal. In some cases 1 per cent. of aluminium oxide was added. The mixture was partially reduced in an atmosphere of hydrogen at a temperature of 400° C. and coated on a hot filament.

He found the variation of positive ion emission with filament temperature to follow Richardson's equation for thermionic emission, the temperature required for emission being lowest in the case of caesium and highest in the case of the alkaline earth metals.

A mass spectrographic analysis of the emission in the case of a Kunsman source of potassium ions showed that the only type of ion emitted was the singly ionized atomic ion of the alkali (or alkaline earth) metal.†

Alkali aluminium silicates‡ have also been used as a coating on hot filaments of platinum or nickel. Thus the mixture $3\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ gives a copious supply of lithium ions, $3\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ of potassium ions. Similar mixtures are available for sodium and caesium.

2.5. Sources employing ions produced by surface ionization

The phenomenon of surface ionization has been used to produce positive ions of the alkali metals.

A jet of the vapour of the metal required is allowed to impinge on a hot surface of a suitable metal (usually tungsten). If the ionization potential of the alkali atom is smaller than the work function of the hot metal, a considerable fraction of the incident atoms will leave the surface as positive ions. The ratio of the number of ions N^+ to the number of neutral atoms, N , leaving the surface in unit time is given by

$$N^+/N = \exp\{-(I-\phi)/\kappa T\},$$

where I , ϕ are respectively the ionization energy of the alkali atom and the work function of the hot surface. For tungsten $\phi = 4.8$ eV, which is greater than the ionization energy of potassium, rubidium, and caesium. For oxidized tungsten the work function is about 7 eV and exceeds even the ionization energy of lithium and sodium. This type of source is therefore available for the production of beams of ions of all the alkali metals but not of other elements because their ionization potentials are still too great.

† This is only the case, however, if great care is taken in the heat treatment of the source prior to use. See Powell and Brata, *Proc. Roy. Soc. A*, **141** (1933), 463.

‡ Jones, *Phys. Rev.* **44** (1933), 707; Blewett and Jones, *ibid.* **50** (1936), 404. The mineral spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) is sometimes used as a source of Li^+ ions.

Poeverlein† has used this method to obtain beams of K^+ ions, but most observers have preferred the filament type positive ion sources.

2.6. Condensation type sources

A source which has proved useful for mobility measurements has been developed by Brata.‡ It has been used for the production of ions of thallium, indium, and gallium.

A layer of the metal whose ions are required is condensed from an atomic beam *in vacuo* on an iron oxide surface. On heating this surface atoms from the layer will re-evaporate, many as ions. The surface area of the iron oxide is so large that a monolayer of the condensed material will contain a large number of atoms—sufficient to provide a steady source of the appropriate ions over a long period.

Powell and Mercer§ have studied the mechanism of these sources using as base an oxidized tungsten strip instead of iron oxide. In these circumstances conditions are more reproducible but the useful lifetime is much shorter. As would be expected, they found optimum positive ion emission to occur for a thickness of about one monolayer when the work function is a minimum. As is the case with other types of filament source, care is needed to eliminate impurities of Na^+ and K^+ ions.

2.7. Sources of fast neutral particles

To prepare fast neutral beams use may be made of charge exchange. It has been pointed out in § 1 that in this process the neutralized ion which has captured an electron has its direction of motion practically unaltered. After an ion beam has passed a short distance through a gas it is therefore accompanied by a parallel neutral beam of nearly the same energy. If the ions are then separated out by some electrical device, a fast neutral beam is available for collision experiments.

Fig. 210 illustrates a typical source of this type used by Amdur and Pearlman|| (§ 4.22) to obtain neutral helium and hydrogen beams of energy ranging from 200 to 800 eV. The appropriate ions were pulled through the grid *E* and accelerated through the ion gun *F* to the required energy. Passing into the collision space *G*, charge exchange occurred with neutral molecules, giving the required neutral beam mixed with the ion beam. This latter was removed by applying a potential difference of 1,500 volts across the plates of the condenser *H*.

† *Ann. der Physik*, **42** (1942), 1.

‡ *Proc. Roy. Soc. A*, **141** (1933), 463.

§ *Phil. Trans. Roy. Soc. A*, **235** (1935), 101.

|| *J. Chem. Phys.* **8** (1940), 7; **9** (1941), 503; **11** (1943), 157.

3. Methods of detection of energetic ionized and neutral molecules

3.1. Positive ions

The detection of positive ions has usually been accomplished by means of a cylindrical collecting electrode and an electrometer. The main difficulty in measurements of positive ion beams arises from the production of secondary electrons when the ions strike surfaces. Errors due to this source are diminished by using a cylindrical collector. In some cases they are still further diminished by placing an insulated grid over the mouth of the collecting cylinder and applying a negative potential to the grid relative to the cylinder.

A convenient method of reducing the effect of secondary electrons on the collected current was used by Keene.† The collector consisted of two long parallel plates (F_1, F_2 in Fig. 217, § 5.12), insulated from each other and maintained at different potentials. Positive ions were collected to the negative plate and any secondary electrons produced went to the positive plate. The electrode F at the end of the collector was connected to the positive plate. The net resultant current to the whole system F, F_1, F_2 was measured. This should give the true positive ion current to the collector.

In a few cases Geiger counters have been used for the detection of positive ions. This method of detection is rendered difficult because the counter has to be separated from the apparatus by means of a window of some kind. In practice this means that the method is available only for relatively fast ions of energy greater than a few thousand electron volts.

3.2. Fast neutral molecules

For the detection of fast molecular beams, three methods have been used.

In the *ionization method*, used, for example, in the experiments of Meyer (§ 6.2) and of Wayland (§ 6.4), the molecular beam enters a cylindrical ionization chamber with an insulated axial rod as a collecting electrode. Ionization is produced by the beam in the gas of the chamber and the ionization current collected by the axial electrode is a measure of the relative intensity of the beam.

In the *thermal method*, used by Rudnick (§ 5.14) and Batho (§ 5.14) and by Amdur and Pearlman (§ 4.22), the intensity of the molecular beam is determined by the heating effect it produces when it is incident

† *Phil. Mag.* **40** (1949), 369.

on a thermo-element. In using this method great care has to be taken to shield the detector from heat radiation from hot filaments and other heated parts of the apparatus.

In the *secondary emission method*, used by Rostagni (§ 5.121) and by Varney and his co-workers (§ 5.22), the molecular beam is allowed to fall on a metal surface and secondary electrons produced by the beam are collected to an electrode held positive with respect to the surface. It is clearly of importance to prevent radiation striking the target surface in order to avoid complicating effects of photo-electric emission.

Rostagni† has estimated the coefficient for secondary electron production by neutral atoms of A, Ne, and He at a target surface of unspecified material. His values are given in Table I.

TABLE I

Secondary Electron Emission Coefficients γ for Atomic Beams incident on an Unspecified Surface

Atom	Energy of incident atoms (eV)						
	600	400	200	100	50	30	25
A . .	0.23	0.17	0.07	0.013	0.004	0.0002	0.0001
Ne . .	..	0.07	0.04	0.01	0.003	0.0002	..
He . .	..	0.43	0.39	0.08	0.008	0.0006	..

The methods described above for the detection of fast beams of neutral molecules are only capable of giving relative intensities of beams of the same kind and of the same energy. For measurements of the total cross-section for molecular beams, such relative measurements are all that are required. Estimation of the absolute intensity of such beams, which would be required for the determination of the cross-section for ionization or excitation, is much more difficult and can really only be made if the charge exchange cross-section is known. Such estimates of absolute intensity from the charge exchange cross-section have been made by Rostagni and were used to determine the secondary electron emission coefficients listed in Table I. It should be remembered, however, that these estimates may be in error appreciably, particularly in the case of the rare gases, since they take no account of the possibility of the production of metastable atoms which also produce secondary electron emission from metal surfaces (see Chap. IX, § 6.1). These metastable atoms may be formed by collisions of ions with the metal surfaces of the accelerating system, a process which is of great importance in the case of helium (see Chap. IX, § 3).

† *Il Nuovo Cimento*, 11 (1934), 99.

4. Elastic collisions

4.1. Introductory remarks

It has already been pointed out in § 1 that the angular resolving power necessary to measure the total elastic cross-section for collision in experiments employing beams of ions or neutral atoms has to be very high indeed. To estimate it reference may be made to Chap. VII, § 5.11, in which the same problem was discussed for measurements at gas-kinetic velocities of impact. The resolving power required increases roughly as the relative velocity, so that for collisions of 100 eV protons with helium atoms deviations less than 7 minutes of arc must be capable of detection in order to obtain a total cross-section correct to within 10 per cent. Table II gives the angular distributions and total elastic

TABLE II

Calculated Differential and Total Cross-sections for Scattering of Protons by Argon and Helium

(i) Differential cross-section in units a_0^2 .

Angle of scattering (relative coordinates)	Argon (72 eV protons)		Helium (110 eV protons)	
	Self-consistent field	Unscreened Coulomb field	Self-consistent field	Unscreened Coulomb field
0°	5.1×10^4	∞	2.87×10^3	∞
12°	7.0	5.04×10^3	2.5	29.6
28°	2.29	246	0.64	1.94
34°	0.88	116.5	0.23	0.91
57°	0.30	16.3	0.07	0.13
80°	0.15	4.8	0.03	0.04
114°	0.05	1.69	0.01	0.01
137°	0.025	1.12	..	0.01
167°	0.015	0.83	..	0.005

(ii) Total cross-section.

Gas	Proton energy in eV	Cross-section in units πa_0^2	Gas-kinetic cross-section in units πa_0^2
He	90	3.75	2.6
	800	2.0	..
A	73	16.4	7.3
	650	10.7	..

cross-sections calculated by Massey and Smith† for the scattering of 110 eV protons in helium and 72 eV protons in argon. In carrying out these calculations the proton was supposed to move in the self-consistent

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

field (see Chap. III, § 2.1) of the atom concerned, polarization being neglected. At all angles except 0° the classical formula for scattering (Chap. VII, § 3.31) could be used, the angular range of validity of this formula increasing with increasing energy of the ion. The corresponding angular distributions for scattering by the unscreened Coulomb field of atomic nucleus are also included. It will be seen how small a proportion of the scattering occurs at angles greater than 12° , and that the total cross-section is comparable with the gas kinetic.

In view of these considerations it is unprofitable to attempt measurement of total elastic cross-sections. It is better to confine such experiments either to observation of the angular distribution of the elastic scattering or of the cross-section for elastic scattering through angles greater than an accurately fixed and known minimum angle. The analysis of such observations may be carried out exclusively using classical theory. Deviations due to quantum theory will only become appreciable at angles of scattering comparable with the angular resolution necessary to measure the total elastic cross-section. As the energy of relative motion prevailing in the beam experiments is so much greater than in gas-kinetic phenomena, the analysis of data acquired in this way provides information about the interaction between molecules, neutral or ionized at much closer separations than the techniques discussed in Chapter VII. Special interest therefore attaches to this work.

4.2. *Measurement of elastic cross-section for scattering through angles greater than a defined minimum*

4.21. *Ion beams.* Fig. 211 shows diagrammatically the apparatus used in an extensive series of measurements by Simons and his collaborators.† *A*, *F*, *C* are respectively the anode, filament, and cathode of a low-voltage arc source of the Lamar-Luhr type (§ 2.13). *P* and *Q* are systems of cylindrical electrodes, forming part of a carefully designed focusing system. Each consists of four coaxial cylinders, $\frac{1}{4}$ in. diameter and of length so adjusted as to subtend the same angle at the slit in *C*.

Approximately a quarter of the ions from the source entered the magnet chamber *M*. The fore-chamber *P* and the main chamber *Q* each had their own pumping system. After deflexion through 90° by an electromagnet the analysed beam passed through focusing and

† Simons, Francis, Fontana, and Jackson, *Rev. Sci. Inst.* **13** (1942), 419; Simons, Fontana, Muschlitz, and Jackson, *J. Chem. Phys.* **11** (1943), 307; Simons, Fontana, Francis, and Unger, *ibid.* 312; Simons, Francis, Muschlitz, and Fryburg, *ibid.* 316.

collimating cylinders, B , G , then entered the scattering cylinder S , and was finally collected in the cylinder R , the collected current being measured by an electrometer valve and D.C. amplifier. Care was taken to provide suitable flanges on all the electrodes so as to screen the beam completely from the glass walls of the tube and so to prevent deflexion by electrostatic charges on the walls.

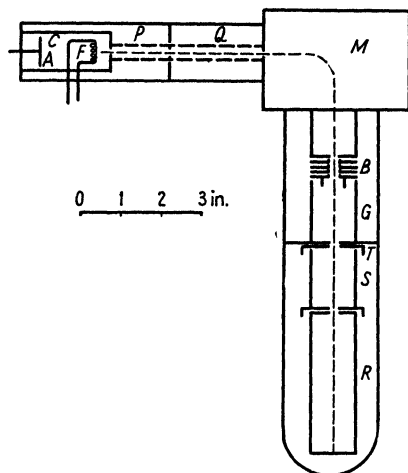


FIG. 211. Simons' apparatus for studying elastic scattering of ionic beams.

By measuring the current collected as a function of the pressure of the gas in S , a collision cross-section could be estimated. This included elastic scattering through angles greater than 4.1° as well as charge exchange. Correction was made for the latter as follows.

The electrode T placed before the scattering cylinder and insulated from it was maintained at a small negative potential (-4 volts) relative to it. It collected slow ions produced by charge exchange and enabled the correction to the measured collision cross-section for this to be made.

With this apparatus the scattering of protons in H_2 and of H_2^+ and H_3^+ ions in H_2 and H_2O has been studied over the energy range from 120 to 5 eV. The data obtained have been analysed by methods similar to those described in Chap. VII, § 5, to obtain information about the interaction energy between the ions and molecules concerned. The interaction was taken to be of the form

$$V(r) = -C/r^n, \quad (6)$$

involving the adjustable constants C , n . With this interaction the relevant cross-section is given by

$$Q' = \int_{\theta_{\min}}^{\pi} I(\theta) \sin \theta \, d\theta, \quad (7)$$

where $I(\theta)$ is given by (23), Chap. VII, and $\theta_{\min}$ is the minimum angle through which deviation must occur in order that the ions will not enter the collector.

The angle $\theta_{\min}$ depends on the position on the ion path in the scattering chamber when scattering occurs. The length of the path in Simons' apparatus was 4.176 cm. To compare with experiment Q' given by (7) had therefore to be averaged over the length of the ion path in the scattering chamber.

For the interaction of H^+ with H_2 Simons and his group found his results could be represented by the following interaction energy:

$$\begin{aligned} V(r) &= -20.37r^{-4} \text{ eV} \quad (r > 1.74 \text{ \AA}), \\ &= -7.72r^{-1.74} \text{ eV} \quad (1.5 \text{ \AA} < r < 1.74 \text{ \AA}), \end{aligned}$$

where r is expressed in $\text{\AA}$.

4.22. Neutral beams. Amdur and Pearlman† have measured the cross-section for elastic scattering, through angles greater than 2.25° , of beams of hydrogen atoms by molecular hydrogen and of helium atoms by helium gas. The beams were obtained by the charge transfer method described in § 2.6 and the energy range investigated was from 200 to 800 eV. There is some uncertainty in their measurements with hydrogen beams because they did not use magnetic analysis of their original positive ion beam. The neutral beam may thus have contained, in addition to H atoms, also H_2 and perhaps H_3 molecules. The experiments with helium beams should have been free from this kind of uncertainty, but the neutral helium beams may have contained a proportion of helium atoms in the metastable state arising from neutralization of He ions at the surfaces of the slit system.

The analysis of the helium-helium atom collisions has already been discussed in Chap. VII, § 4.12. A similar analysis was carried out for the interaction of hydrogen atoms with hydrogen molecules.

4.3. Measurement of the angular distribution of elastic scattering

Measurements of the angular distribution of slow positive ions scattered elastically in gases have been carried out by Ramsauer and Kollath‡ and by Rouse.§

† *J. Chem. Phys.* **8** (1940), 7; see also Amdur, *ibid.* **11** (1943), 157.

‡ *Ann. der Physik*, **16** (1933), 570.

§ *Phys. Rev.* **52** (1937), 1238.

The method of Ramsauer and Kollath† is of special interest in that it provides a direct verification of the distinction between directly scattered ions and those arising from charge exchange. They used the same 'zone' apparatus as they had used earlier for the angular distribution of electron scattering. This apparatus is described in Chap. II, § 7.2 (Fig. 43).

In place of the electrons, a beam of protons, produced by electron bombardment of LiOH, entered the collision chamber after deflexion through 90° in a magnetic field. The scattering took place at the centre of a hollow sphere divided into eleven zones just as before. Each zone represents a definite angle of scattering. The velocity of the scattered particles was measured by a retarding potential experiment. A grid of gold wire, 0.05 mm. diameter, placed 1 mm. in front of the collecting zones enabled these retardation measurements to be carried out.

With this apparatus Ramsauer and Kollath investigated the scattering of protons of energy 30–120 eV in He, A, H_2 , and CH_4 in the range of scattering angles 15 – 167° . The retarding potential curves in He and A showed separate groups of positive ions (Fig. 212). The velocity of the fast group decreased in argon and especially in helium with increasing scattering angle. The number of fast particles decreased in comparison with the number of slow particles for increasing proton energy and increasing angle of scattering. The slow group is, of course, to be identified with the slow positive ions produced as a result of charge exchange. The fast group consists of protons that have undergone elastic scattering.

Fig. 213 shows the results obtained for the scattering of protons of energy 64.5 eV in helium. The results are compared with those to be expected for Rutherford scattering by a Coulomb field and for the calculated angular distribution of Table II. The agreement with this latter curve is seen to be reasonable.

Rouse‡ measured the scattering of K^+ ions in A, Kr, Xe, and Hg vapour. He used a Kunsman source of K^+ ions and measured the scattering into a movable collector which could be rotated to receive ions scattered at different angles out of the incident ion beam. The apparatus was thus very similar in principle to that of Bullard and Massey for electron scattering, described in Chap. II, § 7.1. For the scattering of K^+ ions in argon the angular distribution, shown in Fig. 214, is what might be expected. The scattered intensity decreased monotonically with increase of scattering angle. The scattering was more

† *Ann. der Physik*, **16** (1933), 570.

‡ *Loc. cit.*

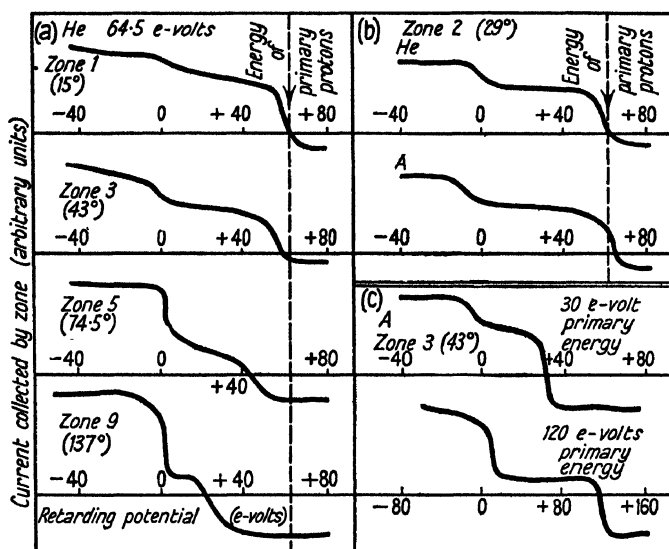


FIG. 212. Retarding potential analysis of the current collected by different zones in Ramsauer and Kollath's apparatus, showing two groups of ions of different velocity.

- Scattering of 64.5 eV protons in helium to illustrate the effect of angle of scattering on the energy distribution of the collected ions. The mean angle of scattering corresponding to each zone is shown on the figure.
- Analysis of current scattered through 29° in He and A.
- Analysis of current scattered through 43° in A for incident protons of energy 30 eV and 120 eV.

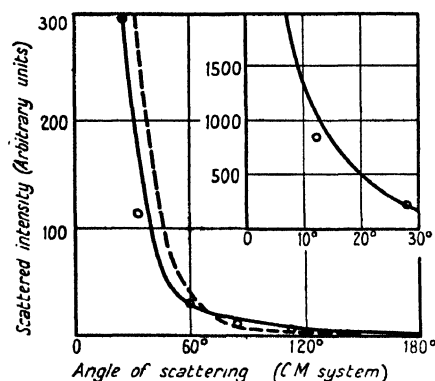


FIG. 213. Angular distribution of 64.5 eV proton scattered by helium. — observed by Ramsauer and Kollath; $\circ$ calculated using the self-consistent helium atomic field; - - - calculated regarding the helium atom as unscreened.

concentrated in small angles as the incident energy increased, and the total scattering decreased with increasing energy. However, for scattering in Kr, Xe, and Hg vapour, a curious increase in scattering was observed for high energies and at large angles. It is likely that this effect was instrumental. No analysis of these results with the aim of obtaining information about ion-atom interaction has been attempted.

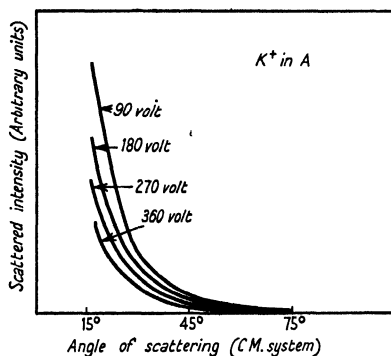


FIG. 214. Observed angular distribution of K^+ ions scattered by argon.

4.4. Diffraction of positive ions by molecules

Experiments on the diffraction of positive ions by molecules are more difficult to carry out than those on electron diffraction because the wave-length of positive ions of a convenient energy is too short. However, the diffraction of protons by CCl_4 molecules has been successfully demonstrated by Yearian† using protons of energy 17.7 keV corresponding to a wave-length of 0.00214 Å. A pattern of the same form as that of Fig. 94 (a) was obtained.

Comparing the values of $s_k = (4\pi/\lambda)\sin(\theta_k/2)$ for the k th ring (see Chap. IV, equation (9)) with the values obtained for electron diffraction, Yearian obtained values of 7.28, 9.20, and 11.33 in units 10^8 cm.^{-1} for $k = 3, 4, 5$ respectively, compared with the corresponding values 7.13, 9.23, and 11.34 for electron diffraction by CCl_4 , thus leaving no doubt of the interpretation of the observations. The difficulties of technique, however, make it unlikely that diffraction by positive ions will prove such a useful tool as electron diffraction for the exploration of molecular structure.

† *J. Chem. Phys.* **8** (1940), 24.

5. Inelastic collisions—the experimental technique

5.1. *Methods used for the experimental determination of charge exchange cross-sections*

5.11. *Measurement of beam absorption coefficient.* The charge exchange cross-section may be measured by a method similar to that used for the apparent total collision cross-section for scattering through angles greater than a definite minimum (§ 4.21). If the angular resolving power of the apparatus is low, very few elastic collisions will be detected and the observed cross-section will be mainly due to charge exchange. This method is especially applicable to beams of moderately high energies, in which case the elastic scattering will be concentrated into very small angles and the cross-section for ionization or excitation is still small. To check whether the elastic scattering contribution is small, the measurements may be carried out using a number of different slit widths. If the observed cross-section is almost independent of the resolving power of the apparatus it may be concluded that the true charge exchange cross-section is being measured in such an apparatus.

Estimates of charge exchange cross-sections using the beam absorption method have been made by Goldmann.†

5.12. *Direct measurement of charge exchange current.* For the direct determination of the cross-section for charge exchange the flux of slow ions produced in the gas by the passage of the ion beam may be measured. This is accomplished by placing in the collision chamber an electrode maintained at a potential a few volts negative relative to the walls of the chamber. It is assumed that the low-energy ions produced in the gas arise from charge exchange and that ions elastically scattered by the gas molecules are scattered only through small angles and without much loss of energy so that they will not in general be collected. In some cases the collecting electrode may simply be a wire, and in that case the applied potential ensures that all the slow ions are collected. In other cases the electrode may be a cylinder in the collision chamber placed so that the incident ion beam moves along its axis. In this case some of the ions collected might be fast ions elastically scattered out of the incident beam. The geometry is such, however, that only the very small proportion of ions scattered through a comparatively large angle could reach the collecting cylinder so that the error arising from elastically scattered ions is likely to be small. It could be avoided altogether by placing an insulated grid in front of the collecting cylinder, thus enabling

† *Ann. der Physik*, **10** (1931), 460.

a velocity analysis of the collected ions to be made. In many experiments the apparatus has also been adapted to measure ionization cross-sections.

5.121. Rostagni's apparatus. An apparatus of this kind has been used by Rostagni† for determining charge exchange and ionization cross-sections. It is shown in Fig. 215. Ions from the source S were

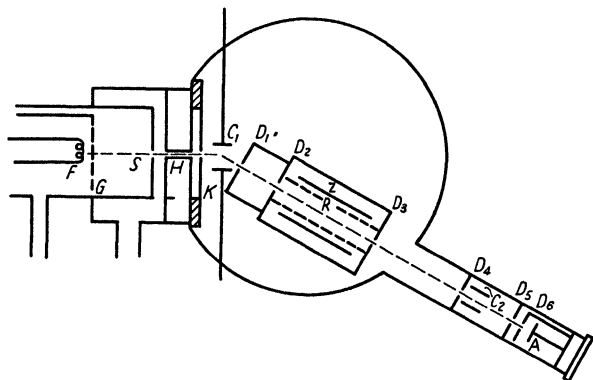


FIG. 215. Rostagni's apparatus for the measurement of charge exchange cross-sections.

collimated by passage through the canal H , 1 cm. long and 1 mm. diameter, and entered the condenser C_1 in which they were deflected through 30° by means of an electrical field. This deflexion ensured that a beam of ions, homogeneous in energy, and free from neutral atoms, was incident on the slit D_1 . To measure the intensity of the beam, an electrode (not shown in the diagram) could be placed in the path of the beam immediately after it entered D_1 . This electrode was constructed on a ground joint so that it could be moved out of the way of the beam from outside the tube when the incident current measurement had been made. The beam then passed through the opening D_2 into the collision chamber. It passed along the axis of the collecting cylinder Z which had in front of it the grid R kept at the same potential as D_2 . By applying a suitable potential difference between Z and R the collected ions could be analysed in velocity. The grid also enabled the measurement of the true ion current independent of secondary electron emission from Z .

After passing out of the collision chamber the beam passed through the system D_4, C_2, D_5, D_6 and eventually was collected at A . This system of slits and condensers was used to centre the beam.

When the current collected by Z was plotted against the potential

† *Zeits. f. Phys.* **88** (1934), 55; *Il Nuovo Cimento*, **12** (1935), 134; **13** (1936), 389.

difference between Z and R , curves of the form shown in Fig. 216 were obtained. Curve (a) of that figure shows the type of curve obtained for an incident ion energy of 50 eV. The saturation current i_c reached for negative potential difference between Z and R represents slow ions produced by charge exchange. In this case no electron current is measured when the potential of Z is positive with respect to K . Curve

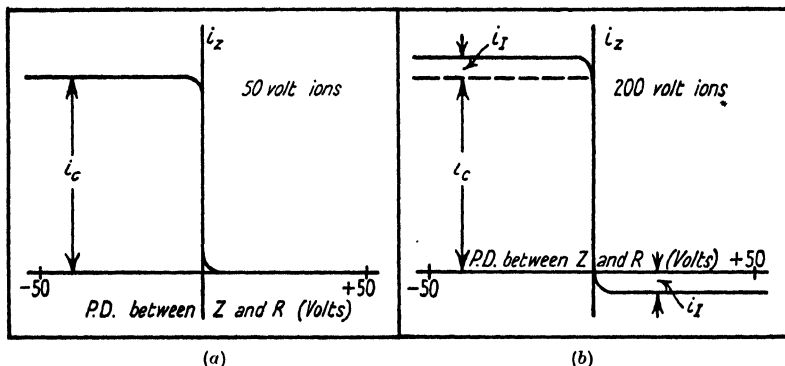


FIG. 216. Retarding potential analysis of ions collected in charge exchange experiments for incident ions of different energies.

(b), however, shows the type of curve obtained for an incident ion energy of 200 eV. In the case shown, obtained for the passage of A^+ ions through argon, a negative current is drawn to Z when it is held positive relative to R . This is an electron current, and arises from the ionization of argon atoms by incident argon ions. From the saturation value of the electron current i_I , the cross-section for ionization may be calculated. In this case the saturation positive ion current will be $i_I + i_c$ so that, knowing i_I , i_c can be obtained and thence the charge exchange cross-section calculated. This shows how both the cross-section for charge exchange and for ionization by positive ions can be obtained in the one set of measurements. Rostagni used incident ions of energy up to 1,000 eV.

5.122. Keene's apparatus. An apparatus somewhat similar to that of Rostagni (§ 5.121), but employing a plate parallel to the beam to collect the ions formed by charge exchange,[†] has been used by Keene[‡] to study charge exchange and ionization in He and H_2 , using ions of those gases of energy up to 35 keV.

Keene's measurements are the most careful that have so far been made of cross-sections for charge exchange of ions in gases. In addition

[†] Rostagni has also used the transverse field method described here in his later work.

[‡] *Phil. Mag.* **40** (1949), 369.

to taking great care to eliminate effects arising from secondary electrons he established in a convincing fashion that the slow ions originating in the collision chamber were actually produced along the path of the beam. Also by conducting a magnetic analysis of the ions formed by charge exchange he was able to identify without ambiguity the actual

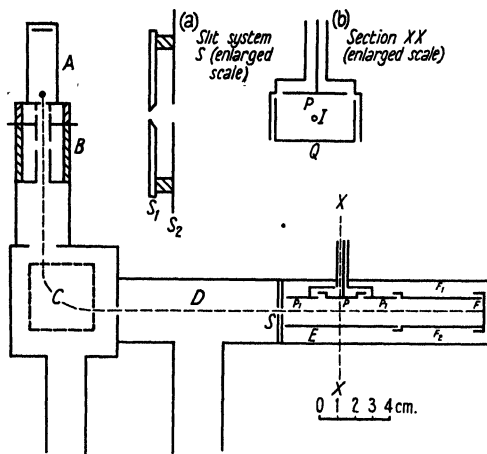


FIG. 217. Keene's apparatus for measuring charge exchange and ionization cross-sections.

- (a) Slit system designed to reduce effect of secondary electrons.
 (b) Section through XX (enlarged), showing ion collector.

processes to which his measured cross-sections referred. Precautions such as these had not been taken in earlier measurements of charge exchange cross-sections. Keene's apparatus is shown in Fig. 217.

The ions were produced in a low-voltage arc A of the Nier type (§ 2.11) operated in a longitudinal magnetic field. They were extracted from the source, accelerated, and focused by means of the focusing system B , and then entered the transverse magnetic field across the chamber C in which they were analysed by deflexion through 90° . After passing through the space D , maintained at a low pressure, the ion beam passed through the slit S and entered the chamber E where ionizing and charge exchange collisions occurred, and it was finally collected in the Faraday cage consisting of the three electrodes F , F_1 , F_2 .

Care had to be taken to prevent secondary electrons and slow charge exchange ions produced in the Faraday cage from passing back into the collision chamber D . A transverse electrostatic field between F_1 and F_2 was used for this purpose. The electrode F was connected to F_1 or F_2 ,

whichever was positive, and the total current to F , F_1 , and F_2 gave a measure of the true beam current. The slit system S was carefully constructed as shown in Fig. 217 (a) to keep secondary electrons out of the collision chamber. It consisted of two slits S_1 , S_2 about 1 cm. apart and insulated from each other. The first slit S_1 was narrower than S_2 and kept at a potential of 30 volts positive relative to S_2 to hold in secondary electrons.

The slow ions produced by charge exchange or ionization were collected by the rectangular plate P . An electrostatic field between the plates P and Q enabled the collection of either electrons or positive ions by P . The direction of the field between F_1 and F_2 was always kept the same as that between P and Q . The plates P_1 , maintained at the same potential as P , ensured that P collected ions from a well-defined length of the beam. Fig. 217 (b) shows a section of the collision chamber at X , illustrating the shapes of the plates P and Q and their position relative to the ion beam I .

By replacing plate P by another plate containing a small hole it was possible to conduct a retarding potential analysis of the velocity of the ions collected to P . Keene was able to show in this way that all the positive ions collected by P originated at the position of the ion beam and were formed with very small energy.

Alternatively it was possible to carry out a magnetic analysis of the ions passing through the small hole. Such an analysis showed that these ions were entirely He^+ ions in the case of a He^+ beam passing through He . For H^+ or H_2^+ in H_2 the H^+ peak was a few per cent. only of the H_2^+ peak, indicating a cross-section for dissociation small compared with the charge exchange cross-section.

A method similar to that used by Rostagni and Keene has been applied by Sherwin† in an extensive series of investigations on the charge exchange and ionization cross-sections of metallic ions. For the production of singly and multiply charged metallic ions Sherwin used a high-frequency spark operated with a potential difference of 12 kV between electrodes of the metal to be studied.

5.123. Wolf's method. An extensive series of investigations of charge exchange for ions of energy up to 1,000 eV has been carried out by Wolf.‡ His apparatus is shown in Fig. 218. It differs from that of Rostagni and Keene in that the measurements were carried out in a magnetic field.

Electrons emitted from the filament F ionized the gas in the ion

† *Phys. Rev.* **57** (1940), 814.

‡ *Ann. der Physik*, **23** (1935), 285, 627; **25** (1936), 527, 737; **27** (1936), 543; **29** (1937), 33; **30** (1937), 313.

chamber *I*. The apparatus was placed in a magnetic field, but the ion source was shielded from the field by the iron cylinder *A*. After acceleration through the slit system *S*, in which the final slit had dimensions 4.5 mm. $\times$ 0.5 mm., the ions entered the analysing chamber *C* where they were deflected through 90° and analysed. The radius of the ion

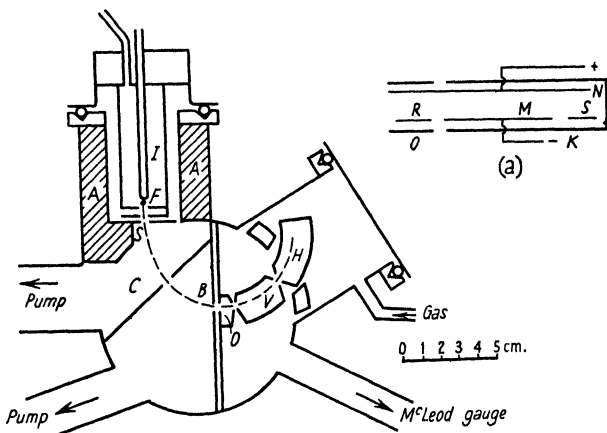


FIG. 218. Wolf's apparatus for measuring charge exchange and ionization cross-sections. (a) Detail of collecting wire system.

path in the magnetic field was 4 cm. They then passed into the small chamber *O*, through a slit *B* of dimensions 12 $\times$ 3 mm. From *O* they entered the collision chamber *V* and after passing out of *V* entered the Faraday cylinder *H*.

Wolf first measured the current i_V collected to *V*, and the current i_H to *H*. By studying $i_H/(i_H + i_V)$ as a function of gas pressure he was able to determine the total collision cross-section. He now replaced the two cylinders *V* and *H* by a single cylinder *K*, curved to conform with the path of the ions in the magnetic field. Into *K* and directly over and under the path of the beam, he introduced two wires *M* and *N* curved into an arc of a circle of radius equal to the radius of the ion beam (Fig. 218 (a)). On either side of *M* were two short lengths of wire, *R*, *S*, curved into an arc of the same circle, which acted like a guard ring for *M*. By studying the current of slow ions collected by *M* as a function of the potential difference between *M* and *N*, he found saturation for positive ions to occur for a potential difference of 4 volts. This was sufficiently low to have little effect on the incident ion beam, so measurements with very low energy beams were quite possible.

In Wolf's earlier work the arrangement of collecting wires was less symmetrical than in that described here. Spurious large charge exchange cross-sections for low ion energies were observed owing to the fact that some of the ions of the incident beam could be deflected to strike the collecting electrode. Since, in the method used by Rostagni, the grid covering the collecting cylinder could be kept at the same potential as the ion beam, his method is superior from this point of view. However, the method used by Wolf has the advantage that it will record very few of the fast scattered ions that could be collected in Rostagni's arrangement.

If l is the length of the wire M , i_M the current collected to it, i_K the total current collected by the cylinder K , and n the number of molecules per c.c. in K , the charge exchange cross-section

$$Q_c = \frac{i_M}{i_K} \frac{1}{nl}.$$

Wolf was able also to measure the ionization cross-section for the positive ions by measuring the saturation electron current to his collector when ionization was occurring.

An extensive and careful series of measurements using a method somewhat similar to that of Wolf has been made recently by Hasted.† These measurements were extended down to ion energies of 25 eV. Other charge exchange measurements have been made by Kallman and Rosen,‡ Sherwin,§ and by Simons, Francis, Muschlitz, and Fryburg.||

5.13. Charge exchange involving multiply charged ions (Arnot's method). An ingenious method for the study of charge exchange involving multiply charged ions has been used by Arnot and McEwen†† and by Arnot and Hart.‡‡ This method is not available, however, in the case of singly charged ions. The apparatus used is shown in Fig. 219(a). The cylinder C_1 was divided into two parts by the nickel gauze G_1 . Electrons were accelerated through the grid G_1 and positive ions were formed in the field free space between G_1 and G_2 . Some of these positive ions, diffusing through G_2 , were accelerated between G_2 and G_3 by a potential V_1 . Between G_3 and G_4 they moved in a field free space where charge exchange could take place. Between G_4 and G_5 a retarding potential V_2 was applied. C_4 was a Faraday cylinder shielded by the cylinder C_3 .

The measurement consisted in the determination of the current i reaching C_4 as a function of the retarding potential V_2 between G_4 and G_5 . It was found that, in order to prevent all the positive ions from reaching C_4 , a retarding potential V_2 had to be applied about equal to twice the accelerating potential V_1 . Plotting the gradient of the i - V_2 curve, the curve of Fig. 219(b) was obtained for the distribution in energy of the ions passing through G_4 . Arnot interpreted the peak at $V_2 = 2V_1$

† *Proc. Roy. Soc. A*, **205** (1951), 421.

§ *Phys. Rev.* **57** (1940), 814.

†† *Proc. Roy. Soc. A*, **169** (1939), 437.

‡ *Zeits. f. Phys.* **64** (1930), 806.

|| *J. Chem. Phys.* **11** (1943), 316.

‡‡ *Ibid.* **171** (1939), 383.

as due to ions which had been accelerated between G_2 and G_3 as doubly charged ions, thereby acquiring a kinetic energy of $2V_1$ eV, but had captured an electron from a gas molecule in passing through the cylinder C_2 and so were retarded between G_4 and G_5 as singly charged ions. This interpretation was supported by the fact that no second peak was obtained unless the potential V_0 between F and G_1 exceeded that required for double ionization of the gas being studied. From the

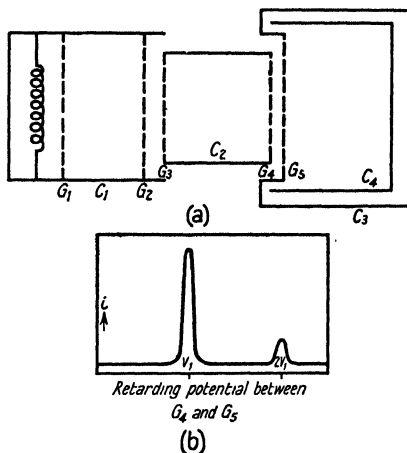
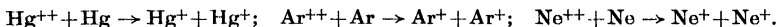


FIG. 219. (a) Arnot's apparatus for studying charge exchange involving doubly charged ions in a gas. (b) Illustrating the analysis of the charge on the ions reaching collector C_4 . The peak at $2V_1$ arises from ions, originally doubly charged, which have captured an electron in C_2 .

known relative probability of the production of singly and doubly charged ions by electrons of a given energy (see Chap. II, § 2.2), and from the pressure in the cylinder C_2 , the cross-section for the capture of electrons by doubly ionized ions could be calculated. Arnot applied this method to the reactions



5.14. Study of equilibrium between ionic and neutral components of a beam. The cross-section for charge exchange has also been determined by studying the relative numbers of positive ions and neutral atoms present in a beam of positive ions after it had passed through a gas. Suppose such a beam originally consists entirely of positive ions. As the beam passes through the gas charge exchange can occur, so the beam will consist partly of ions and partly of fast neutral particles. The concentration of fast neutral atoms will not increase indefinitely because they may themselves be ionized by impact with gas molecules. Thus an equilibrium concentration of the beam will eventually be reached when

the rate of removal of positive ions from the beam by charge exchange is just equal to the rate of removal of the neutral particles by re-ionization.

This method of studying electron capture was first employed for the investigation of the capture and loss of electrons by alpha-particles. Thus Henderson† observed, by a magnetic deflexion method, that a beam of alpha-particles, after passing through matter, had associated with it singly charged He^+ ions and neutral atoms. He and others,‡ by measuring the relative intensities of these beams, were able to calculate the relative mean free paths of He^{++} ions for electron capture and He^+ ions for ionization by the passage through various materials. A summary of the results observed is given in Rutherford, Chadwick, and Ellis, *Radiation from Radioactive Substances* (Cambridge, 1930), 119. The method has been applied by Rudnick§ and Batho|| and more recently by Meyer†† for ions of different kinds in an energy range up to 200,000 eV.

Let N_0 and N_1 be respectively the number of neutral and ionized particles crossing unit area of the beam per unit time and Q_{10} , Q_{01} respectively the cross-sections for charge exchange of the positive ions and re-ionization of the neutral particles. Then we have at a point distant x , measured along the beam from a fixed point in it,

$$\frac{dN_1}{dx} = Q_{01}N_0 - Q_{10}N_1, \quad \frac{dN_0}{dx} = -\frac{dN_1}{dx}. \quad (8)$$

If the path length is sufficiently long so that equilibrium has been attained,

$$Q_{10}/Q_{01} = N_0/N_1.$$

It follows that, if the ratio N_0/N_1 can be measured when equilibrium has been attained, the ratio Q_{10}/Q_{01} can be determined.

Similarly, if a beam is initially composed of a fraction F_0 of neutral atoms, and the remainder, $1 - F_0$, of ions, the fraction F of all the neutral atoms at a point x is obtained by calculating $N_0/(N_0 + N_1)$ at the point x from equation (8). This gives

$$F(x) = F_\infty + (F_0 - F_\infty)\exp\{-(Q_{01} + Q_{10})nx\}, \quad (9)$$

n being the number of gas molecules per c.c. and F_∞ the equilibrium fraction of neutral molecules in the beam.

If a beam is composed initially entirely of neutral atoms and if positive ions are removed by an electric field as they are formed so that there

† *Proc. Roy. Soc. A*, **102** (1922), 496.

‡ Henderson, *ibid.* **109** (1925), 157; Briggs, *ibid.* **114** (1927), 341; Jacobsen, *Nature*, **117** (1927), 858.

§ *Phys. Rev.* **38** (1931), 1342.

|| *Ibid.* **42** (1932), 753.

†† *Ann. der Physik*, **30** (1937), 635; **37** (1940), 69.

is no chance for them to return to a neutral state, the intensity, I , of the beam after passing a distance x when the initial intensity is I_0 is given by

$$I = I_0 e^{-nQ_{01}x}. \quad (10)$$

It is clear from this analysis that the assumption is made that, in the process of re-ionization of the neutral particles, they are not scattered out of the beam. This assumption is probably justified.†

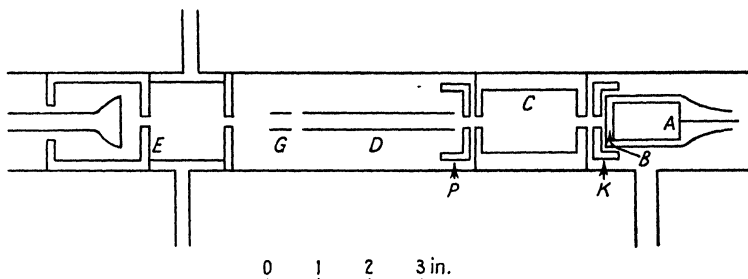


FIG. 220. Apparatus for determining cross-sections for charge exchange and ionization by measuring the relative concentration of neutral atoms and ions in a beam passing through a gas.

Fig. 220 shows the apparatus based on these principles which was used by Rudnick‡ and by Batho.‡ The ion source was a low-voltage arc (filament B , hollow anode A , cathode K) developed by Batho and Dempster.§ Ions drawn out from the arc entered the charge exchange chamber C . The beam issuing from C was a mixture of ions and neutral particles. Potentials applied to the diaphragm P prevented the ions from leaving C so that the beam entering D could be composed entirely of neutral atoms if required. The beam next entered the collision space. Alternatively, by reducing the pressure in C conditions could be realized in which the beam entering D was composed almost entirely of positive ions. The beam entered the collision space, passing through the two parallel plate condensers D and G of different lengths across which electric fields could be applied to remove positive ions, and finally was incident on the detector E , consisting of a thermocouple with a narrow slit. In this way the total number of all particles reaching E could be

† If it were not, the equations for N_0 and N_1 would become

$$dN_0/dx = Q_{10} N_1 - Q_{01} N_0, \quad dN_1/dx = -Q_{10} N_1,$$

giving

$$d(N_0/N_1)/dx = Q_{10}\{(N_1+N_0)/N_1\} - Q_{01} N_0/N_1,$$

so that, for equilibrium, $F_\infty = N_0/(N_1+N_0) = Q_{10}/Q_{01}$ instead of $Q_{10}/(Q_{01}+Q_{10})$ as assumed.

‡ Loc. cit.

§ *Ap. J.* 75 (1932), 34.

measured. At the same time the current collected by E provides a measure of the total number of charged particles arriving.

The total number of particles reaching E was now measured when no electric field was applied across either D or G and the beam entering D consisted either entirely of neutral particles or entirely of positive ions. Let N , N' be the total number of particles per unit time reaching E in these two cases.

The number of neutral particles reaching E per unit time was now measured under the following conditions:

- (1) with a beam consisting entirely of neutral particles entering D , a field applied across the short condenser G , but none across the long condenser D ;
- (2) with a beam consisting entirely of neutral particles entering D , a field applied across D , but none across G ;
- (3) with a beam consisting entirely of positive ions entering D , a field applied across G , but not across D .

Let N_1 , N_2 , N_3 be the number of neutral particles reaching E per unit time in these three cases and let x , y be the lengths of path in the condensers D , G respectively.

Then from (8) and (9) the following relations follow:

$$N_1 = Ne^{-Q_{01}ny}[F_{\infty} + (1 - F_{\infty})e^{-(Q_{01} + Q_{10})nx}], \quad (11)$$

$$N_2 = Ne^{-Q_{01}nx}[F_{\infty} + (1 - F_{\infty})e^{-(Q_{01} + Q_{10})ny}], \quad (12)$$

$$N_3 = N'F_{\infty}e^{-Q_{01}ny}[1 - e^{-(Q_{01} + Q_{10})nx}]. \quad (13)$$

From these equations the quantities F_{∞} , Q_{01} , and Q_{10} can be calculated.

5.2. *Methods used for the study of ionization and excitation by beams of ions or atoms*

5.21. *Introductory remarks.* The measurement of accurate ionization cross-sections is a problem of great difficulty. The ionization currents produced are small, and the electrons which have to be collected in order to measure the ionization are produced in the presence of large quantities of slow positive ions produced both in the ionization process itself, or, more commonly, by charge exchange. These positive ions, when collected, may themselves give rise to considerable quantities of secondary electrons. These can entirely mask the effect of the electrons produced by primary ionization, unless special care is taken to prevent the escape of secondaries, as, for example, by covering all collecting surfaces with insulated metal grids maintained at a negative potential relative to the collecting surface. The collecting system must also be so

designed that saturation electron currents are collected at potentials below that needed to ionize the gas by electron impact.

Another possible source of error in experiments of this kind arises from the possible presence of metastable atoms, which, as described in Chap. IX, § 6.1, have the property of freeing electrons from surfaces on which they are incident. Effects of metastable atoms are particularly likely to cause trouble in measurements with inert gas atoms or ions.

In the measurement of excitation by atom or ion impact the chief difficulty arises from the low intensity of the effects produced. Further losses in intensity occur owing to the necessity of spectral analysis of the radiation emitted. The measurement requires the measurement of such weak intensities that only an integrating method of detection such as the photographic-photometric method is feasible.

In studying collision phenomena of this type the intensities are so weak that an attempt is sometimes made to increase them by increasing the pressure of the gas in which the collisions occur. Care must be taken, however, to work in a region of pressure throughout which the intensity effects are proportional to pressure. At higher pressures more complicated multiple processes may be expected to occur. For a similar reason it is necessary to work in a region of relatively small current density. If the amount of ionization produced by the beam is too large, a plasma may be produced by the beam and some of the observed effects may arise from phenomena occurring in the plasma. Absence of effects such as these may be implied if the current densities employed are such that the ionization or excitation produced is strictly proportional to the ion current.

5.22. Measurement of cross-sections for ionization. The direct method of measuring ionization of positive ions, as used by Keene, Rostagni, Wolf, Sherwin, and others, has already been described (§ 5.11). A different method of studying the ionization, based on the space-charge method used by Hertz† to study the ionization of a gas produced by electron collision (see Chap. II, § 2.4) has been employed by Varney.‡ The principle of this method is shown in Fig. 221.

Two cylinders A and B have axial filaments F_A , F_B which supply electrons. These are pulled out by a potential of about one volt, the electron current to the walls being space-charge limited. The currents in the two cylinders are balanced against each other in a bridge circuit.

Positive ions from a Kunsman source F are collimated by the slits

† *Zeits. f. Phys.* **18** (1923), 307; see also Kingdon, *Phys. Rev.* **21** (1923), 408.

‡ *Ibid.* **47** (1935), 483; **53** (1938), 732.

S_1 and S_2 and enter the cylinder B by means of a hole S_3 . The entrance of the positive ion beam upsets the space-charge limitation condition, but this effect is almost independent of the velocity of the ions provided

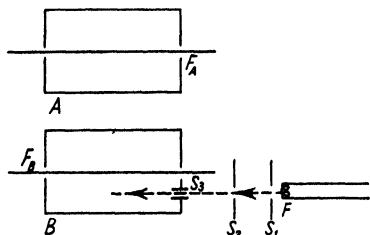


FIG. 221. Balanced space charge method for observing ionization produced by positive ions.

their energy exceeds about 10 eV. If ionization occurs in B the resulting neutralization of space charge causes a sharp rise in the electron current from the filament F_B , so that the device may be made very sensitive for the detection of ionization.

A similar method has been used by Varney† and by Berry, Varney, and Newbery‡ for studying ionization by fast beams of neutral atoms. It appears difficult, however, to

make measurements of this kind quantitative.

It should be noted that in experiments such as those of Berry, Varney, and Newbery, and, in fact, in all experiments employing fast beams of neutral atoms, these beams are produced by neutralization of positive ions. The assumption is invariably made that the energy of the neutral atomic beam is identical with that of the positive ion beam from which it was produced. It is clear from the previous section that there is reasonable justification for this assumption.

5.23. Study of optical excitation by ions and atoms. The measurement of the cross-section for optical excitation employs a type of apparatus essentially similar to that employed to study controlled excitation of spectra by electron impact, described in Chap. II, § 4.2, a suitable ion source replacing the electron source. Typical of the experimental arrangement is that shown in Fig. 222, used by Trittelwitz§ for the study of the optical excitation produced by the collision of helium atoms and ions with neon. As source of He^+ ions a Tuve capillary arc was used (§ 2.12). Ions were drawn out by means of the accelerating electrode E and passed down between the plates of the condenser A . This enabled the removal of all ions from the beam when it was desired to study excitation by neutral atoms alone.

After passing through the slit S_1 , the beam entered the collision chamber containing neon gas and then passed into the Faraday cylinder F . Light produced by excitation in the collision chamber passed through

† *Phys. Rev.* **50** (1936), 159.

§ *Ann. der Physik*, **40** (1941), 131.

‡ *Ibid.* **61** (1942), 63.

S_2 which formed the first slit of a spectrograph and then out through the window W and the collimating lens L of the spectrograph. The light was detected photographically and its intensity measured by a photometer. The sources of error were very large owing to the very weak intensity of the radiation in the wavelength range studied and it is this weak intensity that makes all measurements of this kind very difficult to carry out precisely. For example, when the energy of the incident beam was 4,500 volts, only 20 per cent. of the observed radiation originated from the beam. At 2,500 volts the corresponding figure was only 10 per cent. In this last case the error in any measurement could have been as high as 100 per cent.

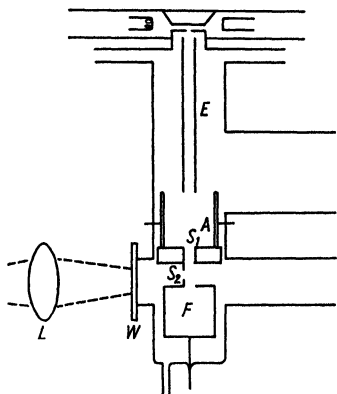


FIG. 222. Apparatus of Trittelwitz for studying optical excitation produced by atomic and ionic collisions.

Another source of uncertainty arises when attempting to distinguish between excitation by atomic and ionic beams. This is usually done by measuring the excitation with and without potentials applied to a condenser such as A in Trittelwitz's arrangement. The difference between excitation observed in these two cases is taken to indicate the effect produced by ions alone. However, in order to obtain measurable light intensities in this experiment a pressure of neon had to be used so high that the mean free path for charge exchange was only 9 mm. Thus a large number of fast neutral atoms were produced between the condenser A and the Faraday cylinder F . Any excitation produced by such neutral atoms could not be distinguished from excitation by positive ions by this method.

5.24. Inner shell ionization by positive ion impact. The inner shell ionization of atoms by protons and alpha particles has been studied by a number of experimenters.† Such investigations involve the study of X-ray excitation, and Fig. 223 illustrates the apparatus used by Peter to study aluminium K radiation excited by fast protons.

The proton beam P of the requisite energy (60–170 keV in Peter's experiments) was incident on a Faraday cylinder F , the base B of which

† Bothe and Franz, *Zeits. f. Phys.* **52** (1928), 466; Gerthsen and Reusse, *Phys. Zeits.* **34** (1933), 478; Peter, *Ann. der Physik*, **27** (1936), 299; Livingston, Genevese, and Konopinski, *Phys. Rev.* **51** (1937), 835; Hoffmann, *Phys. Zeits.* **37** (1936), 694.

was a thin sheet of aluminium foil. X-rays excited by ion impact on the foil could pass through and, emerging on the opposite side, passed into a Geiger-Müller counter *C*. Between the target and the counter, foils *A* of a suitable absorber could be interposed so that the absorption coefficient and hence the wave-length of the X-rays could be determined.

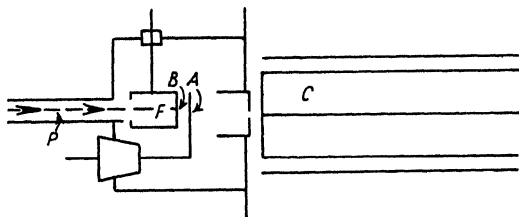


FIG. 223. Peter's apparatus for measuring the intensity of Al *K* radiation produced by fast protons.

As discussed earlier (Chap. II, § 3; Chap. VI, § 3.3) a number of corrections is necessary in interpreting data on inner shell ionization to ensure that they refer to excitation under true thin target conditions. Approximate corrections are less troublesome to make than in the case of inner shell ionization by electrons because in many cases the X-rays produced are not appreciably absorbed in the thin layer of target which the positive ions are able to penetrate.

Let dn_K be the number of *K* electrons ejected per incident positive ion in traversing a layer of thickness dx of the target.

$$\text{Then} \quad dn_K = 2N Q_i(E) dx = 2N Q_i(E) \frac{dx}{dE} dE,$$

where N is the number of particles per unit volume of the target and Q_i the cross-section for ejection of a *K* electron. The quantity usually measured is proportional to

$$n_K = \int_{E=E_i}^E Q_i \frac{dx}{dE} dE,$$

so that

$$Q_i \propto \frac{dn_K}{dE} \frac{dE}{dx}.$$

Knowing dE/dx from stopping power data for charged atomic particles† the form of variation of the true inner shell ionization cross-section with energy of the incident particles may be obtained.

† See, for example, Bethe and Livingstone, *Rev. Mod. Phys.* **9** (1937), 245; Bätznner, *Ann. der Physik*, **25** (1936), 233.

In the measurements of Bothe and Franz on X-radiation excited by alpha particles, the incident energy was varied by interposing absorbing foils of various thicknesses between the alpha-particle source and the target, so that the inner shell ionization was measured as a function of the residual range of the particles. The true form of variation with positive ion energy could then be obtained by differentiating the experimental curve.

Measurements have also been made for K , L , and M shell ionization produced by A^{++} ions of energy up to 420 keV and by Hg^{++} ions of energy up to 2.38 MeV in a number of materials.

6. Inelastic collisions—description and discussion of experimental results

6.1. General discussion

The essential difference which characterizes excitation and ionization of atoms by positive ions as distinct from that by electrons lies in the relation of the velocity of relative motion v to that u of the atomic electrons concerned in the particular excitation process. § Excitation by electron impact is not possible unless $v^2/u^2 > 1$, but may be energetically possible by positive ions even if $v^2/u^2 \ll 1$. In discussing inelastic collisions involving atomic systems we therefore distinguish two regions in which $v^2/u^2 \gg$ and $\ll 1$ respectively.

In the high-velocity region the behaviour is very similar indeed to that for electrons of the same velocity. Born's approximation may be employed|| to give the same formulae as in Chap. III, § 3.5. Thus for an optically allowed excitation this cross-section falls off as $v^{-2} \log \alpha v$ and for one which is optically forbidden, but not involving change of multiplicity, as v^{-2} . The maximum cross-section occurs when v^2/u^2 is somewhat greater than, but of order, unity and is of the same order of magnitude as that for an electron. Strong experimental evidence in support of these conclusions may be adduced from the accuracy with which the Bethe formula for the stopping power of matter for fast particles represents the observed data.††

Although there is no analogue of charge exchange for collisions of electrons with atoms it is still true that Born's approximation gives the correct behaviour of the charge exchange cross-section when $v^2/u^2 \gg 1$.

† Tanaka and Nonaka, *Proc. Phys. Mod. Soc. Japan*, **20** (1938), 33.

‡ Coates, *Phys. Rev.* **46** (1934), 542.

§ Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. XI, § 4.4.

|| *Ibid.*, Chap. XII, § 2.

†† *Ibid.*, § 2.1.

Under these conditions it is found that the cross-section falls off very rapidly with increase of relative velocity. Thus for capture of a $1s$ electron into a $1s$ state it falls as v^{-12} .† The maximum cross-section is of the order of the gas-kinetic provided there are no selection rules operating to reduce it.

The low-velocity region, for which $v^2/u^2 \ll 1$, is the near-adiabatic region which has already been discussed in Chap. VII, § 10. It was shown there that the probability of a transition involving an energy change ΔE in the internal motion in a collision will be very small if

$$a|\Delta E|/hv \gg 1,$$

a/v being the time of collision so that a is of the order of the gas-kinetic radius for the collision. It follows that, in this region, the cross-section for different processes involving two systems A and B should fall off quite rapidly with increase of $a|\Delta E|/hv$. The behaviour should resemble that illustrated in Fig. 199(b) of Chapter VII. Even if the particular systems concerned are not quite the same we might expect that this result would have some general validity. It could not be expected to hold universally as the length a is not well defined and will depend in a rather detailed way on the nature of the colliding systems.

For a particular process the cross-section should therefore rise as $a|\Delta E|/hv$ decreases up to a rather flat maximum of the order of the gas-kinetic cross-section when $a|\Delta E|/hv$ is of order unity, the velocity of relative motion being then comparable with the velocity of the atomic electrons concerned in the transition. It then falls at a rate determined by the nature of the process, being most rapid for charge exchange collisions. This picture is used in considering the stopping in gases of ions which begin with a multiple charge. For this purpose it is necessary to know approximately how the ionic charge will vary due to electron capture from the gas atom as it slows down. It is a good approximation to suppose that the velocity of the most weakly bound electrons in the ion at any point of the path is equal to the relative velocity of the ion through the gas. Slower electrons will be rapidly swept off by ionization, while electron capture will be quite effective until the velocity of relative motion is appreciably greater than that of the captured electron. This approach is the basis, for example, of the theoretical investigation of the stopping power of gases for nuclear fission fragments.‡

The detailed discussion of the high-velocity region is beyond the scope of the present book so that we shall be concerned below mainly with

† Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. XII, § 2.2.

‡ Ibid., § 2.3.

collisions within the near-adiabatic region except for cases in which $|\Delta E|$ is so small that the near-adiabatic region does not extend to high energies. There are also the cases of the charge exchange involving exact resonance such as



in which there is no near-adiabatic region and the cross-section theoretically falls as the time of collision decreases, i.e. there is a monotonic decrease with increase of velocity of relative motion.

6.11. The method of perturbed stationary states. It is not possible to give any general rules concerning the detailed variation of the cross-section with $a|\Delta E|/v$ in the near-adiabatic region. We should expect, however, that it would behave rather like $\exp(-Ca|\Delta E|/v)$, C being a constant. The most suitable theoretical method for calculating cross-sections in the near-adiabatic region, apart from those discussed in Chap. VII, § 10, which are suitable for gas-kinetic collisions and small $|\Delta E|$, is that known as the perturbed stationary state method.† This method makes explicit allowance for the gradual nature of the collision in the near-adiabatic region by treating the kinetic energy of relative motion as a perturbation. If the collision took place infinitely slowly the wave function of the atomic electrons could adjust itself to the very slow rate of change of nuclear separation without any transition occurring. This wave function may be calculated for any given nuclear separation by regarding the nuclei as at rest at that separation (Chap. IV, § 4.1). The fact that the collision does take place with finite, although slow, speed leads to a finite probability of a transition which may thus be regarded as due to the perturbing influence of the kinetic energy of relative motion.

Following the usual perturbation theory of quantum mechanics, the probability of a transition from state i to state f due to a perturbation energy U is proportional to $|U_{if}|^2$, where U_{if} is the average of U over the wave functions of the initial and final states. In the case concerned U is the kinetic energy T of relative nuclear motion which, in quantum theory, is represented by the operator $-\hbar^2 \nabla^2 / 2M$,

where

$$\nabla^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

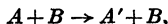
in terms of the relative coordinates (X, Y, Z) , M being the reduced mass. Hence the chance of a transition per collision will be proportional to

$$\left| \iint F_i(\mathbf{R}) \psi_i(\mathbf{r}, R) \nabla_{\mathbf{R}}^2 \{ \psi_f^*(\mathbf{r}, R) F_f^*(\mathbf{R}) \} d\mathbf{r} d\tau_R \right|^2. \quad (14)$$

$\psi_i(\mathbf{r}, R)$, $\psi_f(\mathbf{r}, R)$ are the initial and final electronic wave functions at nuclear separation R , $\mathbf{r}$ referring to the electronic coordinates relative to the centre of

† Ibid., Chap. VIII, § 7.

mass of the two nuclei. These functions are distinguished by the limits to which they tend as $R \rightarrow \infty$ infinitely slowly. Thus, if the reaction is



ψ_i tends to the product of wave functions for the normal states of A and B , and ψ_f to the product of the wave function of the normal state of B and the appropriate excited state of A . F_i and F_f are the respective wave functions of the initial and

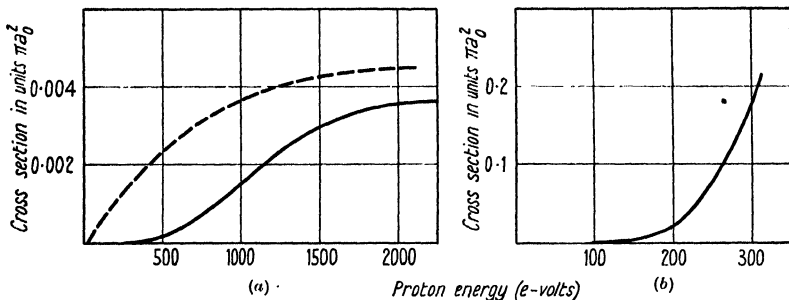


FIG. 224. (a) Excitation curve for the $1P$ state of helium by protons calculated by Massey and Smith. The full curve shows results obtained using the method of perturbed stationary states. The broken curve was calculated using Born's approximation. (b) Cross-section for charge exchange of protons in helium, calculated using the perturbed stationary states method.

final relative motions of the colliding systems and may be represented for present purposes by plane waves $e^{i\mathbf{k}\cdot\mathbf{R}}$, $e^{i\mathbf{k}'\cdot\mathbf{R}}$, $\mathbf{k}$, $\mathbf{k}'$ being the initial and final momenta of relative motion.

It is clear then that the cross-section is determined by the rate of change of the wave function ψ_f (or ψ_i as the integral (14) may readily be transformed to one in which i and f are interchanged) with nuclear separation. If this rate of change is very small it can be shown that (14) reduces to Born's approximation.† When it is not, a pronounced near-adiabatic region appears at low energies of relative motion (see Fig. 225).

This method has been applied in detail to only three reactions: the excitation of the 2^1P state of helium by protons,‡ the capture of electrons from helium atoms by protons,‡ and the excitation of lithium by α -particles.§ Figs. 224 and 225 illustrate the nature of the results. Comparison with the predictions of Born's approximation shows that the latter greatly overestimates the cross-section in the near-adiabatic region. It is important to remember that if the incident ion produces only a small perturbation in the wave functions of the atomic electrons as it approaches, Born's approximation will give nearly the same result as

† Mott and Massey, *The Theory of Atomic Collisions*, 2nd edition, Chap. VIII, § 7.

‡ Massey and Smith, *Proc. Roy. Soc. A*, **142** (1933), 142.

§ Frame, *Proc. Cambridge Phil. Soc.* **33** (1937), 115.

the perturbed stationary states method for excitation or ionization of these electrons. Thus the perturbation of the K electrons of an atom even as light as oxygen by an incident proton will always be small owing to the relatively small charge on the latter. Born's approximation should therefore give satisfactory results for the cross-section for ionization of a

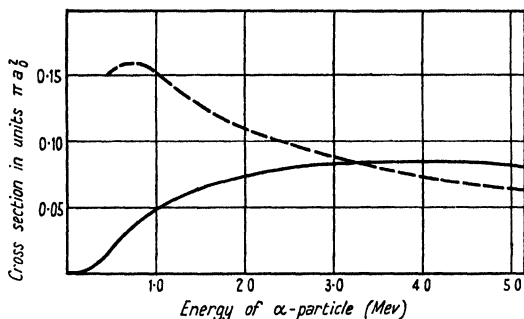


FIG. 225. Calculated cross-section for excitation of the $(1s)^2 3p$ level of lithium by α -particles.

— using perturbed stationary states method; - - - using Born's approximation.

K electron by a proton even though the condition $u^2/v^2 \ll 1$ is not satisfied (see § 6.5).

The foregoing general considerations cannot be expected to agree in detail with the wide variety of possibilities arising in the passage of beams of energetic ions or atoms through gases. A number of complications arise when an attempt is made to allow for the presence of many electrons with various binding energies in the colliding systems. Many regularities of behaviour which have been observed still defy explanation, but there is no doubt of the general correctness of the ideas we have been discussing. It would be of great value if it were possible to set up empirical rules for determining the variation of a cross-section with relative velocity and resonance defect ΔE which could be used in the region where $a|\Delta E|/h\nu$ is very large. At present there is no means of estimating the magnitude of a cross-section on this region where it is so small as to make experimental investigation extremely difficult.

We shall now discuss the experimental information considering the internal consistency of the observed data as well as the relation to theory, and noting all the empirical regularities which have been found. In view of their comparative simplicity we commence by considering collisions in which the colliding system is either helium or atomic hydrogen, neutral or ionized.

6.2. Collisions involving hydrogen and helium only

A number of the possible inelastic collisions which can occur between these systems are listed in Table III with the corresponding energy defect ΔE , defined as the energy which must be transferred from the

TABLE III
Typical Inelastic Collisions involving Helium and/or Hydrogen Atoms or Ions

Reaction	Description	ΔE (eV)	$E_a^\dagger$ (eV)	References to experimental work
(a) $\text{He}^+ + \text{He} \rightarrow \text{He} + \text{He}^+$	Charge exchange	0	0	Rudnick (2), Smith (5), Rostagni (8), Wolf (10), Meyer (12), Keene (14)
(b) $\text{H}^+ + \text{He} \rightarrow \text{He}^+ + \text{H}$	„	10.9	500	Goldmann (1), Smith (5), Meyer (11), Keene (14)
(c) $\text{H}^+ + \text{He} \rightarrow \text{H}^+ + \text{He}'$	Excitation	21.1	1,700	Döpel (4)
(d) $\text{H} + \text{He} \rightarrow \text{H} + \text{He}'$	„	21.1	1,700	Döpel (4), Hanle and Junkelmann (9)
(e) $\text{H} + \text{He} \rightarrow \text{H}' + \text{He}$	„	10.2	400	Döpel (4), Hanle and Junkelmann (9)
(f) $\text{He} + \text{He} \rightarrow \text{He}' + \text{He}$	„	21.1	10,000	Maurer (7)
(g) $\text{He}^+ + \text{He} \rightarrow \text{He}^+ + \text{He}'$	„	21.1	10,000	Hanle and Larche (4)
(h) $\text{He}^+ + \text{He} \rightarrow \text{He}^{++} + \text{He}$	„	40.8	40,000	Hanle and Larche (4)
(i) $\text{H}^+ + \text{He} \rightarrow \text{He}^+ + \text{H}^+ + e$	Ionization	24.5	2,500	Goldmann (1), Keene (14)
(j) $\text{H} + \text{He} \rightarrow \text{H}^+ + \text{He} + e$	„	13.5	700	„
(k) $\text{He}^+ + \text{He} \rightarrow \text{He}^+ + \text{He}^+ + e$	„	24.5	15,000	Brasefield (3), Ros- tagni (8), Wolf (10), Keene (14)
(l) $\text{He} + \text{He} \rightarrow \text{He}^+ + \text{He} + e$	„	24.5	15,000	Brasefield (3), Meyer (12), Berry (13)
(m) $\text{He}^+ + \text{He} \rightarrow \text{He}^{++} + \text{He} + e$	„	29.6	22,000	Rudnick (2), Ros- tagni (8), Meyer (12)

$^\dagger E_a$ is the energy of the incident particle that makes a $\Delta E/h\nu = 1$.

References

1. *Ann. der Physik*, **10** (1931), 460.
2. *Phys. Rev.* **38** (1931), 1342.
3. *Ibid.* **42** (1932), 11.
4. *Ann. der Physik*, **16** (1933), 1.
5. *Proc. Cambridge Phil. Soc.* **30** (1934), 514.
6. *Nuovo Cimento* **12** (1935), 134.
7. *Zeits. f. Phys.* **96** (1935), 489.
8. *Nuovo Cimento*, **13** (1936), 389.
9. *Phys. Zeits.* **37** (1936), 593; **38** (1937), 995; *Zeits. f. Phys.* **107** (1937), 561.
10. *Ann. der Physik*, **29** (1937), 33.
11. *Ibid.* **30** (1937), 635.
12. *Ibid.* **37** (1940), 69.
13. *Phys. Rev.* **62** (1942), 378.
14. *Phil. Mag.* **40** (1949), 369.

relative translation in order that the reaction can proceed. Values are also given of the energy E_a of the incident particle in order that

$$a|\Delta E|/h\nu = 1,$$

a being taken as 10^{-8} cm. The cross-section for the particular process should be small for energies much smaller than E_a .

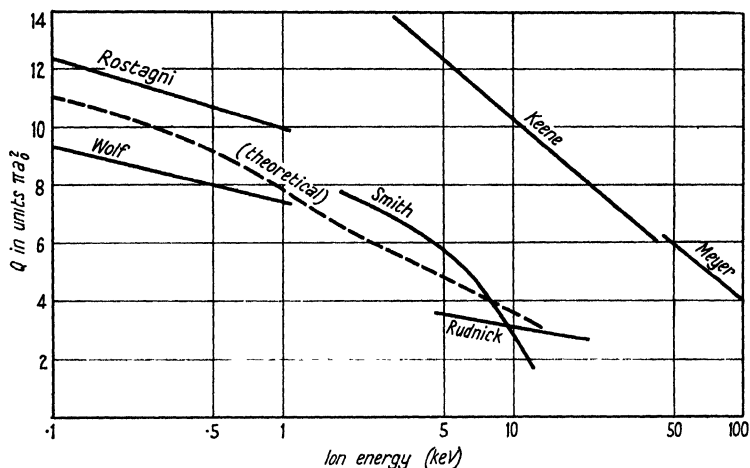


FIG. 226. Observed cross-sections for charge exchange of He^+ in He compared with calculated values.

6.21. Charge exchange and ionization. We consider first the simplest of all the reactions, the resonant charge transfer collision

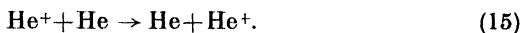
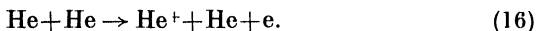


Fig. 226 illustrates the various measurements which have been made of the cross-section for this process as a function of relative velocity. They cover an extensive energy range from 20 to 100,000 eV. Although the measurements by different observers do not agree within a factor of 2 where they cover overlapping energy ranges, there is general agreement that the cross-section is quite high and falls slowly and steadily as the relative energy increases from 20 eV. This is what would be expected from the forgoing considerations. The energy discrepancy is zero, there is no near-adiabatic region, and the cross-section increases with the time of collision. It may be calculated simply by extending to higher energies the method adopted for the calculation of the mobility of helium atoms in helium in which only gas-kinetic energies are involved

(Chap. VII, § 6.52). This has been done by Massey and Smith for the energy range from 500 to 12,000 eV and by Dallaporta and Bonfiglioli† in the energy range from 10 to 1,000 eV. These results are included in Fig. 226. In view of the rather rough estimates of the interaction between helium ions and atoms which they employed and the uncertainties in the experimental results, the agreement is seen to be quite good. On the other hand, it is noteworthy that both Rostagni and Wolf find that the cross-section begins to decrease as the relative energy falls below 20 eV. This has not been confirmed in the later measurements of Hasted‡ and appears most unlikely on theoretical grounds.

To contrast the behaviour in a very similar collision in which the energy defect ΔE is quite high it is only necessary to turn to the data available concerning the cross-section for ionization of helium atoms by helium ion impact. Fig. 227 illustrates the measurements of this cross-section as a function of energy made by Rostagni and by Keene. Again the agreement between the observations is only moderate, but it will be noted that the cross-section is considerably smaller than for charge exchange and is rising as the velocity of relative motion increases. Furthermore, as Rostagni's measurements show, the cross-section becomes very small at impact energies of 100 eV or less. This is in general agreement with the picture of nearly adiabatic collisions. Very similar behaviour would be expected for ionization by impact with neutral helium atoms.

Fig. 227 illustrates also the results of measurements, by different observers, of the cross-section for the process



The absolute value of the cross-section is very difficult to measure in these cases for the reasons discussed in § 3.2, namely the difficulty of determining the incident flux of neutral helium atoms. It will be seen from Fig. 227 that there is indeed a considerable spread in the absolute values obtained by different observers. As far as the observations of Rostagni and of Rudnick are concerned, a likely source of the discrepancy is the difference in the methods of measuring the incident flux, the first author using secondary emission (see § 5.11) and the other a thermocouple for this purpose. Furthermore, in Rudnick's measurements (§ 5.14) only the ionization of the incident beam itself was measured. In contrast with this, Rostagni with his method (§ 5.121) will have measured primarily the ionization of the target atoms. This would give

† *Comm. Pontificia Acad. Scient.* **7** (1943), 141. ‡ *Proc. Roy. Soc. A*, **205** (1951), 421.

equivalent results in this case but, as Rostagni may also have included, in addition, some ionization of the incident beam, his cross-sections might be expected to be larger, for this reason, than those found by Batho and Rudnick. Berry's experiments differed in principle from either of the others in the use of the space-charge method of detection (see § 5.22).

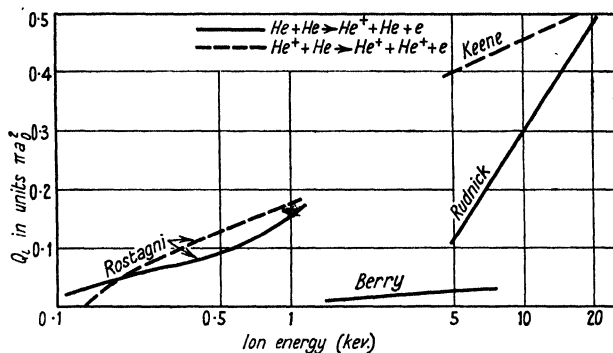
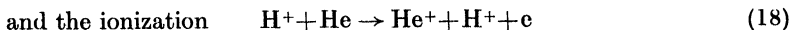


FIG. 227. Measured ionization cross-sections for helium atoms and ions in helium. The full curves refer to ionization by helium atoms, the broken curves to ionization by helium ions.

Allowing for the rather wide range of experimental values it appears that the cross-section for the process (16) is very similar to that for (15), as may be seen from Fig. 227, in which Keene's observed cross-section for ionization by He^+ has been included. This is particularly true if only small weight is given to Berry's measurements. A partial justification for this is provided by the rather unlikely results he obtained by the same method for ionization of argon by neutral argon beams (see § 6.4 and Fig. 233).

The same features characterize the reactions involving protons. Both the charge exchange process



involve considerable energy defects. The first is considerably smaller than for ionization, so we would expect the cross-section for it to rise more rapidly to a flat maximum (at an incident energy of order 500 eV according to column 3 of Table III) than for the second (a maximum at an energy of order 2,500 eV). Keene's results, illustrated in Fig. 228, show that the maximum in the charge exchange case occurs at about 27 keV, while the ionization cross-section is still rising rapidly at 32 kV.

There is qualitative agreement with the predicted relative rate of rise of the cross-sections in the near-adiabatic region. Too much significance should not be attached to the actual numerical value of E_a , the energy of the incident particle that makes a $\Delta E/h\nu$ equal to unity.

Massey and Smith calculated the cross-section for (17) using the

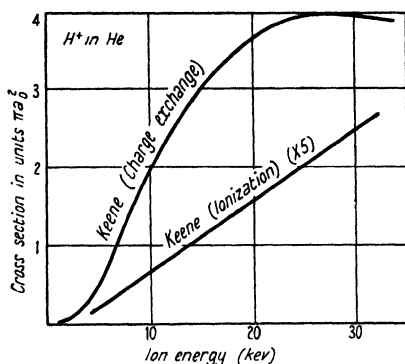


FIG. 228. Charge exchange and ionization cross-sections for protons in helium observed by Keene.

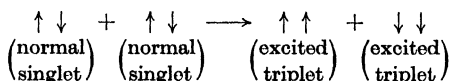
method of perturbed stationary states (§ 6.11) with rather crude approximations for the wave function ψ_i and ψ_f in (14). Their results, which only covered an energy range from 100 to 300 eV, are shown in Fig. 224 (b).

6.22. Excitation. Similar features to those noted above for ionization would be expected in collision reactions leading to excitation. The only additional feature concerns the probability of transitions involving multiplicity changes. Wigner's rule, discussed in Chap. VII, § 8.2, in connexion with gas-kinetic collisions, still applies. We would therefore expect that a proton would be very ineffective in exciting a triplet state of a helium atom from its normal singlet state. This could occur only if an electron spin were reversed. No such restriction would apply to excitation by a hydrogen atom. The presence of the additional electron attached to the proton means that a change of multiplicity of the helium atom may be effected by an exchange of electrons between the colliding atoms. Döpel† has confirmed this argument by showing that the cross-section for excitation of the 3^3P-2^3S line of helium by protons is at most one-tenth of that for excitation by hydrogen atoms.

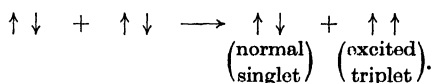
An interesting difference would also be expected to arise between the

† *Ann. der Physik*, **16** (1933), 1.

excitation of helium by helium ions He^+ and by helium atoms He . The effectiveness of the ions in exciting intercombination transitions should be much the same as hydrogen atoms. A collision between two normal helium atoms cannot give rise to excitation of the triplet state of one atom without exciting the other also to a state of the same multiplicity unless an electron spin is reversed. Thus, diagrammatically, in which electron spins are indicated by arrows, electron exchange can lead to the reaction



but not to



The energy required to be transferred from that of relative motion to produce triplet excitation in these encounters should therefore be about twice that for singlet excitation. The near-adiabatic region should therefore extend to higher energies of relative motion in the former than in the latter case. Maurer† has attempted to observe this effect, but his apparatus was not sufficiently sensitive for him to detect it.

The rather meagre evidence from excitation experiments supports the interpretation of the collisions as nearly adiabatic in the energy range concerned. Thus Döpel‡ found with his apparatus that he could detect excitation of hydrogen when a beam of hydrogen atoms of 500 eV energy passed through helium but was unable to detect excitation of the helium until the beam energy reached 2,000 eV. Since the energy required for the former excitation is 10 eV while that for the latter is 21 eV, we would expect, following the condition (13), that the latter collisions would be more nearly adiabatic than the former.

Massey and Smith have applied the perturbed stationary states method outlined in § 6.11 to calculate the cross-section for excitation of the 2^1P state of helium by protons. Their results are illustrated in Fig. 225 (a), in which they are compared with the corresponding results given by Born's approximation. No direct observations with which to test these calculations are yet available, but there is good general agreement with Döpel's observations for the excitation of the 4^1P state, as may be seen from Fig. 229 in which a comparison is made with the excitation curve of the same state by electron impact. The nearly adiabatic character of the

† *Zeits. f. Phys.* **96** (1935), 489.

‡ *Loc. cit.*

collisions at least seems to be well confirmed as also the clear distinction of the cross-section-energy curve from that for electrons.

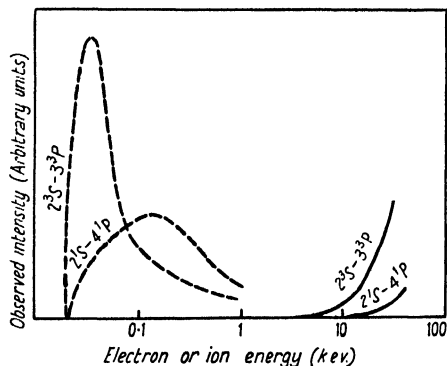


FIG. 229. Observed excitation functions for the helium lines $\lambda 3964$ (2^1S-4^1P) and $\lambda 3888$ (2^3S-3^3P) due to electron and to hydrogen atom impact. The ordinate scale is relative, but is the same for electronic and atomic excitation.

--- electron impact; — H atom impact.

6.3. The experimental data for other atoms—charge exchange

The various charge exchange reactions which have been investigated quantitatively are listed in Table IV, together with the energy defects, the critical energy E_a such that $a\Delta E/h\nu = 1$, and the method used.

The results for cases of exact resonance, illustrated in Fig. 230, are essentially similar to the corresponding results for helium (see Fig. 226). The cross-section increases in going from helium to argon. Although Wolf's measurements for argon do not reproduce in detail the sharp maximum found by Rostagni at low energies, his observed cross-section exhibits a flat maximum near 100 eV incident energy which is equally inexplicable. The more recent, careful measurements of Hasted have failed to show any maximum at low energies.

The observed variation of the cross-section for a particular charge exchange process in which ΔE is finite is frequently found to be of the form expected from the theoretical considerations of § 6.1. It is true that in many cases variations are observed which are not understood. The discrepancies between the results of different observers are such, however, as to raise doubt as to the reality of all of these peculiarities. The divergence between experimental results has already been manifest in the various observations illustrated in Fig. 226. A further illustration

TABLE IV
Charge Exchange Reactions for which Quantitative Data are Available

Reaction	ΔE (eV)	E_a (eV)	References	Reaction	ΔE (eV)	E_a (eV)	References
H ⁺ , He	10.9	500	2, 6, 11, 8	He ⁺ , N ₂	-9.0	1,280	10
H ⁺ , A	2.1	14	2, 8	Li ⁺ , H ₂	10.0	9,700	9
D ⁺ , A	2.1	28	8	Be ⁺ , H ₂	4.2	2,700	16
He ⁺ , He	0	0	3, 6, 7, 10, 15, 19	B ⁺ , H ₂	5.3	6,000	16
He ⁺ , Ne	-3.0	140	10	B ⁺ , H ₂	-11.5	29,000	16
He ⁺ , A	-8.8	900	10	C ⁺ , H ₂	2.3	1,400	10
Li ⁺ , He	19.1	14,000	9	C ⁺ , H ₂	-10.7	31,000	16
Li ⁺ , Ne	-16.1	8,000	9	N ⁺ , H ₂	0.9	280	10
B ⁺ , He	-0.5	32	16	N ⁺ , N ₂	1.1	80	10
C ⁺ , He	0.2	6	16	Ne ⁺ , N ₂	-6.0	3,200	10
N ⁺ , Ne	7.0	4,000	10	Al ⁺ , H ₂	7.6	70,000	16
N ⁺ , A	1.2	80	10	Al ⁺ , H ₂	-5.2	32,000	16
Ne ⁺ , He	3.0	2,700	10	A ⁺ , H ₂	0.3	233	10
Ne ⁺ , Ne	0	0	5, 7, 10	A ⁺ , H ₂	-12.45	128,000	12
Ne ⁺ , Ne	0	0	12	K ⁺ , H ₂	11.1	320,000	9, 16
Ne ⁺ , He	-19.4	45,000	14	Fe ⁺ , H ₂	5.7	160,000	16
Al ⁺ , Ne	5.7	21,000	16	Fe ⁺ , H ₂	-2.6	34,000	16
A ⁺ , A	0	0	5, 7, 10	Fe ⁺ , H ₂	-16.9	1.4 × 10 ⁶	16
A ⁺ , A	-12.1	36,000	14	Cu ⁺ , H ₂	5.9	230,000	16
A ⁺ , A	0	0	12	Cu ⁺ , H ₂	-6.8	300,000	16
K ⁺ , He	20.1	550,000	9, 16	Cu ⁺ , H ₂	-16.0	1.7 × 10 ⁶	16
Fe ⁺ , He	8.3	180,000	16	H ₂ ⁺ , H ₂	0	0	17, 18
Fe ⁺ , He	-6.0	95,000	16	H ₂ ⁺ , N ₂	0.1	0.07	10
Cu ⁺ , He	4.1	56,000	16	H ₂ ⁺ , Ne	0.1	250	10
Cu ⁺ , He	-5.0	80,000	16	H ₂ ⁺ , CCl ₄			17
K ⁺ , Kr	0	0	5	H ₂ ⁺			
Hg ⁺ , Hg	-8.3	85,000	13	C ₂ H ₅ OH			17
H ⁺ , H ₂	1.8	15.8	1, 2, 6, 10, 11, 17, 19	N ₂ ⁺ , A	0.3	0.58	8
				D ₂ ⁺ , A	0.3	1.18	8
H ⁺ , N ₂	2.0	12.8	4	N ₂ ⁺ , H ₂	-0.1	0.93	10
H ⁺ , O ₂	-1.0	3.2	4	N ₂ ⁺ , He	9.0	55,000	10
H ⁺ , CCl ₄			17	N ₂ ⁺ , Ne	6.0	8,000	10
H ⁺			17	N ₂ ⁺ , A	0.2	5.0	10
C ₂ H ₅ OH							

Methods: I. Beam absorption coefficient (§ 5.11).

II. Direct measurement of charge exchange current (§ 5.12).

III. Equilibrium beam concentration method (§ 5.14).

IV. Arnot's method (§ 5.13).

References

1. Bartels, *Ann. der Physik*, **6** (1930), 957 (method III).
2. Goldmann, *ibid.* **10** (1931), 490 (I).
3. Rudnick, *Phys. Rev.* **38** (1931), 1342 (III).
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9. Wolf, *ibid.* **438** (II).
10. Wolf, *ibid.* **30** (1937), 313 (II).
11. Meyer, *ibid.* 635 (III).
12. Wolf, *ibid.* **34** (1939), 341 (II).
13. Arnot and McEwen, *Proc. Roy. Soc. A*, **169** (1939), 437 (IV).
14. Arnot and Hart, *ibid.* **171** (1939), 383 (IV).
15. Meyer, *Ann. der Physik*, **37** (1940), 69 (III).
16. Sherwin, *Phys. Rev.* **57** (1940), 814 (II).
17. Ycarian, *J. Chem. Phys.* **8** (1940), 24.
18. Simons, Francis, Muschultz, and Fryburg, *ibid.* **11** (1943), 316 (II).
19. Keene, *Phil. Mag.* **40** (1949), 369 (II).

is provided in Fig. 231 by comparing the values given by several observers for the cross-section for the process



The general shape which may be synthesized from these data is in agreement with expectation, but there is a considerable spread in the observed values.

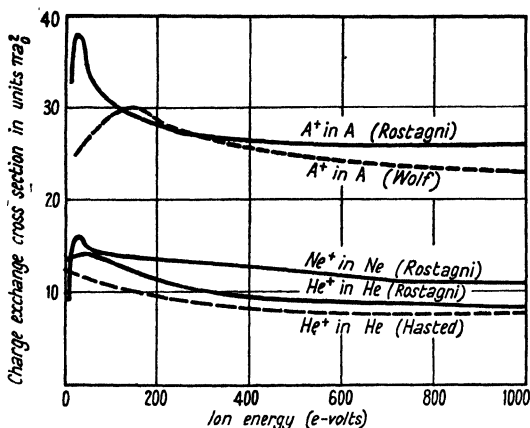


FIG. 230. Charge exchange cross-sections for He, Ne, and A in their own gases, measured by Rostagni, Wolf, and Hasted.

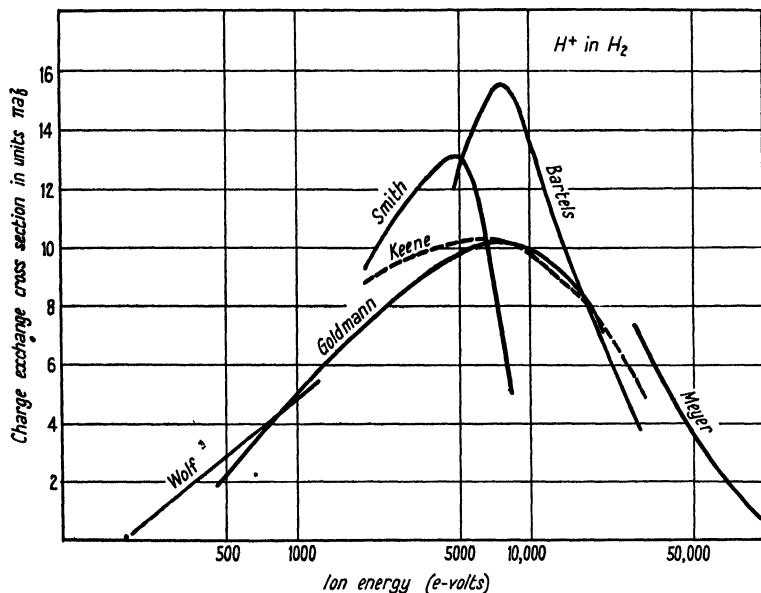


FIG. 231. Charge exchange cross-section for H^+ in H_2 , measured by a number of different observers.

The further analysis of experimental data to test the closeness of the correlation with the discriminating quantity $a|\Delta E|/h\nu$ is hampered by the incompleteness of the available measurements, in particular as regards

variation of the cross-section with relative velocity. To avoid possible complications due to excitation of vibration, etc., it is desirable in the first instance to consider only collisions in which atoms and atomic ions are concerned. For this reason we shall examine first the data obtained by Sherwin for singly and multiply charged metallic ions in helium (see § 5.122).

A number of features of Sherwin's† results are immediately explicable in terms of the near-adiabatic theory. These are as follows.

(a) In the experimental energy range (6–24 keV) charge transfer to B^+ ions was too small to be measured, whereas that for B^{++} corresponded to a cross-section increasing over the energy range from 1.7 to 3.2×10^{-16} cm.² This is clearly due to the fact that for B^+ capture $\Delta E = 16.28$ eV, whereas for B^{++} it is only -0.54 eV, quite close to resonance. In the experimental energy range the adiabatic parameter $a\Delta E/hv$ is therefore $\gg 1$ for the B^+ collisions but $<$ or comparable with 1 for B^{++} . A similar result holds for C^+ ($\Delta E = 13.32$ eV) as against C^{++} ($\Delta E = 0.20$ eV).

(b) The charge exchange cross-section for Fe^+ ($\Delta E = 16.72$ eV) was too small to be measured, that for Fe^{++} ($\Delta E = 8.34$ eV) could just be detected (0.05×10^{-16} cm.²) at the highest energy (18 keV), while that for Fe^{+++} ($\Delta E = -6.02$ eV) was quite large and was falling with increasing energy. The first two results are as expected, and it is likely that for Fe^{+++} there exists an excited state into which capture can occur with nearly exact resonance so that at the energies concerned the near-adiabatic region has been passed and the cross-section is falling rapidly with increasing energy (see § 6.1). For copper a similar result is obtained. Here $\Delta E = 16.9$, 4.10 , and -5.0 for Cu^+ , Cu^{++} , Cu^{+++} respectively. For Cu^{+++} the cross-section decreases only very slightly with energy over the experimental range (6–18 keV). Again it may be that capture takes place to an excited state of Cu^{++} .

It is difficult in some cases, however, to interpret Sherwin's curves in terms of the near-adiabatic theory.

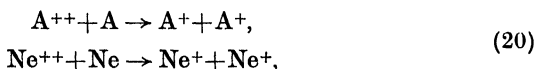
The results of Hasted† provide striking evidence for the usefulness of the near-adiabatic theory in interpreting the charge exchange cross-section, Q . Fig. 232 (b) shows the measured variation of Q with incident ion energy for H^+ in Kr, H^+ in Xe, D^+ in Xe, H^+ in A and D^+ in A. The values of E_a for these cases are respectively, 0.41 eV, 7 eV, 14 eV, 14 eV, and 28 eV, while the corresponding maximum cross-sections occur for ion energies of 100 eV, 150 eV, 400 eV, 850 eV and $2,000$ eV.

The general impression from this analysis of the results of Sherwin

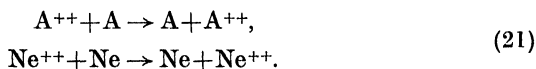
† Loc. cit.

and of Hasted is that the adiabatic parameter $a\Delta E/hv$ is very useful in considering the relative probabilities of collisions between the same or a similar pair of systems. It is no longer so useful in comparing the probabilities of two collision processes which involve substantially different systems. This is probably due to the difficulty of estimating the effective collision range a which is probably a function of v in any actual case.

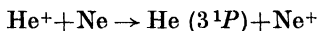
Rather similar conclusions are derived from the study of other evidence on charge exchange between atomic systems. A further interesting example in which the adiabatic parameter may be used effectively concerns reactions between doubly charged rare gas ions and atoms of the same kind. Arnot and Hart† measured the cross-sections for the processes



for which the energy defects are 12.1 and 19.4 eV respectively. For ion energies of 400 eV they found the small values 3.27×10^{-17} cm.² and 7.0×10^{-18} cm.² respectively. On the other hand, Wolf‡ investigated the charge exchange cross-sections for A^{++} in A and Ne^{++} in Ne at the same energies. He obtained the much larger cross-sections 10^{-15} and 3×10^{-16} cm.² respectively, presumably because his measurements applied to the exact resonance collisions



A further example of the influence of the quantity on the charge exchange cross-section for processes involving the same atomic systems is provided by the measurements of Trittelwitz§ on the excitation of the He line $\lambda 5016$ (2^1S-3^1P) in collisions between He^+ ions and Ne atoms. This line must arise from He atoms left in the 3^1P state of excitation energy 23.04 eV after the charge exchange process



for which the energy defect ΔE is 20.04 eV. The cross-section for the process observed by Trittelwitz was 2.8×10^{-19} cm.² for He^+ ions of energy 4,000 eV.

On the other hand, Wolf† has measured the cross-section for the process



for which ΔE is -3.0 eV. Extrapolating his measurements to incident ion energies of 4,000 eV gives for the cross-section 2.8×10^{-16} cm.²,

† Loc. cit.

‡ *Ann. der Physik*, **34** (1939), 341.

§ Ibid. **40** (1941), 131.

about 1,000 times larger than for the process in which excited He is formed.†

As far as the variation of charge exchange cross-section with relative energy is concerned, in many experiments such as those of Sherwin the cross-section increases monotonically with energy (apart from the two exceptions noted above). This is by no means always the case, however, as may be seen by reference to Fig. 232, which illustrates observed

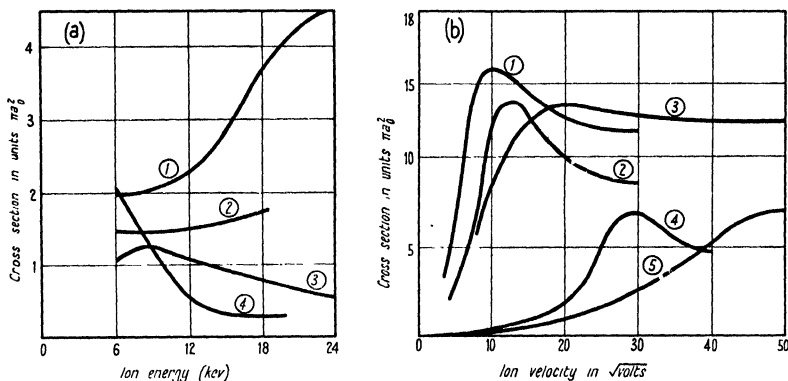


FIG. 232. (a) Sherwin's measurements of charge exchange cross-sections.

(1) C^+ in H_2 (1,400 eV) (2) Fe^+ in H_2 (34,000 eV) (3) Al^+ in H_2 (70,000 eV)
(4) Fe^+ in He ($\times \frac{1}{5}$) (95,000 eV).

(b) Hasted's measurements of charge exchange cross-sections for atomic ions in monatomic gases. These curves illustrate the dependence of the ion velocity at which the cross-section is a maximum on the parameter E_u .

(1) H^+ in Kr (0.41 eV); (2) H^+ in Xe (7 eV); (3) D^+ in Xe (14 eV);
(4) H^+ in A (14 eV); (5) D^+ in A (28 eV).

variations of cross-section with relative energy for a number of cases. As a rough guide, the energy E_u for which the adiabatic parameter $a|\Delta E|/\hbar v$ is equal to unity with $a = 10^{-8}$ cm. is indicated for each.

It is clear that much remains to be done before a clear understanding of all the important factors influencing the chance of charge exchange in a collision has been obtained. With present knowledge it is out of the question to predict the order of magnitude of a cross-section well within the near-adiabatic region. All that can be said is that it will be small compared with the gas-kinetic cross-section. A systematic experimental study of the magnitude of the cross-section for a wide variety of collisions

† A similar effect was observed by Maurer and Mehnert (*Zeits. f. Phys.* **106** (1937), 453) for a charge exchange process between Na^+ ions and He atoms in which excited Na atoms were formed.

between atoms and atomic ions, covering the widest possible range of relative energies, is clearly required to assist in the establishment of a sufficiently comprehensive theory.

6.4. *The experimental evidence for other atoms—ionization*

Table V summarizes the experimental data available on cross-sections for ionization of outer shells of atoms by positive ions and neutral atoms. Apart from these measurements there exists a great body of data concerning so-called threshold potentials for ionization of atoms by heavy particles. It is difficult to see what significance can be attached to such observations. There is no definite threshold potential below which the chance of ionization vanishes apart from the usual ionization potential. For positive ions, however, the cross-section is very small indeed up to energies considerably in excess of the ionization energy. With a particular apparatus it will therefore be impossible to detect the ionization produced until the beam energy attains a value considerably in excess of the true threshold. The apparent threshold energy will thus be determined by the sensitivity and power of discrimination of the particular apparatus employed and has no absolute significance. Comparison of apparent thresholds for different ionization processes measured with the *same* apparatus may sometimes be useful as an indication of the extent to which the particular process approaches adiabatic conditions at the beam energy concerned, but little meaning attaches to comparison of results for different processes obtained with different apparatus.

In general the observed ionization cross-section behaves as anticipated. Over the energy range covered by the observations it is still increasing and is usually still small compared with the gas-kinetic value.

Fig. 233 illustrates the observed cross-sections for ionization of rare gas atoms by collision with their own ions. For each case the variation of the cross-section with relative velocity is as expected. On the other hand, the rate of rise for argon seems to be relatively too great compared with that for helium. Reference to column 3 of Table V shows that the near-adiabatic region should extend over an energy range about four times greater for argon than for helium. It is quite clear, however, that this range is much smaller for argon. The significance of this is not yet understood.

A similar result is found from measurements of the ionization of rare gas atoms by beams of the same atoms, as illustrated in Fig. 233. For the same reasons as those pointed out in § 6.21 in connexion with ionization of helium atoms by beams of the same atoms, results of different observers do not agree very well. In contrast to both the other observers Berry

TABLE V

Available Data on Ionization by Neutral and Ionized Atomic and Molecular Beams

Reaction	ΔE (eV)	E_a (keV)	References	Reaction	ΔE (eV)	E_a (keV)	References
H ⁺ , He	24.56	2.35	8	Cu ⁺⁺ , He	24.56	2,000	23
H ⁺ , A	15.75	0.78	8	Cu ⁺⁺⁺ , He	24.56	2,000	23
He, He	24.56	15.0	5, 6, 13, 24, 27	Kr, Kr	14.00	97.5	7
He ⁺ , He	24.56	15.0	5, 6, 15, 17, 24, 28	Rb ⁺ , Ne	21.56	580	4, 9
Li ⁺ , Ne	21.56	13.7	4, 9	Rb ⁺ , A	15.75	186	4, 9
Li ⁺ , A	15.75	7.1	4, 9	Rb ⁺ , Kr	14.00	97.5	4
Li ⁺ , Kr	14.0	5.6	4	Rb ⁺ , Xe	12.13	68.2	4
Li ⁺ , Xe	12.1	4.3	4	Cs ⁺ , Ne	21.56	1,500	4, 9
Be ⁺ , He	24.56	55	23	Cs ⁺ , A	15.75	400	4, 9
B ⁺ , He	24.56	76	23	Cs ⁺ , Kr	14.00	195	4
B ⁺⁺ , He	24.56	76	23	Cs ⁺ , Xe	12.13	116	4
C ⁺ , He	24.56	90	23	H ⁺ , H ₂	15.4	1.15	8
C ⁺⁺ , He	24.56	90	23	H ⁺ , CCl ₄			25
Ne, Ne	21.56	58	6, 7, 17, 19	H ⁺ , C ₂ H ₅ OH			25
Ne ⁺ , Ne	21.56	58	6	He, H ₂	15.4	11	24, 25
Na ⁺ , Ne	21.56	74	4, 9	He ⁺ , H ₂	15.4	11	24
Na ⁺ , A	15.75	31	4, 9	Be ⁺ , H ₂	15.4	35	23
Na ⁺ , Kr	14.00	20	4	B ⁺ , H ₂	15.4	51	23
Na ⁺ , Xe	12.13	15	4	B ⁺⁺ , H ₂	15.4	51	23
Mg ⁺⁺ , Ne	21.56	77	14	C ⁺ , H ₂	15.4	64	23
Mg ⁺⁺ , A	15.75	77	14	C ⁺⁺ , H ₂	15.4	64	23
Al ⁺ , He	24.56	441	23	Al ⁺ , H ₂	15.4	280	23
A, Ne	21.56	175	19	A ⁺ , H ₂	15.4	280	16
A, A	15.75	62.1	6, 7, 17, 26, 27	K ⁺ , H ₂	15.4	620	10, 23
A ⁺ , A	15.75	62.1	6, 17, 21	K ⁺ , CO			23
A ⁺⁺ , A	15.75	62.1	22	Fe ⁺ , H ₂	15.4	1,190	10
A, Kr	14.00	36	19	Fe ⁺⁺ , H ₂	15.4	1,190	23
A, Xe	12.13	25	19	Fe ⁺⁺⁺ , H ₂	15.4	1,190	23
K ⁺ , He	24.56	260	2, 10, 23	Cu ⁺ , H ₂	15.4	1,550	23
K ⁺ , Ne	21.56	200	2, 4, 9, 10	Cu ⁺⁺ , H ₂	15.4	1,550	23
K ⁺ , A	15.75	62.1	1, 3, 4, 9, 10, 11	Cu ⁺⁺⁺ , H ₂	15.4	1,550	23
K ⁺ , Kr	14.00	36.0	3, 4	H ₂ ⁺ , CCl ₄			21, 25, 27
K ⁺ , Xe	12.13	25	3, 4	H ₂ ⁺ , H ₂	15.4	2.0	25
K ⁺ , Hg	10.38	6	10	C ₂ H ₅ OH			25
Fe ⁺ , He	24.56	1,600	23	H ₂ ⁺ , N ₂	15.6	1.6	16
Fe ⁺ , He	24.56	1,600	23	H ₂ ⁺ , A	15.75	1.6	16
Fe ⁺⁺ , He	24.56	1,600	23	N ₂ ⁺ , N ₂	15.6	42	26, 27
Fe ⁺⁺⁺ , He	24.56	1,600	23	N ₂ ⁺ , N ₂	15.6	42	21, 26
Cu ⁺ , He	24.56	2,000	23	N ₂ ⁺ , A	15.75	37	16

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- Berry, *ibid.* **62** (1942), 378.
- Keene, *Phil. Mag.* **40** (1949), 369.

finds an ionization cross-section for argon decreasing with increase of relative velocity in the energy range from 1 to 5 keV, a most unlikely result. Despite the disagreement in absolute magnitude between the

cross-sections observed by Rostagni and by Batho, their results agree in giving cross-sections with consistent variation with relative velocity. Rostagni's results reveal the same discrepancy with theory as to the relative extent of the near-adiabatic region in argon as compared with helium.

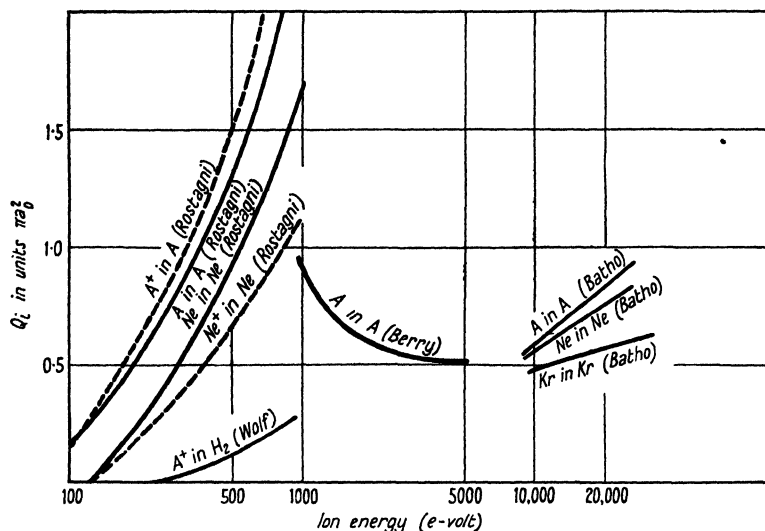


FIG. 233. Observed cross-sections for ionization of A, Ne, and Kr by ions and neutral atoms of A, Ne, and Kr and of H_2 by A^+ ions.

A curious feature of the observed results is that ionization seems to be especially effective when the colliding particles are of nearly the same mass.† Thus argon ions seem to be much more effective in ionizing argon atoms than, say, hydrogen molecules (see Fig. 233). In case this should be regarded as arising in some way when the colliding systems are the same, attention may be drawn to the observations of Frische‡ on ionization by potassium ions (Fig. 234). Here again the effectiveness of ionization of argon atoms as compared with Ne, He, and especially H_2 is very marked. Since ΔE for ionization of H_2 is 15.4 eV as compared with 15.75 for A, this apparent selectivity is not explicable in terms of the usual theoretical considerations. Further evidence in favour of the effect is provided by the observations of Beeck§ and of Varney|| on the apparent threshold potentials, obtained in their respective experiments, for

† Beeck and Mouzon, *Ann. der Physik*, **11** (1931), 737, 858.

‡ *Phys. Rev.* **43** (1933), 160.

§ *Ann. der Physik*, **6** (1930), 1001.

|| *Phys. Rev.* **50** (1936), 159.

ionization of rare gas atoms by alkali metal ions. Thus for Cs^+ the lowest threshold potential was obtained for Xe and for Rb^+ with Kr. With K^+ the results were not so definite. Although in this case the threshold for ionization of A was much lower than for He, Ne, or Xe, it was slightly higher than for Kr. For Na^+ and Li^+ insufficient data were obtained to test the hypothesis. Until further evidence is forthcoming the correlation must still be regarded as suggestive but unproven. No theoretical explanation has been forthcoming.

It is clear that much remains to be done both by experiment and theory

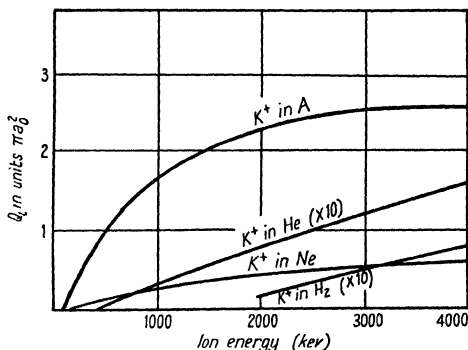


FIG. 234. Cross-sections for ionization of A, He, Ne, and H_2 by K^+ ions measured by Frischo.

before a satisfactory comprehension of all the major factors influencing the magnitude of the cross-section for an ionization for energies of relative motion within the near-adiabatic region is established.

6.5. The experimental evidence for other atoms—excitation†

6.51. *Excitation functions.* Observations have been made of optical excitation functions of different atoms due to beams of ions and neutral atoms in the following cases. In each case the incident particle is given before the target atom.

(H, He) ^(2,15)	(H ⁺ , He) ⁽²⁾	(H, A) ^(7,10,11,12,15)
(D, A) ^(7,11,12)	(H, Hg) ⁽⁶⁾	(H ⁺ , Hg) ⁽⁶⁾
(He, He) ^(4,15)	(He ⁺ , He) ⁽¹¹⁾	(He ⁺ , Ne) ⁽¹⁶⁾
(He, A) ⁽¹⁵⁾	(Ne ⁺ , Ne) ⁽¹⁾	(Ne, Ne) ⁽¹⁵⁾
(A ⁺ , A) ^(1,15)	(Hg ⁺ , Hg) ⁽¹⁴⁾	
{(Li ⁺ , He), (Na ⁺ , He), (K ⁺ , He), (Rb ⁺ , He), (Cs ⁺ , He)} ^(7,8,9,13)		
(Li ⁺ , Hg) ⁽³⁾	(Na ⁺ , Hg) ⁽³⁾	(K ⁺ , Hg) ⁽³⁾
(Rb ⁺ , Hg) ⁽³⁾	(Cs ⁺ , Hg) ⁽³⁾	

† An excellent summary of the position with respect to optical excitation by heavy particles as it was in 1939 was given by Maurer, *Phys. Zeits.* **40** (1939), 161.

References

1. Hanle and Laroche, *Phys. Zeits.* **33** (1932), 884.
2. Döpel, *Ann. der Physik*, **16** (1933), 1.
3. Jones, *Phys. Rev.* **44** (1933), 707.
4. Maurer, *Zeits. f. Phys.* **96** (1935), 489.
5. Gailer, *Ann. der Physik*, **24** (1935), 421.
6. Maurer, *Zeits. f. Phys.* **104** (1936), 113.
7. Hanle and Junkelmann, *Phys. Zeits.* **37** (1936), 593.
8. Bumann, *Zeits. f. Phys.* **101** (1936), 1.
9. Maurer, *ibid.* 323.
10. Lutze, *ibid.* **105** (1937), 445.
11. Hanle, *Phys. Zeits.* **38** (1937), 995.
12. Junkelmann, *Zeits. f. Phys.* **107** (1937), 561.
13. Maurer and Mehnert, *ibid.* **106** (1937), 453.
14. Moser, *Ann. der Physik*, **28** (1937), 97.
15. Neumann, *ibid.* **34** (1939), 603.
16. Trittelwitz, *ibid.* **40** (1941), 131.

As a whole the evidence leads to conclusions similar to those provided by the ionization and charge exchange studies. The cross-section for excitation of a particular spectrum line varies with the energy of the exciting beam more or less in the way expected. Fig. 235 (a) illustrates results obtained by Neumann† for the excitation cross-section of various He lines in He-He collisions. For these excitations the adiabatic parameter $a \Delta E/h\nu$ with $a = 10^{-8}$ cm. is of order unity when the energy of the incident He atoms is about 15 keV. The curves show well the gradual rise of excitation cross-section with incident atom energy extending over a region of several thousand volts above the excitation potential. For an incident energy of 4,000 eV all the curves are seen to be flattening out as the upper end of the near-adiabatic region is approached.

Fig. 235 (c) illustrates results obtained by Maurer for the relative excitation cross-sections of certain Cs⁺ lines by collision with helium atoms. The cross-section falls rapidly when the energy decreases within the near-adiabatic region. For these excitations the adiabatic parameter $a \Delta E/h\nu$ with $a = 10^{-8}$ cm. is of order unity when the energy of the incident Cs⁺ ions is about 5×10^6 eV. Thus all Maurer's measurements refer to the extreme low-energy end of the near-adiabatic region. On the other hand, the sharp decrease observed for the $\lambda 4501.5$ line as the energy increases beyond 12 keV is difficult to understand.

Fig. 235 (b) shows the cross-sections measured by Trittelwitz‡ for various Ne lines excited by impact of He⁺ ions. These measurements also lie within the near-adiabatic region (with $a = 10^{-8}$ cm., $a \Delta E/h\nu$ is of the order unity for an incident energy of about 5,000 eV) and show the rising characteristic to be expected theoretically.

† *Ann. der Physik*, **34** (1939), 603.

‡ *Loc. cit.*

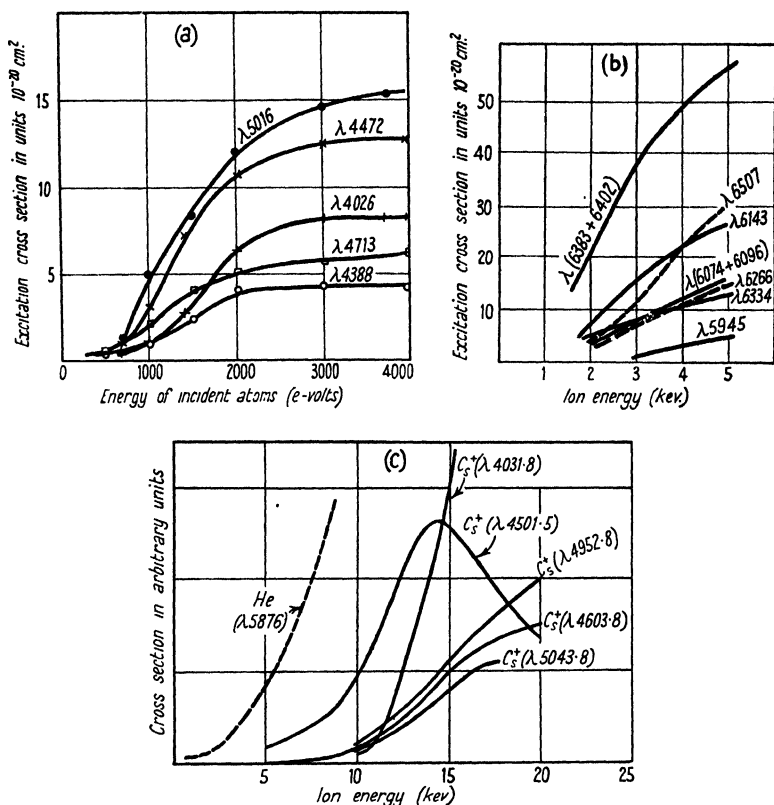


FIG. 235. Optical excitation functions of certain lines due to impact of atoms and positive ions.

(a) Measurements of Neumann for the He lines: $\lambda 4026$ (2^3P-5^3D), $\lambda 4388$ (2^1P-6^1D), $\lambda 4472$ (2^3P-4^3D), $\lambda 4713$ (2^3P-4^3S), $\lambda 5016$ (2^1S-3^1P), excited by impact of He atoms.

(b) Measurements of Trittelwitz for Ne lines: $\lambda 5945$ ($3P_2-3D_2$), $\lambda 6074$ ($1^1S_0-3^1P_1$) + $\lambda 6096$ ($3P_1-3D_2$), $\lambda 6143$ ($3P_2-3P_2$), $\lambda 6266$ ($3P_0-3D_1$), $\lambda 6334$ ($3P_2-1D_2$), $\lambda 6383$ ($3P_1-3P_1$) + $\lambda 6402$ ($3P_2-3D_3$) and $\lambda 6507$ ($3P_1-1D_2$) excited by impact of He^+ ions.

(c) Measurements of Maurer for He line: $\lambda 5876$ (2^3P-3^3D) and Cs^+ lines: $\lambda 4032$, $\lambda 4501$ (1_1-6_0), $\lambda 4953$, $\lambda 4604$ ($3P_2-3_0$) and $\lambda 5044$ (1_1-5_2), excited by impacts of Cs^+ ions with He atoms. (The spectral notation is that used by Laporte, Miller, and Sawyer, *Phys. Rev.* **39** (1932), 458.)

Optical excitation studies provide an especially good check on the usefulness of the adiabatic parameter. The value of this parameter in each case should enable one to decide which of the possible levels of the target atom or incident ion will be the most strongly excited, provided

the relative energy falls in the near-adiabatic region. In particular the strongest lines should be those for which the excitation of the upper level corresponds to the smallest value of ΔE . With given apparatus of definite sensitivity these should also be the lines which will be the first observed as the energy of the incident beam is gradually increased. Table VI gives the apparent threshold beam energies for excitation of the target atom and exciting ion found by Maurer with a particular apparatus.

TABLE VI

Incident particle	Ionization energy (eV)	Target particles		
		Ho ($\Delta E \simeq 24.5$ eV)	Hg ($\Delta E \simeq 10.4$ eV)	H ₂ ($\Delta E \simeq 15.6$ eV)
		Apparent threshold energies† (eV)		
Li ⁺	75.3	≤ 500 $\geq 22 \times 10^4$	< 500 $\geq 9 \times 10^3$	— $\geq 1.75 \times 10^4$
Na ⁺	47.0	$\geq 2 \times 10^4$	< 500 $\geq 9 \times 10^3$	—
K ⁺	31.7	< 750 1,100	< 500 $\geq 9 \times 10^3$	$< 10^3$ $\geq 8 \times 10^3$
Rb ⁺	27.3	—	< 500	$\sim 10^3$
Cs ⁺	23.4	$\sim 3,000$ $\sim 1,000$ 7,000	$\sim 2,500$ < 500 $\sim 1,400$	$\geq 10^4$ — —

† Upper values refer to excitation of the struck atom, lower to that of the incident ion.

The apparent appearance potentials were measured for a number of lines of the incident and struck particles in each case. Little difference was detected between the potentials at which any of the lines of a given atom or ion could first be detected in any given type of impact. Table VI gives therefore the ionization potentials of the incident ion and struck atom. The excitation potentials will be roughly proportional to these.

In all cases except that of Cs⁺ in He the level with the smallest value of ΔE is excited first. The exception is not a very serious one as the resonance defects are not very different for the two excitations. Other examples are provided from the work of Döpel, who, as pointed out in § 6.22, was unable to detect excitation of helium atoms by hydrogen atoms until the energy of the latter exceeded 2,000 eV, whereas the incident atoms themselves were excited to a detectable extent at an energy as low as 500 eV. However, a number of exceptions have also been found showing once more that the adiabatic parameter does not always provide a complete test.

An effect similar to that pointed out in § 6.4 in which the cross-section for ionization of a given atom is a maximum when the incident particle

has approximately the same mass as the struck atom has also been observed by Neumann† for excitation. Thus for the excitation of the argon line $\lambda 4300$ by atoms of 4,000 eV energy Neumann obtained cross-sections of 1.2×10^{-20} cm.², 2.4×10^{-20} cm.², and 7.5×10^{-20} cm.² for excitation by He, H, and A atoms respectively.

6.52. Intercombination transitions. The possibility of exciting intercombination transitions by impact of atoms or atomic ions has already been discussed in § 6.22. It was shown there that excitation of a triplet state of a helium atom by impact of a second helium atom could only take place with appreciable probability if the second atom were also excited to such a state. The same result would be expected for collisions between other two-electron systems provided Wigner's rule holds, i.e. provided the chance of reversal of electron spin in impact is negligible. Döpel and Gailer‡ have investigated this point by examining impacts of helium atoms with other two-electron atoms (Be, Mg, Ba, Sr, and Hg). They found, however, that, in all cases, triplet excitation of the target atoms occurred without corresponding triplet excitation of the incident helium atoms. This result is not surprising for such heavy atoms as Hg, Sr, and Ba for which spin-orbit coupling is not so weak (see Chap. III, §§ 3.3, 3.53) that spin reversal is unlikely. It is remarkable, however, for Mg and particularly for Be. A possible explanation is that metastable helium atoms were present in the incident beam, formed by collision of He^+ ions with metal surfaces (see Chap. IX, § 6.1). Such atoms, being already in a triplet state, could excite a triplet state of another two-electron system by electron exchange without reversal of spin.

There is no marked distinction between the excitation functions of the singlet and triplet levels of He produced in collisions with He atoms (see Fig. 235(a)). This is in sharp contrast to the position with respect to electron collisions (see Chap. II, Fig. 24).

6.53. Doppler effect in lines excited by heavy particle impact. Another special feature of optical excitation studies is provided by the Doppler effect. This enables limits to be placed on the kinetic energy of the emitting source. Thus it can be used not only to distinguish between excitation of the incident or target system but also to place limits on the momentum acquired by the struck system in an impact involving excitation. In this way Wien§ was able to show that very little kinetic energy transfer occurs in such a collision. For excitation of the incident particles

† Loc. cit.

‡ *Phys. Zeits.* **34** (1933), 827; **35** (1934), 336 (with Wigner); see also Gailer, *Zeits. f. Phys.* **103** (1936), 303; **108** (1938), 580; *Phys. Zeits.* **39** (1938), 407.

§ *Ann. der Physik*, **43** (1914), 955.

the Doppler line is very sharp and corresponds to the whole velocity, while for the target atoms there is almost no Doppler effect.

6.54. Comparison of excitation functions for electrons and heavy particles. It was pointed out with reference to Fig. 235 that the rapid decrease of intensity of the Cs^+ ($\lambda 4501$) line as the energy increased beyond that for maximum excitation is difficult to explain. This is by no means an isolated feature of the optical excitation data. Thus Hanle†

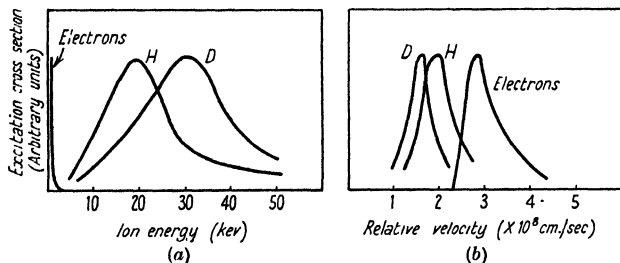


FIG. 236. Excitation functions measured by Hanle and Junkelmann for the helium line $\lambda 4259$ excited by impact of electrons, H atoms, and D atoms. (a) Cross-sections plotted against energy of the incident particles. (b) Cross-sections plotted against the relative velocity. The maxima of the three curves have been adjusted to agree arbitrarily.

compared the optical excitation functions of the A line ($\lambda 4259$) for electron impact with those for impact of hydrogen and deuterium atoms respectively. According to the theory outlined in § 6.2 the three functions should coincide when the relative velocity of the atom and exciting system is the same provided the condition $u^2/v^2 \ll 1$ is satisfied, i.e. beyond the maximum. It will be seen from Fig. 236 that this is by no means the case. A similar discrepancy has been found for the excitation of helium lines by hydrogen and deuterium atoms. No explanation has yet been proposed.

In general the maximum cross-section appears to be of the same order of magnitude for electron or heavy particle excitation, as would be expected theoretically, but there are exceptions to this. For example, the excitation cross-section for Ne lines appear to be much greater for heavy particles, both charged and uncharged, than for electrons.

Table VII shows a comparison of the cross-section for excitation of a number of Ne lines by electrons of energy 125 eV measured by Herrmann‡ with the excitation cross-sections of the same lines by the impact of 4,000 eV He^+ ions measured by Trittelwitz§ and by 4,050 eV Ne atoms

† *Phys. Zeits.* **38** (1937), 995; also Hanle and Junkelmann, *ibid.* **37** (1936), 593; Junkelmann, *Zeits. f. Phys.* **107** (1937), 561.

‡ *Ann. der Physik*, **25** (1936), 143.

§ *Loc. cit.*

measured by Neumann.† The excitation cross-section by electron impact is near its maximum at 125 eV, while in the other cases the excitation cross-section is still rising at 4,000 eV.

TABLE VII

Excitation Cross-sections for Ne Lines in Units 10^{-20} cm.²

<i>Line</i>	<i>Transition</i>	<i>Cross-section for excitation by electrons of 125 eV energy</i>	<i>Cross-section for excitation by He⁺ ions of 4,000 eV energy</i>	<i>Cross-section for excitation by Ne atoms of 4,050 eV energy</i>
5945	$^3P_2-^3D_2$	0.96	3.30	28.7
6074	$^1S_1-^3P_1$	2.19	10.8	43.2
6096				
6143	$^3P_2-^3P_2$	2.48	21.1	30.2
6266	$^3P_0-^3D_1$	1.18	10.7	24.2
6334	$^3P_2-^1D_2$	1.61	9.9	18.9
6383	$^3P_1-^1P_1$	3.94	48.5	64.8
6402				
6507	$^3P_2-^3D_2$	2.87	21.7	24.0

For the excitation of A lines by A neutral atoms, Neumann† found cross-sections at 4,000 eV from $\frac{1}{2}$ to $\frac{1}{3}$ of the maximum observed for electron impact, while for the excitation of He lines by He neutral atoms of energy 4,000 eV the cross-sections observed were only about 1 per cent. of the maximum for electron impact. This last result is surprising, since it is clear from Fig. 235 (a) that at 4,000 eV the cross-sections for the helium lines are near their maximum.

6.6. Inner shell ionization by positive ion impact

Special interest attaches to the excitation of X-radiation by proton impact as Born's approximation may be used to calculate the cross-section for inner shell ionization in this case (see § 6.11), even when the condition $u^2/v^2 \ll 1$ is not satisfied, since the perturbation can be treated as small owing to the proton charge being small compared with the effective nuclear charge near the K orbit.

Fig. 237 (a) illustrates the comparison of the calculations of Henneberg‡ using Born's approximation for the K-shell ionization of aluminium with the excitation curve observed by Peter† for the Al K radiation excited in a thin aluminium foil by proton impact.

The agreement is remarkably good even allowing for the arbitrary choice of scale to produce agreement at 130 kV. The agreement in absolute value is also quite reasonable. Peter estimates that, for proton

† Loc. cit.

‡ *Zeits. f. Phys.* **86** (1933), 592.

energies of 132 keV, each proton produced 1.55×10^{-4} *K*-ionized atoms, while the value estimated for Peter's arrangement from Henneberg's calculations was 3.27×10^{-4} .

Fig. 237 (b) shows the comparison with theory of the curve obtained by Livingston, Genevese, and Konopinski† for the *K* ionization of Zn by protons in the energy range 0.7 to 1.8 MeV.

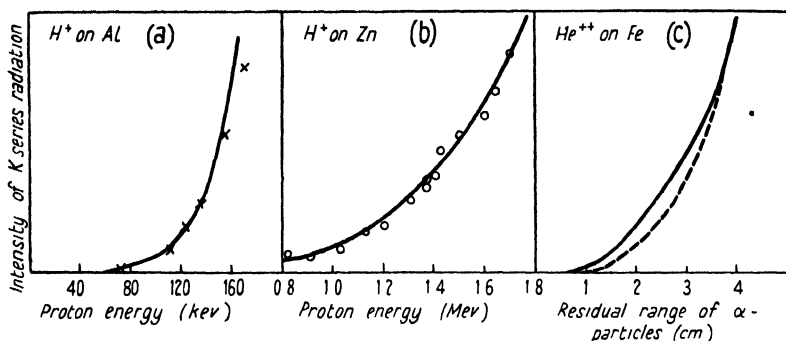


FIG. 237. Comparison of observed and calculated variation with ion energy of cross-section for inner shell ionization produced by positive ions.

- (a) Al *K* radiation excited by protons. × observed relative cross-section; ——— calculated relative cross-section. The curves were fitted at 130 keV.
 (b) Zn *K* radiation excited by protons. ○ observed relative cross-section; ——— calculated. (Curves fitted at 1.37 MeV.)
 (c) Fe *K* radiation excited by α-particles. ——— observed; - - - - calculated.

Bothe and Franz† have investigated ionization produced by particles from Po (energy up to 5.25 MeV) in the *K*-shell of Mg, Al, S, Ca, Fe, Zn, and Se and in the *L*-shell of Se, Mo, Pd, Sn, Sb, Ta, Ir, Au, and Bi. In Fig. 237 (c) their curve for the *K* ionization of Fe is compared with Henneberg's calculations.

In each case the agreement is quite good. Measurements of the variation of the cross-section for inner shell ionization with atomic number also agree with that expected theoretically.

† Loc. cit.

IX

THE COLLISION OF POSITIVE IONS AND NEUTRAL ATOMS WITH SURFACES

1. Introduction

WHEN a beam of positive ions is incident on a solid surface it may give rise to a variety of phenomena.

In the first place secondary electron emission may occur. Such emission takes place largely in the backward direction, just as in the case of the impact of beams of electrons on surfaces. It therefore cannot wholly arise from the direct interaction between the incident ions and the electrons of the metal but must involve interaction with the crystal lattice.

In the case of very slow ions it is believed electron ejection may occur in two stages, the first stage corresponding to the capture of a metal electron into an excited state of the ion, the second to a radiationless transition of the excited atom so formed to its ground state, liberating energy which is used to eject another electron from the metal.

When positive ions bombard thin metal foils, secondary electrons are also observed to emerge from the side of the foil remote from the entrance side. These secondaries could, of course, have been produced by direct ejection of an electron from the metal, but it appears likely that most arise through a process involving interaction with the crystal lattice.

The impact of positive ions on a solid surface gives rise also to the process of sputtering. Atoms, or clusters of atoms, are ejected from the surface as a result of the impact. These sputtered particles appear usually to be slow moving and are sometimes, but not usually, electrically charged.

Many positive ions striking a solid surface will simply be scattered back with loss of energy. Such 'reflected' positive ions are observed at all angles of reflection although there is some evidence to show that the specular angle of reflection is most probable. The energy of the reflected ions depends on the angle of reflection.

A further process that may occur when a positive ion is incident on a surface is capture of an electron from the solid. The neutral atom so formed may then either be adsorbed on the surface, or it may be reflected from the surface, giving rise to a fast neutral atom.

Closely linked to this mechanism is the production of negative ions

by the impact of positive ions of the same kind on surfaces. In this process, which has been observed particularly in the case of mercury, the positive ion captures two electrons from the solid and goes off as a negative ion.

An important practical effect of the bombardment of a surface with positive ions consists in the liberation of adsorbed layers of gas on the surface. Account has to be taken of this phenomenon in all experimental investigations of the interaction of positive ions with surfaces. The adsorbed gas may be liberated from the surface as a negative ion. This alternative mode of production of negative ions by positive ion impact is distinguished from the aforementioned process in that a given positive ion does not necessarily produce a negative ion of the same kind.

A number of interesting phenomena are also associated with the impact of neutral atoms on surfaces.

It has been already mentioned that excited atoms, formed by neutralization of a positive ion at a solid surface, may eject an electron from the solid in undergoing a transition to a lower state. In particular this may occur with metastable atoms. As such atoms are usually present in appreciable concentration in association with rare gas ions, the effect is often of considerable importance.

Atoms impinging on a surface with gas-kinetic energies may be captured in forming an adsorbed layer or, if the surface is sufficiently regular, may undergo diffraction. The exchange of energy between a solid and atoms of a surrounding gas depends on the chance of vibrational energy of the solid lattice being transformed into translational energy of the gas atom or vice versa. This probability determines the so-called accommodation coefficient of the surface for the gas atoms.

In the following sections we discuss these various phenomena in some detail.

2. Secondary electron emission by positive ion bombardment

2.1. *Historical introduction*

Much of the early work on secondary emission from solids was carried out using alpha-particles as the incident positive ions.†

The secondary emission coefficient, γ , is defined as the number of ejected electrons per incident positive ion. Values of γ from 3 to 30 were found for alpha-particles of different energies, tending to increase with decrease of alpha-particle energy in a manner reminiscent of a Bragg curve for ionization.

† An account of the early work on secondary emission from solids by alpha-particles is given in an article by Geiger, *Handbuch der Physik*, 24 (1927), 171.

The value of γ did not appear to be very sensitive to the nature of the solid surface, although McLennan and Pound† observed it to be influenced markedly by the presence of an adsorbed gas layer. Later work has shown that, when the solid surface is suitably outgassed, γ varies with the nature of the solid material.

The early work using positive ions of lower energy produced by artificial means‡ is of little quantitative value because magnetic analysis was not employed and there was usually uncertainty about the nature of the incident ion beam. For example, most of the experiments used as source a platinum wire coated with aluminium phosphate under the impression that the ions so produced were of hydrogen. Much later it was shown that most of the positive ions emitted by sources of this type were actually ions of sodium or potassium§ (see Chap. VIII, § 2.4).

The application of really good vacuum technique to the study of the phenomena was made by Penning|| and by Oliphant.††

In the meantime, however, interest in the value of γ was aroused from another point of view. In his original theory of the breakdown in a gas, Townsend had attributed to positive ions the possibility of ionizing the molecules of the gas by collision. The so-called 'second Townsend coefficient' was introduced as a measure of the effectiveness of positive ions in this collision process. Holst and Oosterhuis‡‡ suggested, however, that the generation of electrons by positive ions occurred rather as a result of the bombardment of the cathode by these ions. If this is the major process, the second Townsend coefficient should be practically identical with the secondary electron emission coefficient.

It is now known that very little ionization can in fact occur in the dark space of a usual type of glow discharge as a result of positive ion impact, because the energy of the incident ions will be too small (see Chap. VIII, § 6), so that the mechanism postulated by Holst and Oosterhuis is almost certainly correct. This phenomenon provides us then with an alternative means of investigating the secondary electron emission.

2.2 *Experimental methods of measurement of the secondary emission coefficient, γ*

2.21. Direct measurement of the secondary emission. The principle employed in this method of investigation is very similar to that already described in the case of secondary emission by electron bombardment

† *Phil. Mag.* **30** (1915), 491.

‡ This work is summarized in an article by Ruchardt, *Handbuch der Physik*, **24** (1927), 105. § Dempster, *Phys. Rev.* **11** (1922), 316.

|| *K. Akad. Amst. Proc.* **31** (1928), 14; **33** (1930), 841.

†† *Proc. Roy. Soc. A*, **127** (1930), 373.

‡‡ *C.R.* **175** (1922), 577.

(Chap. V, § 2.1). A beam of positive ions drawn from a discharge tube or filament source is incident on a target of the material being investigated. Another electrode is available merely to collect the secondary emission from the target. The current to this electrode is studied over a range of potentials above and below the potential of the target. A typical

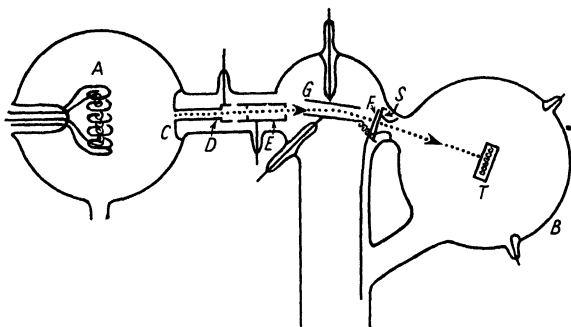


FIG. 238. Oliphant's apparatus for studying secondary electron emission from a surface by positive ion bombardment.

arrangement is that used by Oliphant† and shown diagrammatically in Fig. 238.

The source of ions consisted of a low-voltage arc *A* (see Chap. VIII, § 2.13) from which the positive ions were drawn through the hole in *C* by a negative potential of about 1,500 volts. In the gap between *D* and *E* the positive ions were retarded to the potential required. In this way a beam of ions with energy independent of the drawing-out potential of *C* could be obtained.

Since it had been found in earlier experiments that, with positive ions, the beam issuing from *E* was accompanied by fast moving neutral atoms, electrostatic deflexion was applied to the electrode *G* to separate the charged and neutral beams. After deflexion the positive ion beam passed through the slit *S* on to the target *T*. The slit *S* could be closed by means of the shutter *F*, actuated from outside the tube by a magnet.

The target *T* in the form of a box could be outgassed by heating to a temperature of about 1,200° C. by means of a tungsten filament. The target was situated at the centre of a glass bulb *B* which was covered with a conducting film of platinum, deposited by evaporation in a vacuum, contact being made by wires sealed through the wall of the bulb. Various potentials could be applied between the target and the

† Loc. cit.

platinized bulb and the currents to the target and bulb measured as functions of this potential difference.

If, in an experiment of this type, the current to the bulb is plotted as a function of this potential difference, a curve similar to that shown in Fig. 239 is obtained. Saturation currents result for both sufficiently

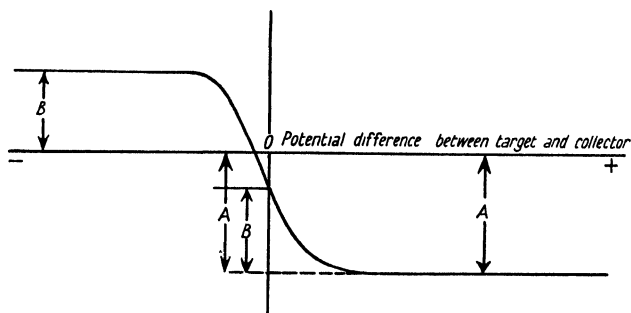


FIG. 239. Typical curve obtained in the retardation analysis of the reflection and secondary emission accompanying impact of positive ions on a surface.

large positive and negative potentials applied to the collector (relative to the target). These are due to the collection of the secondary electrons and reflected ions respectively, so that the measurements give the total positive ion reflection coefficient as well as the secondary electron emission coefficient.

Analysis of the curve obtained for small negative potential differences between collector and target enables the energy distribution of the ejected electrons to be deduced. One difficulty in determining this energy arises, however, from the presence of contact potential differences between the target and the collector, leading to uncertainty as to the true difference of potential.

Paetow and Walcher† obtained the true position of the zero in these curves by noting that, at this position, the current to the collector is just equal to the difference between the saturation secondary electron and reflected ion curves—i.e. it occurs for the point *O* of Fig. 239.

Some observers‡ have determined the energy distribution of the ejected electrons by deflecting them in a magnetic field, and Oliphant obtained good qualitative agreement between measurements of this nature and those made by applying the retarding field technique.

With a few exceptions little attention has been paid in these experi-

† *Zeits. f. Phys.* **110** (1938), 69.

‡ Oliphant, loc. cit.; Schneider, *Ann. der Physik*, **11** (1931), 357.

ments to ensure that the composition of the incident ion beam was definite. In their experiments with high-energy ions, Hill, Buechner, Clark, and Fisk† used magnetic resolution to define their incident beam, while Koch‡ and Paetow and Walcher§ used electrostatic focusing to provide a beam homogeneous in energy.

2.22. The calorimetric method. In the direct method of measurement of γ , the true incident positive ion current, undisturbed by secondary emission, may prove difficult to measure. This has sometimes been done by a calorimetric method. Thus Güntherschulze and others,|| in a series of investigations, used as cathode of a glow discharge the bottom of a hollow cylindrical vessel which could be filled with water. They then obtained the rate of heat input, H , into the cathode by measuring the rate of rise of the temperature of the water in the vessel when the discharge was running. If i is the measured current to the cathode and V the cathode fall, γ is given by the relation

$$\gamma = (iV - H)/H. \quad (1)$$

This relation implies that all the ions reach the cathode with the full energy corresponding to the cathode fall of potential. This would only be the case if they suffered no collisions in the cathode dark space. However, Güntherschulze points out that the effect of charge exchange collisions in the dark space will be to produce fast neutral atoms which will strike the cathode. The energy input to the cathode will therefore be the same as it would have been if the ion had reached the cathode with the full energy corresponding to the cathode fall and without suffering any collisions. The occurrence of collisions will mean, however, that the ions reaching the cathode will not be homogeneous in energy and the measured value of γ will correspond to such a beam of ions with a mean energy less than the full cathode fall.

Measurements based on a somewhat similar principle have been carried out by Oliphant,†† who measured the energy input to a Langmuir probe consisting of a wire, in one case, and a small copper cylinder in another, held at a negative potential relative to the plasma. In each case the probes were maintained at a constant temperature by means of electrical heating. The difference in the amount of energy which had to be dissipated in the heating coil, with and without the discharge running, in order to maintain this constant temperature, is equal to the energy of positive ion bombardment and thus leads to a determination of the true positive ion current. Difficulty was experienced in these experiments, however, owing to changes in the surface conditions of the wire probe due to the positive ion bombardment. These changes affected the thermal accommodation coefficient (see § 10.32) between the gas and the wire, and therefore the heat losses from the wire.

In general it can be said that measurements of γ made using calorimetric methods are unlikely to be as accurate as measurements by the direct method.

2.23. The current amplification method. Kingdon and Thomson‡‡ found that the photo-electric currents from a composite silver oxide-caesium cathode could be greatly increased by filling the photo-tube with argon at a pressure of a fraction

† *Phys. Rev.* **55** (1939), 463.

‡ *Zeits. f. Phys.* **100** (1936), 685.

§ *Loc. cit.*

|| Güntherschulze and Bär, *ibid.* **107** (1937), 730; **109** (1938), 121; Güntherschulze and Betz, *ibid.* **108** (1938), 780.

†† *Proc. Roy. Soc. A*, **132** (1931), 631.

‡‡ *Physics*, **1** (1931), 343.

of a mm. of Hg and applying a field of a few hundred volts per cm. The amplification arises from two sources—the ionization by collision produced in the gas by the ejected photo-electrons and the secondary electron emission from the cathode following bombardment by the positive ions moving towards the cathode in the electric field.

Townsend's theory of ionization by collision† gives for the current i , flowing between two electrodes distant x apart when i_0 is the photo-current in the absence of the gas,

$$i = \frac{i_0 e^{\alpha(x-\delta)}}{1 - \gamma\{e^{\alpha(x-\delta)} - 1\}}. \quad (2)$$

δ is the distance the electrons must have travelled before the beginning of the ionization, and α and γ are respectively the first‡ and second Townsend coefficients— γ being almost identical with the secondary electron emission coefficient for positive ions striking the cathode.

By measuring the current amplification for a given field between the electrodes for a number of different electrode separations x , it is possible to calculate both α and γ . Measurements of this kind have been carried out by a number of different authors.§ The defect of the method is that it determines γ as a function of the field between the electrodes and not as a function of the energy with which the ions strike the surface. In fact each measurement of γ will be an average for a large range of positive ion energies.

2.24. Determination of γ by measuring breakdown potential between two electrodes in a gas. Huxford has also determined γ for a cathode by measuring the minimum striking potential between two parallel electrodes distant x apart, in the absence of light. According to Townsend's theory breakdown will occur when the denominator of equation (2), § 2.23, becomes zero so that the ratio i/i_0 increases indefinitely, i.e. the condition for breakdown is

$$1 + \gamma - \gamma e^{\alpha(x-\delta)} = 0.$$

If the potential at which breakdown occurs is known and if α is known for the corresponding value of F/p , γ can be determined.† This method suffers from the same defect as that of § 2.23 since ions of a wide range of energy are incident on the cathode in any given measurement.

2.3. Results of the measurement of γ

The ions and target materials for which measurements of γ are available are shown in Appendix 3. There are considerable discrepancies between the values of γ obtained by different authors for the same ion and target material. This undoubtedly arises mainly from the presence of adsorbed surface layers. There is general agreement that the value of γ obtained is very sensitive to the condition of the surface under bombardment. Since the procedures employed for outgassing the surface vary greatly in different experiments it is difficult, in assessing the results of different observers, to say how effective the outgassing procedure has been.

† *Phil. Mag.* **3** (1902), 557; **5** (1903), 389; **6** (1903), 598.

‡ See Chap. II, § 4.54.

§ Kruithoff and Penning, *Physica*, **3** (1936), 515; Jones and Willott, *Proc. Phys. Soc.* **48** (1936), 830; Huxford, *Phys. Rev.* **55** (1939), 754.

Appendix 3 includes measurements of γ made using the methods which involve the determination of Townsend's second coefficient. In such methods, as has been pointed out in § 2.22, γ is determined in terms of F/p and not of the ion energy, and represents an average value over a large range of incident ion energies. Such methods are of value in the study of the glow discharge but, owing to the difficulty of relating them to values obtained by the direct method, we shall base the discussion of the factors influencing γ on measurements by the direct method only.

The observed values of γ range from very small values for low-energy ions up to values of over 20 for the impact of very fast Hg^+ ions on surfaces of sodium and potassium.

2.31. Dependence of γ on the energy of the incident ion. Fig. 240 shows the type of variation of γ with energy observed in a number of different experiments, covering a wide range of incident ion energies and a variety of incident ions and target surfaces. It is seen that in all cases γ increases with ion energy up to energies of some thousands of electron volts. Usually this increase is linear. In some cases the linear part of the curve, if produced, would cut the γ -axis on the positive side for zero electron energy (see Fig. 240 (a) for He^+ on Ni), but usually γ is very small for low-energy ions.†

At higher energies the increase of γ with ion energy is less rapid and over a wide range of energy γ remains practically constant (see Fig. 240 (d)). For still higher energies γ decreases slowly with increase of ion energy (see Fig. 240 (e)).

Referring to Chap. VIII, § 6.4 (Figs. 233, 234), it will be seen that the variation, with energy of the bombarding ions, of the secondary emission coefficient γ is very similar to that of the cross-section for ionization of an atom by positive ion impact, i.e. a rather flat maximum at a high ion energy with a gradual fall at higher energies and a rather more rapid decrease on the low-energy side so that ions of, say, 100 eV energy are quite ineffective.‡

Large differences exist between the values of γ found by different investigators using similar ions and similar target materials. This is clear, for example, from Fig. 240 (e), which shows that for protons of energy 100 keV incident on copper, Allen found values of γ about half those found by Hill, Buechner, Clark, and Fisk. Usually the results obtained by any one set of observers are consistent in themselves, but may differ

† The apparent secondary emission due to low-energy ions is probably due to metastable atoms present in the beam (see § 6.1).

‡ Except for rare gas ions where the presence of metastable atoms associated with the beam may produce emission at low energies (see § 6.1).

in absolute value from those of other observers who met with a different degree of success in removing the layer of adsorbed gas from the target surfaces.

2.32. Dependence of γ on the nature of the surface. It is difficult to draw reliable conclusions about the influence of the target surface on

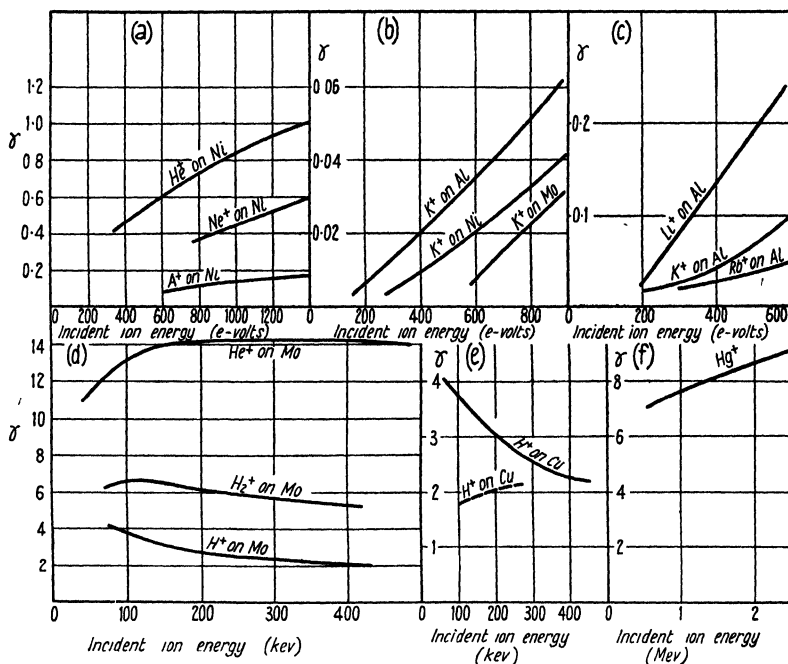


FIG. 240. Variation of γ with incident energy.

- (a) He⁺, Ne⁺, and Ar⁺ on Ni (Healea and Houtermans).
- (b) K⁺ on Al, Ni, Mo (Jackson).
- (c) Li⁺, K⁺, Rb⁺ on Al (Chenoy).
- (d) H⁺, H₂⁺, He⁺ on Mo (Hill, Buechner, Clark, and Fisk).
- (e) H⁺ on Cu (Hill, Buechner, Clark, and Fisk, Allen).
- (f) Hg⁺ on Ni, Cu, Sn, Na, Mo, Al, W, Ag, Mg, Cd (Linford).

the measured values of γ . Some observers who have bombarded a number of metal surfaces with the same kind of ion have in general found very little difference between the values of γ for different metal surfaces. Where γ for a certain ion has been measured for different targets by different observers different values have often been obtained, but one cannot rule out the possibility that these values may correspond to different adsorbed surface layers and not be characteristic of the

underlying material. Some observers have found higher values of γ for surfaces which oxidize readily and one is tempted to suppose that the high values arise from the presence of an oxide layer. For instance, for Hg^+ ions of very high energy, Linford† found indistinguishable results with targets of Na, Cu, Mo, A, W, Ag, Sn, Mg, Cd (see Fig. 240 (f)) but very much higher values for K and Na targets. Similarly Allen‡ found that surfaces of C, Cu, Ni, Pt gave comparable values of γ over a large range of incident ion energy, whereas the values found for a Be surface were much larger.

In a few cases, notably for impact of alkali metal ions, there seems to be some evidence that the value of γ decreases with increasing atomic number of the target. Thus Fig. 240 (b) indicates the variation of γ with ion energy in the case of K^+ ions bombarding surfaces of Al, Ni, and Mo.§

2.33. Dependence of γ on the nature of the ion. For bombarding ions having a similar structure and thus a similar external field, there seems to be a consistent tendency for the value of γ to decrease with increasing mass of the ion. Thus Fig. 240 (a) shows the curves obtained for the impact of ions of the inert gases on a target of nickel by Healea and Houtermans.‡ The measurements of Cheney‡ for the impact of ions of the alkali metals on a target of aluminium also indicate a similar trend as shown in Fig. 240 (c). For dissimilar types of ions, however, no simple relationship was found to hold.

For ions of very high energy the mass of the ions seems to have a marked effect opposite to that in the lower energy range. Thus Hill, Buechner, Clark, and Fisk‡ bombarded a molybdenum surface with high-energy ions of H^+ , H_2^+ , and He^+ . Their results are illustrated in Fig. 240 (d). It is seen that at these energies the value of γ is almost proportional to the mass of the ion. Also it seems that the curve of γ against incident ion energy passes through a very flat maximum at high ion energies and then decreases. But the position of this maximum moves farther towards the region of high energy as the mass of the ion is increased.

Fig. 240 (f) shows the results obtained with very high energy Hg^+ ions bombarding a surface of Mo (Linford‡). It is seen that the value of γ is still increasing for an ion energy of 3 million electron volts.

2.34. Effect of adsorbed layers on γ . As is clear from what has already been stated, all observers have found that adsorbed layers have a

† *Phys. Rev.* **47** (1935), 279.

§ Jackson, *Phys. Rev.* **30** (1927), 473.

‡ Loc. cit.

marked effect on the secondary emission by positive ion bombardment of a surface. The effect is markedly greater than for secondary emission by electron impact in which it was possible to explain the change produced by a monolayer at the surface of a metal as arising from a change of work function (Chap. V, § 4.2).

A detailed study of the effect of an adsorbed surface layer has been carried out for tungsten by Pactow and Walcher.[†] The ions used were

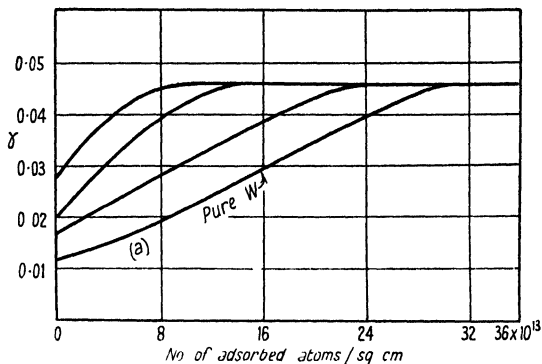


FIG. 241. Illustrating the increase of γ with time of bombardment for Cs ions on a tungsten surface. The time of bombardment is shown in terms of the total number of Cs^+ ions striking 1 cm.^2 of the surface. A concentration of 30×10^{23} atoms/sq. cm. represents a monatomic layer. Curve (a) refers to a pure W surface. The other curves refer to surfaces for which the oxide layer had been removed to varying extents.

Cs^+ . Starting with a tungsten surface which had only been partly freed of its adsorbed layer of oxygen, they found that the value of γ rose with time of bombardment until, after a certain time, a steady value was reached. With a tungsten surface for which the oxygen layer had been completely removed by preliminary heat treatment, the initial value of γ was much lower, but after bombardment the final value reached was identical with that reached finally in the former case. Fig. 241 shows a number of curves obtained starting with tungsten surfaces on which the oxygen layer had been removed to varying extents. For each curve the energy of the incident ions was the same (500 eV). The abscissa of Fig. 241 is the number of Cs atoms per sq. cm. adsorbed on the tungsten surface. This can be calculated from the known current of Cs^+ ions, the time of bombardment, and the fraction of ions reflected from the surface. The surface density of the adsorbed film at which the saturation

[†] Loc. cit.

value of 0.046 is attained for γ with the pure tungsten surface is 3×10^{14} atoms/sq. cm. This is just equal to the concentration required for a single monolayer.

Paetow and Walcher conclude that in those cases where the surface has not initially been freed of all its oxygen, a composite film of Cs+O

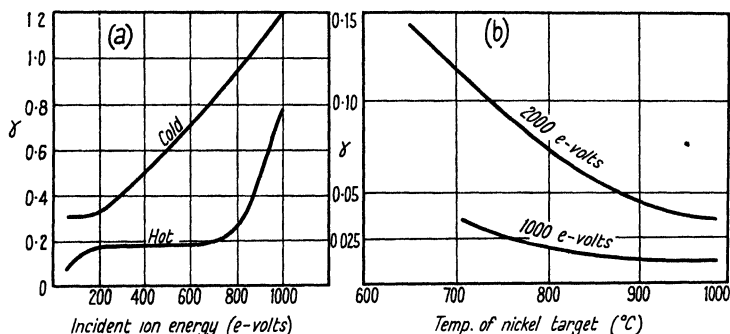


FIG. 242. (a) Variation of γ with incident ion energy for He^+ ions on hot and on cold nickel. (b) Variation with temperature of γ for Cs^+ ions of energy 1,000 eV and 2,000 eV incident on nickel.

is formed and that the saturation value of γ is reached when this composite film is one monolayer thick. In view of the big difference between the work function for caesium and oxygen, it would follow that the electron emission cannot depend much on the work function of the adsorbed atoms and the extra electrons must come from the adsorbed layer itself.

Paetow and Walcher also measured γ for tungsten surfaces with an adsorbed monolayer of potassium and of hydrogen. Of the three combinations W+Cs, W+K, W+H, the last has the lowest work function and would be expected to show the greatest value of γ if the effect of the adsorbed layer on emission arose from difference in work function. In fact the values of γ for the three cases are 0.046, 0.049, and 0.018 respectively, thus being smallest for the surface of lowest work function. Paetow and Walcher interpret the low value of γ for the W+H surfaces as arising from the relatively small electron density in that case.

2.35. Effect of target surface temperature on γ . The measured value of γ appears to depend markedly on the temperature of the target surface. Fig. 242 (a) shows the variation of γ with ion energy obtained by Oliphant† for He^+ ions bombarding a cold and a 'red hot' surface of molybdenum.

† *Proc. Roy. Soc. A*, **127** (1930), 373.

Moon† has found a similar decrease of γ with increase of target temperature for Cs^+ ions of a given energy incident on nickel (see Fig. 242(b)). It is probable that this effect is associated with the adsorbed surface layer, but this has not been established definitely.

2.36. Dependence of γ on the angle of incidence of the primary ions. Studies of the dependence of γ on the angles of incidence of the primary

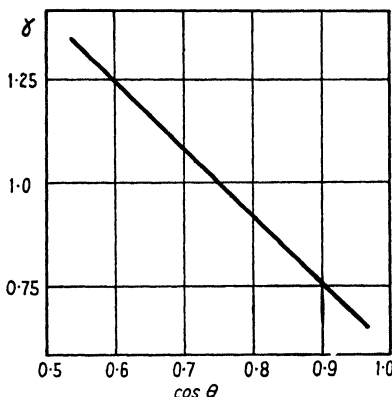


FIG. 243. Illustrating the variation of γ with angle of incidence for He^+ ions on nickel.

ions on a metal surface have been made by Oliphant‡ for low-energy He^+ ions on a well-polished molybdenum surface and on a roughly polished nickel surface, and by Allen§ for high-energy protons on surfaces of Be, C, Cu, Ni, Pt. Allen finds that the value of γ corresponding to ions incident at an angle θ to the normal to the target surface is roughly proportional to $\sec \theta$. A curve obtained by Oliphant using a nickel target for ions of energy 1,000 eV is shown in Fig. 243. He found for γ a relation of the form $(a - b \cos \theta)$, where a , b are constants. Actually, however, Oliphant's results, over the range for which he gives values in his paper, do not depart far from the proportionality to $\sec \theta$ obtained by Allen in his measurements with ions of much greater energy.

2.4. The energy distribution of the ejected electrons

Most of the secondary electrons ejected by positive ion bombardment possess very small energies. Thus, in 1913, Baerwald§ studied the ejected electrons produced by the canal rays from a hydrogen discharge falling on a variety of targets. With a potential of 24,000 volts across

† *Proc. Camb. Phil. Soc.* **27** (1931), 570.

‡ *Loc. cit.*

§ *Ann. der Physik*, **41** (1913), 643.

the discharge the maximum energy of the secondary electrons observed was only 22 eV.

Later investigators have found that the energy distribution of the secondary electrons depends on the state of the surface. Before a surface has been properly outgassed secondary electrons of very low energy are much more prominent than after thorough outgassing.

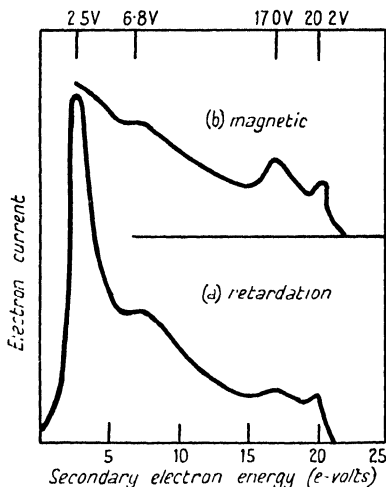


FIG. 244. Energy distribution of electrons ejected from Mo by impact of He^+ ions. Curve (a) shows the distribution determined by a retardation analysis, curve (b) by a magnetic analysis.

Fig. 244 shows typical curves obtained by Oliphant† for the energy distribution of electrons ejected by the impact of He^+ ions of 400 eV energy on a gas-free molybdenum surface. The fine structure exhibited by these curves was quite reproducible. Oliphant found a very similar energy distribution, with the peaks in the same position to within a fraction of a volt, for Ni, Mo, and W targets.

Veith‡ studied secondary energy distributions produced by the impact of K^+ ions on an outgassed platinum target. He found the ejected electrons to fall into two groups, viz. (a) a group of small velocity which, at all primary energies, lay between 1 and 3 eV, and (b) a relatively narrow group of greater energy depending on the energy of the primary ions. Table I shows the energy range of this second group for different primary energies.

† Loc. cit.

‡ *Ann. der Physik*, **29** (1937), 189.

TABLE I

Energy Range of Fast Group of Secondaries observed by Veith for K⁺ Ions on Platinum

Primary energy (eV)							Energy range of group (eV)
280	.	.	.	.	.	.	16-19
440	.	.	.	.	.	.	17-20
560	.	.	.	.	.	.	19-23
720	.	.	.	.	.	.	23-28
900	.	.	.	.	.	.	35-42
1,140	.	.	.	.	.	.	52-58

Veith found that the energy range of the fast group of secondary electrons depended on the nature of the target material. For K⁺ ions of 560 eV energy incident on a target of aluminium he found the energy of the fast group to be about 50 eV.

The energy distribution of secondary electrons ejected by positive ions of very great energy has been studied by Hill, Buechner, Clark, and Fisk,[†] who have found that, even for He⁺ ions with energy 300 keV, the great bulk of the ejected electrons have energies below 30 eV.

2.5. Concluding remarks

It is clear that a great deal more reliable experimental information needs to be accumulated in this field. Results obtained by different observers show a wide disagreement. Very few measurements are available for the emission of secondary electrons from non-metallic surfaces and too little care has been taken in many cases to ensure that the surfaces of the materials studied have been clean and free from surface gas. No measurements seem to be available concerning the angular distribution of the ejected electrons.

The study of this process provides an interesting insight into the mechanism of the interaction of positive ions with surfaces and is of great practical importance in view of the extensive employment of fast moving beams of ions for nuclear disintegration and for the understanding of the mechanism of the glow discharge.

3. Neutralization of positive ions on impact with a metal surface

In the course of measurements of the secondary electron emission produced by He⁺ ions striking a metal surface, Oliphant[‡] was able to show that much of the effect he was observing arose from metastable helium atoms formed by neutralization of the He⁺ ions on their way from the source to the target, either by collision with other gas atoms or

[†] Loc. cit.

[‡] *Proc. Roy. Soc. A*, **124** (1929), 228.

by collision with the walls of the canal which defined the beam. He established that such collisions with a solid surface were capable of giving rise to a considerable intensity of metastable atoms and that the earlier work of Penning (§ 2.3) on secondary electron emission by Ne^+ ions must have contained a contribution from metastable Ne atoms.

Fig. 245 shows the apparatus used by Oliphant to show that He^+

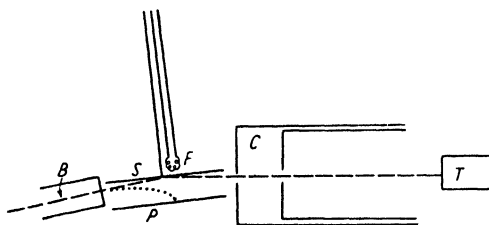


FIG. 245. Apparatus used by Oliphant for investigating the production of metastable helium atoms by the impact of He^+ ions on a metal surface.

ions were able to extract electrons from a metal surface to give rise to metastable atoms. The beam B , consisting of a mixture of He^+ ions and metastable He atoms, was incident on a metal surface S ,† which could be outgassed by heating with a filament F . After scattering from S the beam entered a collector system C and was incident on the target T . The total positive ion current entering the collector could then be measured and also the secondary electron current emitted by T . The electron emission was more than 3 times the incident positive ion current. The incident ion beam had an energy of the order of 1,000 eV, and this high secondary electron emission would not be expected for ions of this energy (see § 2.31). Oliphant concluded that metastable atoms, as well as positive ions, were entering the collector. To investigate the matter further a field was applied between the condenser plates S , P , large enough to prevent ions reaching the plate S and forcing them to follow the dotted path in Fig. 245. It was found that the electron emission was decreased by 40 per cent. From the known value of γ it was estimated that the positive ion current could not have accounted for more than a 15 per cent. decrease. It was concluded that the balance of the decrease arose from metastable atoms formed by the incidence of the positive ions at S (see § 6.1).

The electron emission still observed from the collector when a field

† The nature of the metal surface is not specified in Oliphant's paper.

was applied across the condenser evidently arose from the reflection of metastable atoms from S .

Rostagni† tried to detect neutral atoms produced by the glancing impact of A^+ and H_2^+ ions of energy between 100 and 600 eV on the walls of a narrow canal, by looking for electrons ejected by them from a copper target. He failed to obtain any evidence of neutral atoms in this case and claims that he could have detected a current of neutral atoms in the beam issuing from the canal of magnitude only 10^{-4} times the ion current.

Little work seems to have been done on the systematic study of the process of metastable atom formation by the impact of positive ions on surfaces since the investigations of Oliphant. The process must be of considerable importance in gas discharge phenomena on account of the high probability of electron extraction from surfaces on which metastable atoms are incident.

4. Production of negative ions by the impact of positive ions on a metal surface

The impact of positive ions with a metal surface has been observed by Arnot and his collaborators‡ to give rise also to the formation of negative ions. They found that many of the negative ions produced in this way were ions of the same material as the bombarding positive ions. In particular, negative ions of mercury and hydrogen were observed as a result of the impact of positive mercury and hydrogen ions with a nickel surface. However, Sloane and Press,§ using an apparatus that could be thoroughly outgassed, failed to obtain evidence of the production of Hg^- ions arising from the impact of Hg^+ ions on a nickel-chrome surface. They identified, however, the negative ions CO^- and $C_3H_3^-$ which they attributed to adsorbed layers on the nickel surface. Evidence of light negative ions produced by positive ion impact on adsorbed layers has also been obtained by Arnot and Beckett.|| These writers, however, differ from Sloane and Press in their interpretation of the mass spectrum of these negative ions.

This work has been extended recently by Sloane and Watt,†† who have investigated negative ions emitted from a tantalum gauze bombarded by positive ions of the residual gases present in a sealed-off tube. They identified the negative ions H^- , C^- , O^- , F^- , C_2^- , C_2H^- , CN^- , Al^- , O_2^- , C^- , and possibly K^- .

† *Zeits. f. Phys.* **88** (1934), 55.

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

§ *Ibid.* **168** (1938), 284.

|| *Loc. cit.*

†† *Proc. Phys. Soc.* **61** (1948), 217.

The study of this phenomenon is of some importance in the design of cathode-ray tubes, because it has been shown that the 'black spot' which forms on the screen of such tubes is due to negative ions produced in the cathode region, either by positive ion bombardment of the electrodes or by thermionic emission from the cathode itself. These negative ions are focused on the screen by the electrostatic lens.

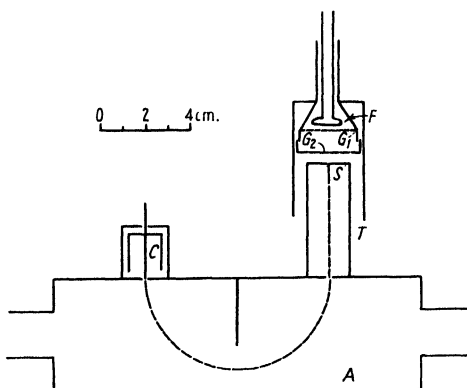


FIG. 246. Apparatus used by Arnot and Beckett for studying negative ions produced by positive ion impact on a metal surface.

4.1. *Experimental methods of studying the negative ion production*

A typical apparatus used by Arnot and Beckett is shown in Fig. 246. Electrons from the filament F were accelerated through the grid G_1 and ionized the gas or vapour in the region between G_1 and G_2 . A negative potential of a few hundred volts (relative to G_1) was applied to the grid G_2 so that positive ions produced in the space between G_1 and G_2 were accelerated to G_2 while electrons, or any negative ions produced at the filament F , were prevented from reaching G_2 . The slit S was kept at a potential of a few hundred volts positive with respect to G_2 so that the positive ions could not pass through it. Instead they were turned round and passed back and forth through the grid G_2 . Negative ions formed by impact of the positive ions on the grid G_2 , or by any other means, however, were accelerated between G_2 and S and entered the soft-iron tube T . After passing through T they entered the analysing chamber A , which could be placed between the poles of an electromagnet. By appropriate choice of the magnetic field and the accelerating potential between G_2 and S they could be deflected into the Faraday cylinder C . In this way the mass spectrum of the negative ions could be measured. In

addition, by placing on the Faraday cylinder a retarding potential relative to the grid G_2 , the energy distribution of the negative ions leaving G_2 could be obtained.

Sloane and Press† extended Arnot's work by using a double mass spectrograph arrangement, shown diagrammatically in Fig. 247. A low-voltage arc discharge was run between four indirectly heated cathodes, K , and a cylinder of nickel gauze, C , which served as anode. Positive ions were pulled out from the discharge through the flat gauze G and further accelerated by a potential of about 100 volts through the slit S_1 . Passing along the soft-iron tube T they entered the analysing chamber A , where they were deflected through the slit S_2 on to the nickel-chrome disk D . In order to study the effect of positive ions of different velocities, the disk D could be made several thousand volts negative with respect to S_2 . Negative ions produced at D were then accelerated in the reverse sense by this same field and were deflected in A through the slit S_3 and into the Faraday cylinder F . This arrangement has the disadvantage that the incident ion energy on D cannot be adjusted arbitrarily since the potential difference between S_2 and D must be such as to deflect the negative ions through the slit S_3 . By varying the potential on F relative to that of D it is possible to study the distribution in energy of emission of the negative ions.

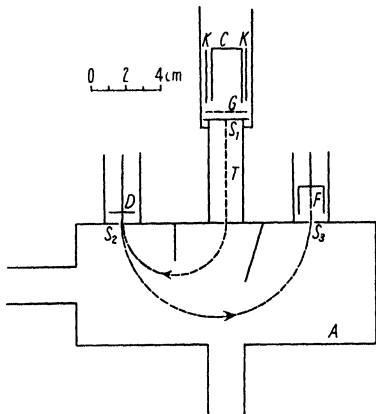


FIG. 247. Apparatus used by Sloane and Press for studying negative ion production by the impact of positive ions on a metal surface.

4.2. The yield of negative ions

It is very difficult to make an accurate estimate from the available experimental data of the number of negative ions produced at a surface per incident positive ion. This is because of the difficulty of estimating the actual positive ion current incident on the nickel surface.

However, Arnot and Milligan made the rough estimate that for incident Hg^+ ions of 200 eV energy, 0.64×10^{-3} Hg^- ions were formed per incident Hg^+ ion, whereas for hydrogen they estimated the corre-

† Loc. cit.

sponding figure of 1.04×10^{-5} H^- ions per incident H_2^+ ion of 200 eV energy striking the surface.

Fig. 248 shows the observed variation of negative ion yield with positive ion energy in these cases.

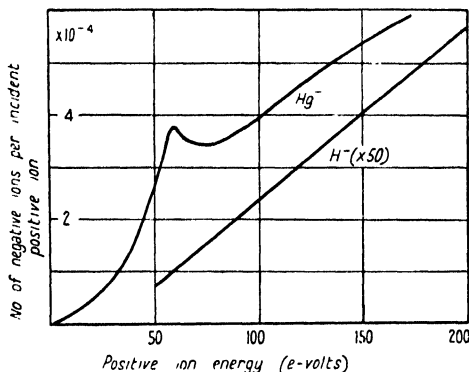


FIG. 248. Observed variation with ion energy of the negative ion yield resulting from bombardment of a nickel surface by Hg^+ and H_2^+ ions.

4.3. Energy distribution of the ejected ions

Most of the negative ions leave the surface with an energy of a few electron volts only, but some were found to have energies of some tens of e-volts. Thus Fig. 249 shows curves obtained by Sloane and Watt† for the energy distribution of H^- , O^- , and CN^- ions obtained in one of their experiments with a sealed-off tube. The nature and energy of the incident positive ions was uncertain, but they may have had energy up to 200 eV. The H^- and CN^- were ejected from a tantalum gauze. The O^- was ejected from an oxide-coated cathode, and O^- ions of energy more than 100 eV were observed.

In some cases, in addition to a peak in the energy distribution corresponding to ions of a few electron volts energy, a second peak was observed for ions of higher energy.‡ This is seen from Fig. 250, which shows the energy distribution observed for H^- ions ejected by H^+ impact and for O^- and O_2^- ejected by O^+ and O_2^+ impact.

5. Reflection of positive ions from surfaces

Positive ions incident on a solid surface may be reflected without neutralization. As has been pointed out in the discussion in § 2.21 of the measurement of secondary electron emission by positive ions, the

† Loc. cit.

‡ Arnot, loc. cit.

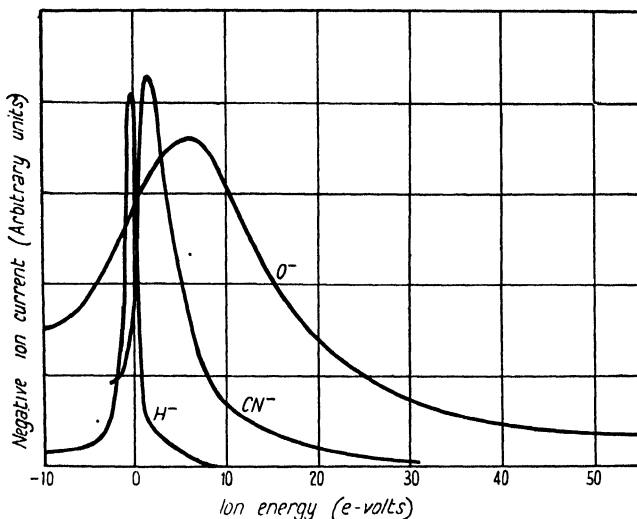


FIG. 249. Energy distribution of H^- , O^- , and CN^- negative ions ejected by impact of positive ions in a sealed-off apparatus. The energy and precise nature of the positive ions are uncertain.

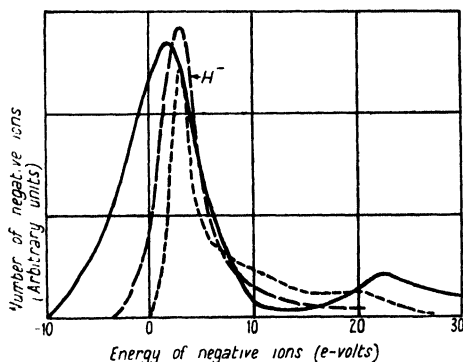


FIG. 250. Energy distribution of H^- , O^- , and O_2^- ions ejected respectively by H^+ , O^+ , and O_2^+ impact on a metal surface. — H^- ; --- O^- ; O_2^- .

same type of measurement employed there will also yield the total positive ion reflection current if the saturation current to the collectors is measured for high negative potentials relative to the target.

When the positive ions are incident normally on the target the positive ion reflection coefficient R has been found to be very small in the case of

alkali ions. Thus for incident ion energies up to about 1,000 eV it turns out to be usually of the order 0.02 or 0.03.†

For rare gas ions incident on nickel Healea and Houtermans‡ find much greater values of R even at quite low energies. Fig. 251 illustrates the results obtained by these investigators. It is seen that the reflection

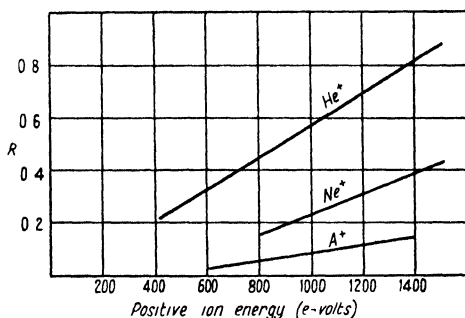


FIG. 251. Reflection coefficient R for A^+ , Ne^+ , and He^+ incident normally on a nickel surface.

coefficient for He^+ is very large but that, for these three ions of a similar type, it decreases markedly with increase of atomic weight of the ion.

Some interesting measurements of the effect of the nature of the surface on the reflection coefficient for Cs^+ ions have been made by Paetow and Walcher in the work discussed in § 2.34.

In contrast to the result for secondary electron emission they found that the work function was of great significance for the reflection of positive ions from a surface. The ratio of the probability of reflection of an incident ion as an ion to the probability of its reflection as a neutral atom is given by

$$\exp\{(\phi - I)/\kappa T\},$$

where ϕ is the work function, and T the temperature, of the surface and I is the ionization energy of caesium. If the work function exceeds the ionization energy of caesium, as is the case, for example, for an oxidized tungsten surface, the ion reflection coefficient R would be expected to be comparatively large, while if the work function is less than the ionization energy of caesium, many of the incident Cs^+ ions will leave as neutral atoms and R will be correspondingly lower.

Fig. 252 illustrates the values of R obtained by Paetow and Walcher for the reflection of Cs^+ ions from pure and oxidized tungsten and from

† Jackson, *Phys. Rev.* **30** (1927), 473; Paetow and Walcher, *Zeits. f. Phys.* **110** (1938), 69.

‡ Loc. cit.

tungsten with monolayers of adsorbed caesium. It is seen that R decreases with decrease of work function of the surface. In each case R is seen to increase linearly with ion energy.

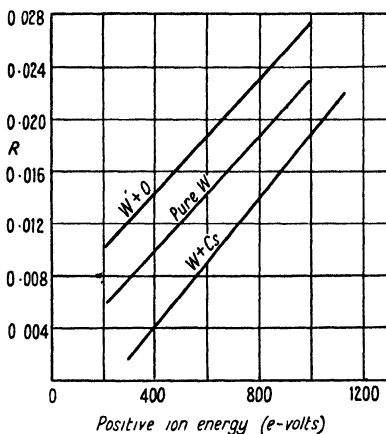


FIG. 252. Reflection coefficient R of Cs^+ ions incident on a clean tungsten surface and on a tungsten surface with monatomic layers of oxygen and caesium.

The reflection coefficient of positive ions incident on a solid surface depends markedly on the angle of incidence of the ions. This effect has been studied by several investigators.† In Gurney's apparatus, ions from a source (of a Kunsman type) emitting K^+ , Cs^+ , or Li^+ ions were incident on a target which could be rotated to vary the angle of incidence. The reflected ions were analysed with respect to their energy by deflecting them through 180° in a magnetic field. It was found that, for angles of incidence near the normal, the value of R was very small, but it increased markedly with increasing angle of incidence. Most of the scattering occurred in the forward direction and it tended to be centred in a broad beam (width at half maximum about 45°) about the direction of specular reflection.

The spread in angle of the reflected beam is illustrated by the curve of Fig. 253 obtained by Read for the reflection of Li^+ ions of different energies incident on a platinum target at an angle of incidence of 45° . The curves which show the relative intensity of the reflected ions as a function of the angle of deviation indicate that the total intensity of reflection passes through a sharp maximum for incident ions of 48 eV energy. A similar result was obtained by Gurney for Cs^+ , K^+ , or Li^+ ions incident on platinum.

It is not clear how these results link up with those for normal incidence (Figs. 251 and 252) which show a linear increase of R with incident ion energy up to energies about 1,000 eV.

If the incident ion beam is homogeneous in energy, the ions scattered at a given

† Read, *Phys. Rev.* **31** (1928), 629; Gurney, *ibid.* **32** (1928), 467; Sawyer, *ibid.* **35** (1930), 1090; Woodcock, *ibid.* **38** (1931), 1696; Longacre, *ibid.* **46** (1934), 407.

angle are also nearly homogeneous. The mean energy retained by the ions varies continuously with angle of incidence, rising from 20 per cent. of the incident energy

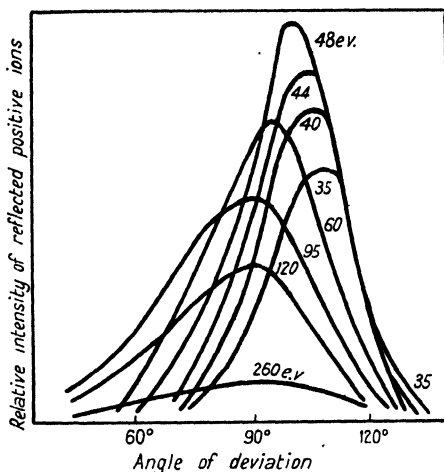


FIG. 253. Relative intensity of Li^+ ions of energy from 35 to 260 eV reflected from a platinum target, illustrated as a function of the angle of deviation. A deviation of 90° corresponds to specular reflection.

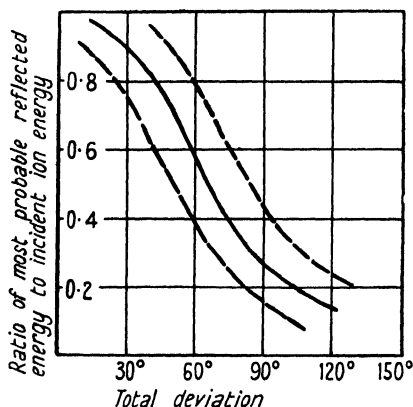


FIG. 254. Variation of the ratio of the most probable reflected energy to incident ion energy with the total angular deviation for Li^+ ions of a few hundred eV energy incident on a nickel target. The broken lines indicate the scatter of the experimental points.

to 90 per cent. or more of it as grazing incidence is approached for a properly outgassed target. The condition of the surface of the target has a marked influence on the energy distribution of the reflected ions. If the target has not been properly

outgassed, large numbers of reflected ions of very low energy are found at normal incidence and the energy retained rises only to about 40 per cent. of the initial energy near grazing incidence.

Fig. 254 shows the results obtained by Longacre for the ratio of the most probable reflected energy to the incident ion energy for Li^+ ions of a few hundred electron volts energy incident on an outgassed surface of nickel. This ratio is plotted against the angle between the incident and reflected ion beams (the total deviation). It is seen that the ratio decreases markedly as the total angle of deviation increases.

6. The collision of metastable atoms with surfaces

6.1. *Electron extraction by metastable atoms*

Electron extraction from a metal surface following the impact of metastable atoms seems first to have been established definitely by Webb† in 1924, for mercury atoms and a nickel surface. He showed that a time-interval of about 2×10^{-4} sec. elapsed between the excitation of a Hg atom and the arrival of the radiation from it at a surface with the subsequent emission of an electron. This is just the time that would be needed for such an atom to travel across the discharge, so that it was reasonable to suppose that the electron emitted was not a true photo-electron, but arose from the interaction of the excited atom with the surface.

A little later Messenger‡ showed that some of the apparent critical potentials for Hg observed in the measurements of Franck and Einsporn,§ which had been somewhat puzzling because they pointed to a number of states for which there was no spectroscopic evidence, could be interpreted as arising from spurious inflexions in the current-potential curves due to electrons ejected from surfaces by metastable Hg atoms.

These writers studied the relative importance of emission due to impact of metastable atoms and to radiation, by placing screens of quartz and fluorite of known optical transmission between the excited gas and the electrode from which electron emission was being observed. They found that extraction by metastable atoms was, under some conditions, more effective than photo-electric emission.

Other investigations on metastable Hg atoms were made by Couliette|| and Sonkin.†† Sonkin studied the extraction from a tungsten surface and showed the phenomena to be very complicated and critically dependent on the nature of the surface. A complex adsorbed Hg-O layer appeared to be necessary for any emission. Sonkin concluded that the maximum efficiency of emission observed was not greater than a few per cent.

† *Phys. Rev.* **24** (1924), 113.

‡ *Ibid.* **28** (1926), 962.

§ *Zeits. f. Phys.* **2** (1920), 18.

|| *Ibid.* **32** (1928), 636.

†† *Ibid.* **43** (1937), 788.

Much higher efficiencies of emission have been found in the case of metastable rare gas atoms. A number of experimenters† have investigated electron extraction from a nickel surface by metastable atoms of Ne, but the most comprehensive investigation is still that of Oliphant‡ on metastable atoms of helium. It is now clear that metastable atoms play a vital role in the mechanism of electric discharge in the rare gases.

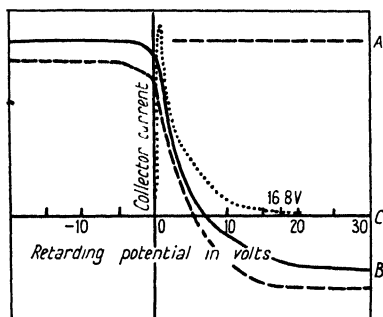


FIG. 255. Retarding potential curves for secondary electrons ejected by the impact of metastable He atoms on a magnesium surface. — freshly deposited surface; - - - surface four hours after deposition; energy distribution of the ejected electrons.

The apparatus used by Oliphant in his investigations was very similar to that shown in Fig. 245, except that the metastable atoms passed right along the axis of the tube and were not reflected from *S*. The tube was originally designed to study secondary electron emission by positive ions, but it was soon evident that electron emission from the target *T* was occurring even when retarding fields prevented any ions from reaching it and that the effects could not have been due to radiation.

By applying different retarding potentials between the collecting cylinder *C* and the target *T* it was possible to study both the energy distribution of the ejected electrons and also the reflection coefficient of the metastable He atoms from the target surface. In most of these experiments the target material was molybdenum, but targets of nickel and magnesium were also studied.

Fig. 255 shows retarding potential curves obtained with a magnesium target. Two curves are shown, one corresponding to a freshly deposited magnesium film, the other to a magnesium film 4 hours after deposition.

† Uytterhoeven, *Phys. Rev.* **31** (1928), 913; Uytterhoeven and Harrington, *ibid.* **36** (1930), 709; Found, *ibid.* **34** (1929), 1625; Langmuir and Found, *ibid.* **39** (1932), 237.

‡ *Proc. Roy. Soc. A*, **124** (1929), 228.

The magnesium was deposited in a thick layer over the target and inside walls of the collecting cylinder by evaporation in the apparatus itself. Since the collector and target were of the same material, errors due to contact potential differences were avoided in this particular measurement.

The gradient of the retardation curve for the freshly deposited film is also plotted in Fig. 255. This curve gives the distribution in energy of the ejected electrons. The maximum energy is 16.8 eV. For helium the energy of the metastable level is 19.7 eV. The work function of a clean magnesium surface is 3.01 eV. The difference between these quantities, which one would expect to be the maximum energy available to the ejected electrons, is 16.7 eV, in good agreement with the measured value of the maximum kinetic energy of the ejected electrons, 16.8 eV.

Oliphant could not measure the number of electrons set free per incident metastable atom since he was unable to measure the flux of metastable atoms incident on his target. He noted, however, that the ejected electron current was the same for metals as widely different in work function as Mo and Mg.

The number of electrons ejected per incident metastable atom has been estimated by Dorrestein† in his experiments on the excitation of the 2^3S and 2^1S metastable states of He by electron impact (Chap. II, § 5.4). For the 2^3S state which could be excited by electrons of energy 19.8 eV—too small to excite the 2^1S state—he estimated that 0.24 electrons were ejected per incident metastable atom incident on a surface of platinum. The corresponding figure for the 2^1S state was 0.48. These estimates were based on the absolute value of helium excitation cross-sections measured by Maier-Leibnitz (Chap. II, § 5.2). They are admittedly rough, but likely to be of the right order of magnitude.‡

6.2. *Reflection of metastable atoms at surfaces*

Referring again to Fig. 255 it seems that the retarding potential curve falls below the voltage axis, the current reversing at about 6 volts, indicating that electrons are being collected also by the target from the collector. These electrons must arise from the collision, with the collector, of metastable atoms scattered from the target. If one can assume that the fraction of metastable atoms which eject electrons is the same for

† *Physica*, **9** (1942), 433, 447.

‡ Fast stable neutral atoms can also eject electrons from surfaces. The process is evidently similar to that of ejection by fast positive ions. Very little work has been done on this effect, but it has been used as a means of detection in studies of ionization by fast neutral atoms (see Chap. VIII, § 3.2, Table 1).

impact on the target or the collector, the ratio of the saturation electron current from the collector to the sum of the saturation electron currents from the target plus collector, i.e. BC/AB in Fig. 255, is a measure of the fraction of the metastable atoms scattered still in an excited state. For fresh magnesium this ratio was about 0.23, but it is clear from Fig. 255 that the ratio is larger for older magnesium surfaces.

For reflection from a molybdenum surface it was found that the ratio varied considerably according to whether the surface had been properly outgassed. Immediately after outgassing it was 0.50, but had dropped to about 0.10 after some hours for metastable atoms of the same energy.

In any given experiment it is very difficult to measure the velocity of the metastable atoms. It would be expected, however, to rise in proportion with the velocity of the positive ions that produce them. Table II shows the reflection coefficient of the metastable He atoms at a molybdenum surface in terms of the energy of the positive ions which produce them.

TABLE II

Reflection Coefficient for Metastable Helium Atoms from a Molybdenum Surface

<i>Energy of ions which produce the metastable atoms (eV)</i>	<i>Reflection coefficient</i>
2,100	0.05
800	0.10 to 0.20
400	0.40 to 0.50
120	0.50

Thus the reflection appears to fall sharply as the energy of the incident metastable atoms is increased.

Oliphant also studied the effect on the reflection coefficient of varying the angle of incidence of the metastable atoms on the surface, and found that it increased markedly with increase of angle of incidence as shown in Table III.

TABLE III

Effect of Angle of Incidence on Reflection Coefficient for Metastable Helium Atoms from a Molybdenum Surface

<i>Energy of positive ions which produce the metastable atoms (eV)</i>	<i>Angle of incidence</i>	<i>Reflection coefficient</i>
600	0°	0.10-0.30
„	45°	0.15-0.40
„	75°	0.40-0.60
200	0°	0.40
„	45°	0.40-0.70
„	75°	0.60-0.90

It is clear that much more experimental work is called for in the study of the interaction of metastable atoms with surfaces.

7. The theory of the interaction of positive ions and metastable atoms with surfaces

7.1. *Introductory remarks*

A clear distinction can be made at the outset between two ways in which a positive ion may supply sufficient energy to a metal electron to enable it to leave the metal. In the first the energy comes from the kinetic energy of translation of the ion relative to the metal, whereas in the second it is made available by changes in the electronic structure of the ion, no change in the translational energy being involved.

The first mechanism, which is responsible for a large part of the secondary electron emission, is similar to that involved in the ionization of an atom by ion impact, and should exhibit the same general features. For slow ions the reaction will be nearly adiabatic and the resultant yield of ejected electrons very small. This yield will increase with ion energy up to a flat maximum at an energy of some thousands of electron volts, after which it will decline slowly. It has already been pointed out in § 2.31 that this is in general agreement with the observations. The low-energy side of the maximum, the near-adiabatic region, cannot be treated theoretically by Born's approximation, the perturbed stationary state method being required. Wooldridge's theory of secondary electron emission by electron impact, which employs Born's approximation, cannot be extended to such conditions.† At energies beyond the maximum Born's approximation may be used, but so far no detailed theoretical treatment has been forthcoming even in this region. It has been suggested by Kapitza‡ that the secondary electron emission due to fast ions could be regarded as a thermionic emission arising as a result of very intense local heating of a surface by the kinetic energy of an incident ion. This theory of intense local heating has been developed by Hippel§ to account for the phenomenon of cathode sputtering and it will be discussed later in that connexion, when its application to the theory of secondary electron emission by positive ions will also be considered.

† The mechanism of collisions with free electrons of the metal, the basis of Kadyshovich's theory of secondary emission by electron impact, could not be of importance for secondary emission by slow ions because the maximum energy communicated to an electron in such a collision is $4m/M$ times the incident ion energy, where m , M are respectively the masses of the electron and the ion. In order to obtain sufficient energy in such a collision to leave the metal incident ions with many thousands of e-volts energy would be needed.

‡ *Phil. Mag.* **45** (1923), 989.

§ *Ann. der Physik*, **81** (1926), 1043; **86** (1928), 1006.

The second mechanism is responsible for the capture of electrons by a positive ion and for the ejection of electrons by metastable atoms. In the former case an electron of the metal is captured into an energy level of the same energy in the field of the ion. The process is exactly analogous to a charge exchange collision in the gas phase:



in which the ionization potentials of the atoms A and B are exactly equal. The ejection of an electron from a metal by a metastable atom is analogous to the ionization of, say, an argon atom by a metastable neon atom, as discussed in Chap. VII, § 9. The energy released by the transition from the metastable to the ground state of the atom is communicated to a metal electron and may be sufficient to raise it out of the metal potential 'box'. In both the analogous gas-phase reactions the probability falls off very slowly with velocity of the ion or atom and is quite large per impact. A similar result should hold for impact with a metal, in agreement with observed data.

7.2. *Energetic relations in resonance transitions near a metal surface*

The energetic relations for these 'resonance' transitions were first discussed by Oliphant and Moon† in terms of the potential box model of a metal described in Chap. V, § 3.1.

The metal is regarded as a box within which the potential energy of an electron is lower than in the surroundings by an amount D . The metal electrons are distributed as a Fermi-Dirac gas so that, at absolute zero, the maximum energy of a metal electron is μ . At higher temperatures there will be some electrons with higher energies, but we shall ignore these. The minimum energy required to remove an electron is then $D - \mu$, which is the work function ϕ of the metal surface.

Suppose now that a positive ion A^+ approaches the surface. Let V_i be the ionization potential of the atom A and V_e the excitation potential of an excited level of this atom. The field and system of energy levels when the ion is at a distance a from the edge of the metal are shown schematically in Fig. 256. If the atom A has a level (either the ground state or an excited level) whose energy is just equal to that of an occupied level of the Fermi distribution, a transition may take place between the electron in the metal and the unoccupied atomic level, through the potential barrier. Such a transition might be expected to have a high probability when the ion is sufficiently close because it occurs between

† *Proc. Roy. Soc. A*, **127** (1930), 388.

two states of equal energy. The condition for it to occur into a level whose excitation potential is V_e can be written

$$D > \epsilon(V_i - V_e) > \phi. \quad \text{I (Capture by a positive ion)}$$

As an example, for a He^+ ion near a surface of Mo, $V_i = 24.47$ volts, $V_e = 19.77$ volts, $\phi = 4.3$ eV, $D = 14$ eV, so that the conditions I are

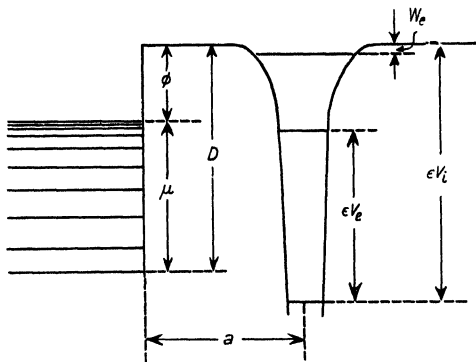


FIG. 256. Schematic representation of the potential energy and energy levels of an electron in the combined field of a metal and an atom at a distance a from the surface.

satisfied. The level for which $V_e = 19.77$ volts is the metastable 2^3S level. Thus the neutral He atom formed in this process will be in a metastable state. Some ions will leave the surface in this state and will account for the observations of Oliphant on the production of metastable He atoms by collision with a metal surface.

An excited atom may itself interact with the metal, however, and a transition may occur in which a second metal electron is ejected as a result of the energy gained when the excited atom falls to its ground state. Equating initial and final energies

$$\epsilon V_e = D - E_i + E_f,$$

where E_i , E_f are respectively the initial energy of the electron in the metal and its final kinetic energy after ejection. The condition for such a transition to occur is

$$\epsilon V_e > \phi. \quad \text{II (Ejection by excited atom with excitation energy } \epsilon V_e)$$

The maximum energy of an ejected electron will be given by

$$E_f(\text{max}) = \epsilon V_e - \phi.$$

In general it will not be possible to distinguish this process from the exchange process in which the metal electron passes to the vacant ground

state of the excited atom and the energy gained is used to eject the electron in the excited state, and in calculations of the transition probability the problem has to be considered as a two-electron system and proper account taken of symmetry. For metastable helium the direct process is very improbable since it would involve a change of spin of the electron in the excited state. Only the exchange process then has to be considered.

An excited atom may be able to capture an electron from a metal, thus forming a negative ion. The condition for this process to occur is

$$D > \epsilon V_e + A > \phi. \quad \text{III (Capture of an electron by an excited atom to form a negative ion)}$$

A is here the electron affinity of the atom.

In some circumstances, if the electron affinity is sufficiently large and the work function of the surface small enough, negative ion formation can occur by the interaction of unexcited neutral atoms with a metal. The condition is

$$D > A > \phi. \quad \text{IV (Capture of an electron by an unexcited atom to form a negative ion)}$$

The only case in which this condition will be satisfied is that of halogen atoms incident on a clean alkali metal surface.†

A positive ion can thus eject an electron from a surface in two stages, represented by process I followed by process II. Alternatively the process may occur in one stage, involving the interaction of two metal electrons moving in the combined field of the metal and the positive ion whereby one electron is captured into the vacant ground state of the ion and the other is ejected. We refer to this as process V.

Similarly, a positive ion can be reflected as a negative ion by a combination of the process I followed by the process III. The probability of this process is reduced by the fact that, in general, $A < \phi$ and there will be a considerable probability of the transition of an electron back into the metal into a vacant state of the Fermi distribution, as is apparent from Fig. 256.

The formation of a negative ion can also occur in a single process involving the interaction of two metal electrons in a manner analogous to process V. We refer to this as process VI.

† This process can occur when neutral, unexcited halogen atoms strike a hot tungsten or molybdenum surface, because, although $A < \phi$, some of the metal electrons will be excited by the high temperature into states from which a transition to the atom to form a negative ion can occur.

7.3. Approximate evaluation of 'resonance' transition rates

It is difficult to develop a detailed theory capable of predicting the chance that a given positive ion will capture an electron, or a given metastable atom will be deactivated, on collision with a given metal surface. In any case insufficient reliable experimental data are available to justify an elaborate analysis. All that has been done up to the present is to calculate approximately the rate $p(a)$, at which electrons are captured from the metal by a positive ion He^+ to form a metastable He atom, when at a distance a from the metal surface, and the corresponding rates $m(a)$, $m^-(a)$ for the ejection of electrons by a metastable atom and capture by the atom to form a negative ion respectively.

As the relative velocity of the ion and metal is very small compared with that of the metallic electrons, it is a good assumption to suppose that the relative motion of ion and metal has a negligible effect on the rate of transition. The chance that a positive ion moving with velocity v which has approached to a distance a from the metal will be neutralized in approaching a distance da may therefore be taken as $p(a) da/v$. What is required is the probability $P(a) da$ that an ion will be neutralized when at a distance between a and $a+da$ from the metal. Since the chance that the ion reaches to a distance a without neutralization will be

$$1 - \int_a^\infty P(a) da,$$

we must have
$$P(a) = \left[1 - \int_a^\infty P(a) da \right] p(a)/v.$$

From this integral equation $P(a)$ may be determined if $p(a)$ is known. The average distance at which neutralization will occur is

$$\bar{a}_p = \int_0^\infty a P(a) da.$$

A similar analysis applies to determine the probabilities $M(a)$, $M^-(a)$ for the respective transitions involving metastable atoms and the corresponding average transition distances $\bar{a}_m$, $\bar{a}_m^-$.

Cobas and Lamb† have made approximate calculations of $p(a)$ and $m(a)$ for helium using standard quantal formulae for the transition probability but, of necessity, rather crude approximations for the wave functions of the metal electrons. They find that $\bar{a}_p$, the mean distance for neutralization of a positive ion, has the respective values

† *Phys. Rev.* **65** (1944), 327.

5.8 and 3.2×10^{-8} cm. for ions of 0.02 and 1,800 eV energy respectively. These distances are considerably greater than the corresponding ones, 1.0 and 0.05×10^{-8} cm., for deactivation of a metastable atom.

These values are consistent with the assumption that the extraction

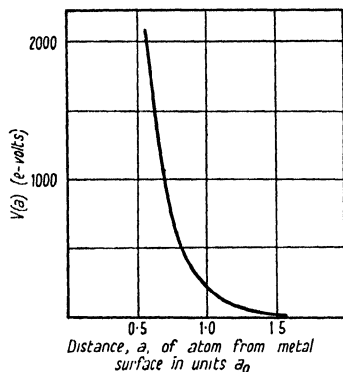


FIG. 257. Interaction energy $V(a)$ between a metal and a metastable helium atom at a distance a from its surface derived from observed reflection coefficients for metastable atoms of different energies.

of electrons by He^+ ions takes place in two stages. On the average the ion is first neutralized at a comparatively large distance from the surface to form a metastable atom. If this atom penetrates close enough it will be deactivated in ejecting a metallic electron. The rather large value of $\bar{a}_p$ suggests that an ion beam should be completely transformed into metastable atoms if the process is energetically possible. The fact that this does not occur completely (see § 3) must mean that the chance of the reverse transition, ionization of the atom by capture of an electron into the vacant state within the metal, is large.

If the chance $r(E)$ that a metastable atom of given energy E be reflected without deactivation from a surface is known, it is possible, by solving the equation

$$\int_{a_c}^{\infty} M(a) da = 1 - r(E),$$

to determine the closest distance of approach a_c of a metastable atom of energy E to the metal surface. If this can be done for a sufficiently wide range of energies E , the potential field $V(a)$ exerted by the metal on the atom at distance a may be determined. Cobas and Lamb have illustrated this procedure for He by using the rough reflection coefficients found by Oliphant (see § 6.2, Table II). Their results, which must be regarded as illustrative only, are shown in Fig. 257.

No satisfactory theory of the angular dependence or velocity distribution of the ejected electrons has yet been given.

The alternative process in which an excited atom gives up its energy to extract an electron from a metal surface to form a negative ion (process III above) has been investigated by Smith,[†] who calculated $m^-(a)$ for the case of Hg^+ and H^+ ions and a nickel surface. For Hg^+ ions

[†] *Proc. Roy. Soc. A*, **168** (1938), 19.

approaching a nickel surface with energy 200 eV, he calculates the average probability that they should leave as negative ions as 1.4×10^{-3} , compared with the experimental value of 0.64×10^{-3} , obtained by Arnot and Milligan.[†] He pointed out also that the probability of the formation of H^- ions from H_2^+ ions incident on nickel would be expected to be very small (as observed) since the only available mechanisms appear to involve excitation of the incident H_2^+ ion on impact with the surface, or the simultaneous capture of two electrons from the metal (process VI). No calculations for such a process have been made.

One of the difficulties of the above calculations is that no account is taken of loss of energy of the incident ion in interaction with the crystal lattice of the metal. This would imply that the particles move away from the surface with the same velocity as they approach it. It has been seen, however, that, at least in the case of positive ion reflection and of the production of negative ions, this is certainly not the case. In his theory of negative ion production Smith introduces an empirical expression to take account of this change in velocity.

No calculations have been made of the probability of ejection of negative ions from an adsorbed layer on the surface of a metal by incident positive ions. This process probably occurs in three stages. First the incident positive ion captures a metal electron into a metastable state (process I). The metastable atom then transfers its excitation energy to an adsorbed atom on the surface by a collision of the second kind, and the latter then captures an electron from the surface to form a negative ion.

It is clear that while the calculations show that the processes described above are important, a great deal more work is required for the full interpretation of experimental results on the interaction of positive ions with a metal surface.

8. The role of positive ion-cathode surface interaction in the mechanism of the Geiger-Müller counter

The considerations of § 7 have an interesting application in the interpretation of the quenching mechanism of a Geiger-Müller counter. These counters consist of a fine wire, a few thousandths of an inch diameter, stretched along the axis of a metal cylinder a few cm. in diameter, the whole tube being filled with a gas such as argon at a pressure of about 10 cm. Hg. A potential of the order of 1,000 volts is applied between the two electrodes with the cylinder as cathode. If an ionizing particle passes through the counter, the electrons produced are accelerated towards the wire and in the intense field near the fine wire a large number of additional ions are produced. Amplification factors between 10^8 and 10^{12} are common in actual counters.

[†] Loc. cit.

The sheath of positive ions produced round the wire moves to the cathode and current flows through an external circuit.

Some of the positive ions arriving at the cathode will eject secondary electrons which, being accelerated towards the wire, will start the process all over again. Thus generally the breakdown, once started, will continue. In the earlier counters the discharge was interrupted by passing the cathode current through a high resistance (10^9 – 10^{10} ohms) which reduced the wire-cathode potential difference and stopped the discharge. However, with such a high external resistance the time constant of the counter circuit was of the order of 0.1 sec. and counting rates above a few hundreds per minute were not possible.

Trost† showed that by introducing a certain amount of alcohol vapour or some other polyatomic gas the counter could be made self-quenching, the external high resistance could be dispensed with, and very high counting rates employed. Successful self-quenching counters can be made using as filling a gas such as methane, or a mixture of 90 per cent. argon with 10 per cent. alcohol vapour.

The role of the polyatomic gas in the self-quenching counter discharge has been discussed by Korff and Present.‡

Since the discharge in an argon-filled counter is carried on after the passage of the initial sheath of positive ions by secondary emission from the cathode, the presence of the polyatomic gas or vapour in the self-quenching counter must prevent this secondary emission. Owing to the comparatively high gas pressure in the counter the mean kinetic energy of the positive ions reaching the cathode is only of the order of 0.1 eV, so that the mechanism of secondary electron emission must consist of a combination of processes I and II of § 7.2. The positive ion is first neutralized by the capture of an electron from the cathode into an excited state at a distance of about 5×10^{-8} cm. from the wall. To eject an electron from the metal in process II, the excited atom must approach closer, to a distance of the order of 10^{-8} cm. from the surface. If the excited atom has an energy of about 0.1 eV, the time after neutralization before electron ejection occurs is of the order of 2×10^{-12} sec. If the counter gas is argon, the radiative lifetime of the excited state formed on neutralization is 10^{-7} sec. Accordingly many of the argon atoms will give up their energy by liberating electrons from the cathode surface.

If, on the other hand, the counter gas is methane for which the ionization energy I is 14.5 eV, and the cathode is copper, for which the work function is 4.2 eV, neutralized methane molecules may be formed in a state of excitation 10.3 eV. But spectroscopic evidence indicates that methane molecules with an excitation energy above 8.5 eV dissociate in a time of the order of 10^{-13} sec.§ Combining this figure with the time of 2×10^{-12} sec. before secondary emission from the surface can occur, only about one molecule in 10^9 will give rise to secondary emission.

The average number of ions in the sheath reaching the cathode as a result of the initial avalanche is of order of 10^9 . Although these figures are approximate only, they suffice to show that a considerable fraction of the particles counted will produce single pulses not prolonged by secondary emission from the cathode.

To explain the self-quenching action of counters containing a mixture of argon

† *Zeits. f. Phys.* **105** (1937), 399.

‡ *Phys. Rev.* **65** (1944), 274.

§ Excited molecules could also be formed with any excitation energy down to $I - D$, where D is the depth of the Fermi distribution. If this is less than 8.5 eV an excited level could be formed in a state that does not lead to dissociation. This would invalidate some of the following arguments. From the fact that self-quenching does occur one should perhaps conclude that no such level is available.

and alcohol vapour, it is assumed that although many of the initial positive ions are A^+ ions, charge exchange is possible with the alcohol molecules since the ionization potential of the ethyl alcohol is less than that of argon. On the other hand, since the mean energy of the positive ions is only a fraction of an e-volt, the inverse charge transfer process is not possible energetically. Consequently by the time the cathode is reached the positive ion beam is composed almost entirely

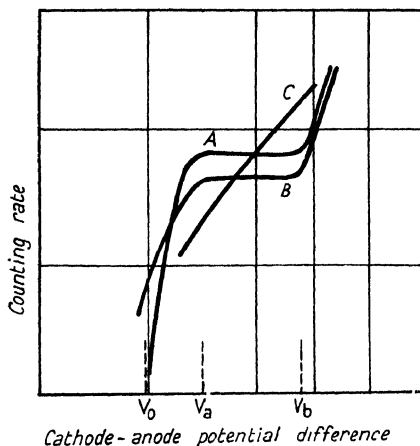


FIG. 258. Counting rate as a function of cathode-anode difference of potential for a methane-filled counter.

Curve A: pure methane at pressure of 9 cm. Hg.

Curve B: methane at a partial pressure of 9 cm. Hg together with argon at a partial pressure of 1.5 cm. Hg.

Curve C: methane at a partial pressure of 9 cm. Hg together with water vapour at a partial pressure of 1.5 cm. Hg.

of alcohol ions which dissociate on electron capture by the same process as that described for methane.†

There is considerable experimental evidence in support of the theory of Korff and Present. If for a given counter exposed to a constant radiation source the counting rate is plotted as a function of potential difference between cathode and anode, a curve such as that of Fig. 258, curve A is obtained. This represents an actual curve obtained for a counter filled with pure methane at a pressure of 9 cm. Hg. Until a certain minimum potential difference V_0 is reached no pulses are obtained. The counting rate then increases rapidly until the potential difference is V_a . Between V_a and V_b , a range of about 50–100 volts, the counting rate is independent of the potential difference, while above it increases rapidly. The region between V_a and V_b is the working region of the counter and is referred to as the plateau. In passing from V_a to V_b the average number of positive ions reaching the

† The discharge could also be continued in counters containing a mixture of gases by photons emitted from excited argon atoms produced in the initial avalanche. It is suggested that this radiation is absorbed by the alcohol molecules and photo-dissociation results before the excited molecules can eject photo-electrons from the cathode.

cathode in a single pulse increases from 10^9 to 10^{10} . As a result one would expect the number of multiple pulses to increase between V_a and V_b . This is exactly as observed.

Curve *B* of Fig. 259 is for the same counter but containing in addition to the methane, argon at a partial pressure of 1.5 cm. Hg. There is no change in the extent of the plateau. The argon has a higher ionization potential than the methane and the positive ions reaching the cathode are still almost entirely those of methane. Curve *C* shows a similar curve with water vapour of pressure 1.5 cm. Hg added. The plateau has disappeared. Water vapour has a lower ionization potential than methane and the positive ions reaching the cathode are now predominantly those of water vapour which cannot quench the secondary emission.

The most convincing evidence for the theory has been obtained by Friedland† and by Farmer and Brown,‡ who examined by means of a mass spectrograph the nature of the molecules present in a counter at different stages in its lifetime. They showed conclusively that during the lifetime of the counter the concentration of the polyatomic gas decreases markedly and the products of its dissociation increase. The disappearance of the quenching vapour in this way is one of the reasons for the eventual failure of counters of this type.

9. Cathode sputtering§

9.1. *The measurement of the rate of sputtering*

The phenomenon of cathode sputtering has been known for nearly a century, since the observations of Grove|| in 1852 and Plücker†† in 1858. Many hundreds of investigations of the phenomenon have been carried out during that time. It is therefore rather surprising that even today the phenomenon cannot be said to be fully understood, and reliable data on its magnitude are still available for only a limited number of cathode materials and types of ion.

The difficulty with most of the measurements of cathode sputtering is that they have generally been made in a gaseous discharge at pressures of the order of 1 mm. of Hg, and under these conditions the gas-kinetic mean free path l is small compared with the dimensions of the sputtering chamber. Sputtered atoms, after leaving the cathode, undergo collisions with the gas molecules in the discharge tube so that many of them diffuse back to the cathode. The rate of loss of material is then determined by the difference between the rate of sputtering and this rate of rediffusion. The rediffusion rate clearly depends on the gas pressure in the discharge and on the geometry. As a result the apparent sputtering rate increases as the pressure decreases until the mean free path is of the

† *Phys. Rev.* **74** (1948), 898.

‡ *Ibid.* 902.

§ A chapter on sputtering is to be found in Glockler and Lind, *Electro-chemistry of Gases and other Dielectrics*, pp. 400–29 (John Wiley, New York, 1939).

|| *Phil. Trans. Roy. Soc.* **142** (1852), 87.

†† *Pogg. Ann.* **103** (1858), 90; **105** (1858), 67.

order of the dimensions of the apparatus in which the sputtering occurs, below which it will be independent of pressure.

The effect of discharge tube geometry is shown clearly in Fig. 259, which represents the results of measurements by Güntherschulze and Meyer,[†] plotted by Penning and Moubis.[‡] In this figure the sputtering rate for positive ions of energy 500 eV is plotted against the product pd

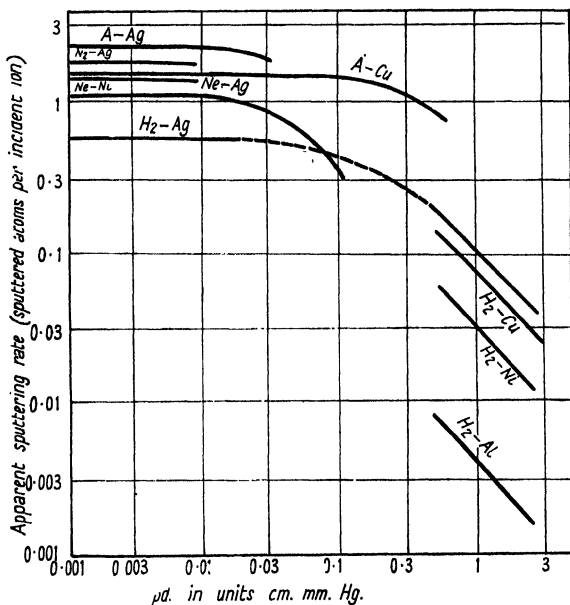


FIG. 259. Apparent sputtering rate as a function of the product of the pressure and cathode-anode separation, illustrating the effect of diffusion.

of the gas pressure p in mm. Hg and the cathode-anode separation d in cm. The ordinates in this figure represent the apparent number of sputtered atoms per incident positive ion as estimated by the current to the target. This is not quite equal to the true sputtering rate because correction is not made for the contribution to the cathode current arising from secondary electron emission, nor for the fraction of the sputtered atoms returning to the target.

For small values of pd , when $l \gg d$, the apparent sputtering rate is independent of pd . As pd increases, however, and l becomes comparable with or less than d the apparent sputtering rate decreases markedly owing to diffusion back to the target.

[†] *Zeits. f. Phys.* **62** (1930), 607.

[‡] *Proc. Amst. Acad.* **43** (1940), 41.

Some investigators have sought to overcome the effect of back diffusion by using a wire as cathode in a sputtering arrangement. If the wire is made sufficiently fine, one would expect that the chance of it being struck by a sputtered atom diffusing back would be very small. Thus Kingdon and Langmuir† used a wire to study the sputtering of thorium from the surface of a thoriated tungsten cathode, measuring the rate of loss of thorium from the cathode by the change in thermionic emission that occurred. Similarly in a careful series of measurements carried out by the research staff of the General Electric Company (London)‡ a triode was employed, the sputtering of the tungsten wire grid being measured. In this arrangement ionization was produced by means of a potential applied between cathode and anode, the negatively charged grid pulling in ions from the gas, and the rate of sputtering was measured by the change in electrical resistance of the grid.

Fetz§ has shown, however, that, even in the case of positive ion bombardment of a wire in a good vacuum, when no question of diffusion could arise, the sputtering rate of a very fine molybdenum wire was 4 or 5 times as great as the rate for a plane sheet of molybdenum, so that sputtering rates observed using the 'wire' technique would be expected to be different from those observed for plane cathodes.

Although the rate of sputtering observed from the cathode of a glow discharge would be expected to be very dependent on the discharge conditions and geometry, one might expect that the relative rates of sputtering of different materials in the same gas would be unaffected. Different observers, however, differ considerably in assigning the relative rates of sputtering. The reason is that the surface conditions of the cathode play a considerable role in the sputtering phenomenon. The presence of a layer of oxide will greatly reduce the sputtering rate.

Most observers have found that the rate of sputtering increases to a steady value after the cathode has been subjected to positive ion bombardment for some time and have assumed this to arise from the removal of an absorbed layer of gas on the cathode surface by the bombardment. Güntherschulze|| has suggested, however, that the change of rate of sputtering with time of bombardment may arise from a change in the nature of the surface of the cathode as a result of material diffusing back to the target and depositing there in the form of a powder.

It is clear from these considerations that the most reliable measure-

† *Phys. Rev.* **20** (1922), 108; **21** (1923), 210; **22** (1923), 148.

‡ *Phil. Mag.* **45** (1923), 98.

§ *Zeits. f. Phys.* **119** (1942), 590.

|| *Ibid.* **36** (1926), 563.

ments on cathode sputtering are those carried out at pressures so small that diffusion is not an important consideration. For this purpose it is necessary to pull the ions away from the discharge plasma and accelerate them on to the sputtering electrode away from the discharge. Güntherschulze and Meyer† carried out measurements along these lines under conditions in which the pressure near the sputtering apparatus was in the neighbourhood of 10^{-3} to 10^{-4} mm. Hg. Their apparatus is illustrated in Fig. 260. The discharge took place between the hot cathode K and the anode A , of silver. Ions were pulled out of A and accelerated to the sputtering electrode Z . This was suspended from the spring F which served as a spring balance to determine the loss of weight of Z . Three small markers, B , on the suspension of Z and three stationary marks, C , on the glass served to measure the displacement of Z due to the loss of weight. G was a glass plate which prevented the discharge reaching the upper part of the tube and also facilitated centring. It was found that the rate of sputtering of silver by argon ions was independent of pressure at pressures below 0.01 mm. Hg.

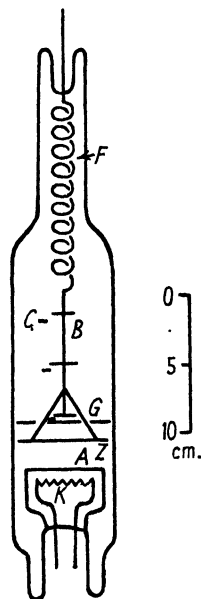


FIG. 260. Apparatus used by Güntherschulze and Meyer for the study of sputtering rate.

Studies of sputtering processes in a good vacuum have also been made by Oliphant‡ using positive alkali ions from a Kunsman source, and more recently Timoshenko§ has studied the sputtering produced by argon ions drawn out from an argon discharge into a region of high vacuum. Penning and Moubis|| have also carried out careful measurements of the sputtering rate in a good vacuum for argon ions on copper.

One of the difficulties in the determination of the sputtering rate is the measurement of the actual positive ion current incident on the metal. Allowance has to be made particularly for the contribution to this current arising from secondary electrons. Timoshenko was able to measure the secondary emission by application of a retarding field, and Penning and Moubis bent many of the secondary electrons back to the

† Loc. cit.

§ *J. App. Phys.* **12** (1941), 69.

‡ *Proc. Camb. Phil. Soc.* **24** (1928), 451.

|| *Proc. Amst. Acad.* **43** (1940), 41.

cathode by means of a magnetic field, but secondary electrons were included in the currents measured by Güntherschulze and Meyer.†

The apparatus used by Penning and Moubis is shown in Fig. 261. The cathode *C* consisted of a water-cooled copper cylinder with two

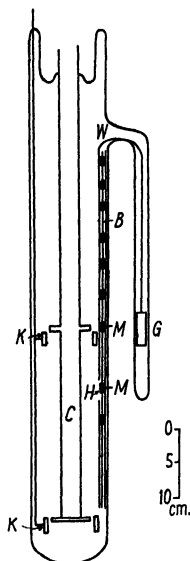


FIG. 261. Apparatus used by Penning and Moubis for the measurement of sputtering rate.

flat end-plates. It was coated electrolytically with the material being studied. The amount of sputtering was determined by measuring the increase in weight of small mica disks *M* during the experiment. These disks were attached to a wire *W* which moved inside a tubular holder *B*, with a small window *H* in it. Different mica disks could be brought opposite this window by using a magnet outside the tube to move the weight *G*. The two rings *K* constituted the anode of the discharge. An axial magnetic field, by increasing the electron paths to the anode *K*, made possible the operation of the discharge at a lower pressure than would have been possible without it. The magnetic field also had the advantages of greatly reducing the importance of secondary electron emission from the cathode and of enabling the current density, potential difference, and pressure of the discharge to be varied independently. In ordinary glow discharges only two of these three quantities may be varied independently.

An interesting alternative arrangement which enables the measurement of sputtering rates in a glow discharge to be made, in spite of diffusion effects, has been described by Güntherschulze.‡ A tube *T* of the material whose sputtering rate is being investigated constituted the cathode and a copper wire *F* along the axis of the tube, the anode. The sputtered material built up a pressure inside the apparatus until equilibrium was reached. In these circumstances the amount of material deposited per unit time per sq. cm. of cathode was equal to the amount sputtered per unit time per sq. cm. If it is assumed that the pressure of the sputtered material is the same throughout the discharge, then the rate of deposition per unit area on the wire is also equal to the rate of sputtering per unit area. By measuring the increase in weight of the wire after a certain time he was able to calculate the sputtering

† Loc. cit.

‡ *Zeits. f. Phys.* **118** (1941), 145; **119** (1942), 79.

rate, making suitable allowance for secondary electron emission. Using this method Güntherschulze obtained a value for the rate of sputtering of copper by argon ions agreeing within $1\frac{1}{2}$ per cent. with that obtained by Penning and Moubis† using good vacuum conditions.

It is clear, however, that there is considerable need for more accurate sputtering measurements using good vacuum conditions, and in view of the facilities for producing ion beams now existing in many laboratories such measurements should not be long delayed.

9.2. *Results of measurements on sputtering*

9.21. *Dependence of the rate of sputtering on the ion energy.* In the region of incident ion energies up to a few thousand eV, most observers have found a relation of the type

$$S = a(V - V_0),$$

where S is the number of sputtered atoms per incident ion, V the potential difference between cathode and anode, and a and V_0 constants. For most materials V_0 has a value of the order of 100 volts. It should be remembered, however, that in the types of experiment in which this relation has been found to hold, the sputtering electrode was the cathode of a glow discharge so that the positive ions incident on the cathode were spread over a considerable range of energies.

In his experiments on the sputtering of copper by ions of Ne, A, He, and H_2 using the 'equilibrium' method described above, Güntherschulze also obtained a relation of this type, V_0 being about 300 volts, but in his earlier experiments with Meyer, employing a better vacuum, the curves of S against ion energy were usually found to be straight lines passing through the origin for energies up to about 1,000 eV. At higher energies the increase of sputtering rate with energy was less rapid.

Fig. 262 shows typical results obtained by Güntherschulze and Meyer† and Penning and Moubis† for the variation with incident ion energy of the sputtering rate of various materials by A^+ , N^+ , Ne^+ , H_2^+ , and Hg^+ ions. Quite a different kind of variation has been obtained by Timoshenko† for the sputtering of silver by argon ions. His curve showed a sharp rise with voltage at about 3 kV. There is some uncertainty, however, in Timoshenko's measurements about the actual current striking his sputtered specimen. It was not measured directly but was estimated on the assumption that his ion beam was uniform over its section. Departure from validity of this assumption at some ion energies could cause uncertainty in the sputtering rate-energy curve.

† Loc. cit.

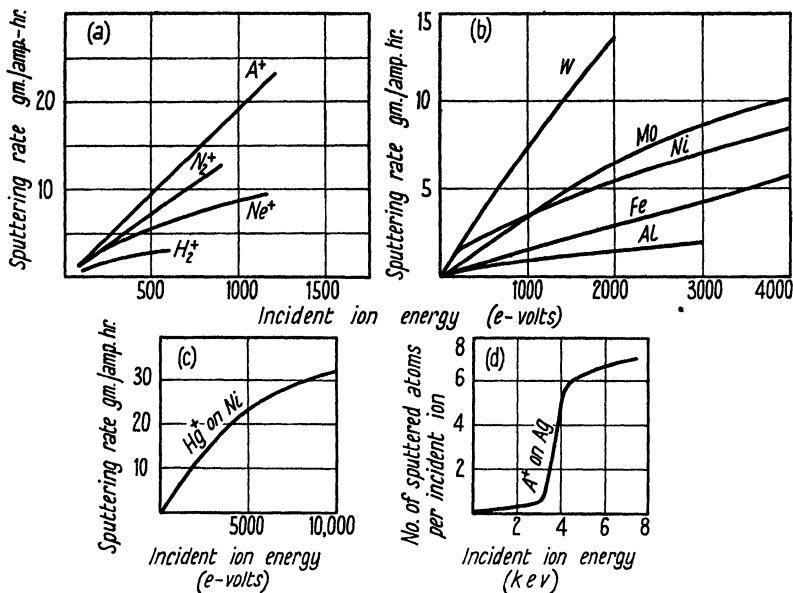


FIG. 262. Observed variation of rate of sputtering with ion energy.

- (a) Ag target sputtered by H_2^+ , Ne^+ , N_2^+ , A^+ ions.
 (b) Targets of W, Mo, Ni, Fe, Al sputtered by Hg^+ ions.
 (c) Ni target sputtered by Hg^+ ions.
 (d) Ag target sputtered by A^+ ions (observed by Timoshenko).

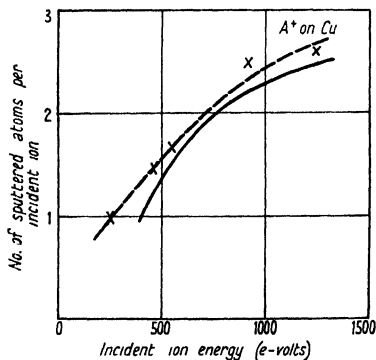


FIG. 263. Variation with ion energy of sputtering rate of Cu by A^+ ions. ——— Penning and Moubis;
 - - - - Güntherschulze and Meyer.

It should be remembered that the curves given in Fig. 262 show the measured sputtering rate. In the experiments giving these results the

apparent positive ion current included a contribution from secondary electrons. This contribution will increase with incident ion energy (§ 2.31). The true sputtering rate will accordingly be greater than the apparent sputtering rate and the ratio of the two will increase with increasing ion energy. Thus the true sputtering rate would probably show a more linear variation with ion energy than appears to be the case in Fig. 262.

Fig. 263, which shows the results of measurements of sputtering of Cu by A^+ ions by Güntherschulze and Meyer and by Penning and Moubis, gives an indication of the compatibility of results obtained by different investigators in experiments of this type.

The values given in Fig. 263 are not corrected for secondary electron emission.

9.22. *Variation of the rate of sputtering with the nature of the sputtered material.* Table IV shows the influence of the sputtered material on the sputtering rate for a number of different ions. This table does not contain all the measurements that have been made. Only those measurements are included for which the effect of diffusion in reducing the apparent rate of sputtering is unimportant. ϑ_{500} and γ are respectively the true number of sputtered atoms per ion and secondary electron emission coefficient for ions of energy 500 eV.

In Table IV the elements marked with an asterisk are those that amalgamate with mercury. The sputtering rate of these materials by Hg^+ ions is appreciably greater than that for materials that do not amalgamate. In fact for the latter group the sputtering rate, expressed as numbers of sputtered atoms per incident ion, is nearly constant. These measurements suggest strongly that, provided chemical action does not occur at the sputtering electrode, the number of sputtered atoms per incident ion is nearly independent of the electrode metal.

9.23. *Influence of the nature of the sputtering ion on the rate of sputtering.* Most observers agree that the sputtering rate increases with the atomic weight of the bombarding ion, but at a rate considerably less than proportional to the atomic weight. This tendency is clearly evident in the curves of Fig. 262.

Chemical action between the sputtering gas and the target material may, however, cause anomalies, as is the case for the sputtering of some materials by H_2^+ or O_2^+ ions, owing to hydride or oxide formation.†

9.24. *Influence of target temperature on sputtering rate.* The evidence

† Güntherschulze, *Zeits. f. Phys.* **38** (1926), 575; Blechschmidt, *Ann. der Physik*, **81** (1926), 999.

TABLE IV

Sputtering by Ions of Energy 500 eV

<i>Sputtering ion</i>	<i>Sputtered metal</i>	<i>Sputtering rate gm./amp. hr. for 500 eV ions</i>	$\delta_{500}/(1+\gamma)$	δ_{500}	<i>Heat of evaporation cal./gm.</i>	<i>References</i>
He ⁺	Cu	0.97	0.40	..	50.8	4
Ne ⁺	Cu	4.06	1.67	..	50.8	4
Ne ⁺	Ag	5.5	1.34	..	45	1
A ⁺	Al	0.78	0.75	0.83	48	3
A ⁺	Cu	4.13	1.7	1.9	50.8	3
A ⁺	Cu	4.08	1.67	..	50.8	4
A ⁺	Ni	9.5	1.2	1.35	..	3
A ⁺	Ag	5.7	1.4	1.5	45	3
A ⁺	Ag	9.5	2.32	..	45	1
H ₂ ⁺	Cu	0.97	0.40	..	50.8	4
H ₂ ⁺	Ni	0.31	0.14	0.15	..	3
H ₂ ⁺	Ag	2.7	0.67	..	45	1
H ₃ ⁺	Ag	1.92	0.47	0.56	45	3
N ₂ ⁺	Ag	7.0	1.71	..	45	1
Hg ⁺	Be*	0.24	0.62	..	..	2
Hg ⁺	Al	0.55	0.53	..	48	2
Hg ⁺	Si	0.56	0.52	..	44	2
Hg ⁺	Cr*	1.75	0.89	..	..	2
Hg ⁺	Mn	1.13	0.54	..	..	2
Hg ⁺	Co*	1.72	0.77	..	..	2
Hg ⁺	Cu*	3.45	1.42	..	50.8	2
Hg ⁺	Zr	1.70	0.49	..	..	2
Hg ⁺	Mo	1.96	0.54	..	177	2
Hg ⁺	Pd*	5.21	1.28	..	45	2
Hg ⁺	Ag*	10.23	2.50	..	45	2
Hg ⁺	Ta	3.70	0.54	..	..	2
Hg ⁺	W	3.83	0.55	..	218	2
Hg ⁺	Pt*	7.88	1.07	..	127	2

References

1. Güntherschulze and Meyer, *Zeits. f. Phys.* **62** (1930), 607.
2. Meyer and Güntherschulze, *ibid.* **71** (1931), 279.
3. Penning and Moubis, *Proc. Amst. Acad.* **43** (1940), 41.
4. Güntherschulze, *Zeits. f. Phys.* **118** (1941), 145.

concerning the influence of temperature on the sputtering rate is a little conflicting. Most earlier workers found no effect that could not be explained as due to the removal of adsorbed layers of gas at higher temperatures. However, Ingersoll and Sordahl† reported an increase with temperature near 1,000° C. in the sputtering rate of Au, Ni, and Pt by A⁺ ions, and the measurements of Fetz‡ on the sputtering of a very fine Mo wire by Hg⁺ ions indicated that the sputtering rate practically doubled when the temperature rose from 400° C. to 1,000° C.

† *Phys. Rev.* **32** (1928), 649.‡ *Loc. cit.*

9.25. Influence of surface conditions on sputtering rate. Surface impurities and adsorbed layers of gas have a marked influence on the rate of sputtering. Fig. 264 illustrates the variation with time of the rate of sputtering of a Mo wire by Hg^+ ions of energy 150 eV obtained by Fetz.† It is necessary therefore, in accurate determinations of sputtering rates, to avoid measuring until surface layers have been removed.

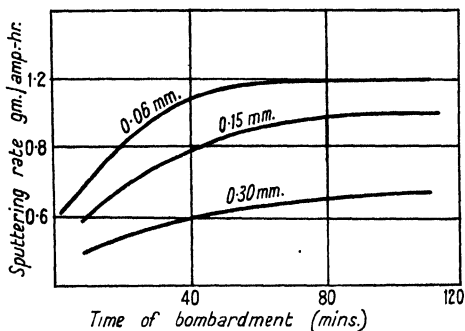


FIG. 264.

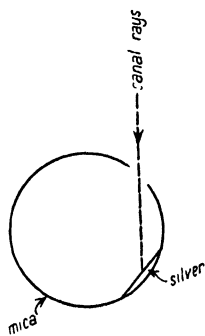


FIG. 265.

FIG. 264. Variation with time of the sputtering rate of a Mo wire by Hg^+ ions of energy 150 eV. The numbers on the curves refer to the pressure in mm. Hg.

FIG. 265. Illustrating the arrangement of Seeliger and Sommermeyer for studying the angular distribution of the sputtered material.

The effect of the presence of surface layers appears, in general, to be to decrease the sputtering rate from that characteristic of the underlying metal. For example, it was long thought that the rate of sputtering from aluminium was extremely small. It has been shown, however, that when care is taken to remove the oxide layer the sputtering rate from aluminium is quite normal.‡

9.26. Angular distribution of sputtered material. Seeliger and Sommermeyer§ studied the angular distribution of atoms sputtered by a beam of A^+ ions of energy between 5,000 and 10,000 eV impinging on a surface of silver or of liquid gallium.

The apparatus used is shown diagrammatically in Fig. 265. A beam of argon canal rays entered a mica cylinder *in vacuo* and were incident on a narrow strip of silver or molten gallium lying along a generator of the cylinder.

They found that the mica cylinder was covered uniformly with a sputtered deposit. The uniform deposit indicated a cosine law of

† Loc. cit.

‡ See, for example, Kueck and Brewer, *Rev. Sci. Inst.* **3** (1932), 427.§ *Zeits. f. Phys.* **93** (1935), 692.

distribution of the sputtered material. The direction of the canal rays in the energy range investigated has no influence on the angular distribution of the sputtered atoms.

9.27. Nature of the material ejected by sputtering. Baum† studied the sputtering of silver in a hydrogen discharge in the presence of a magnetic field and concluded that the sputtered particles left the cathode uncharged. On the other hand, Sommermeyer‡ studied the transport of sputtered metal from the cathode to the anode and found that some of it at least appeared to follow the lines of force, behaving as if negatively charged. It may be that some negative ions are formed in processes similar to those discussed in § 4.

Hippel§ found that sputtered metal such as Cd, Zn, or Ag gave characteristic atomic spectra in the neighbourhood of the cathode.

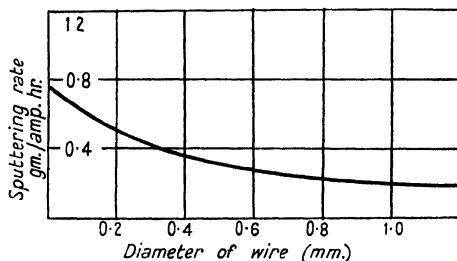


FIG. 266. Variation with wire diameter of the sputtering rate of Mo wires by Hg^+ ions (Fetz).

9.28. Influence of angle of incidence of the ion beam on the sputtering rate. As has been mentioned above, Fetz,|| in a study of the sputtering of molybdenum wire by Hg^+ ions in a discharge of pressure 10^{-3} mm. Hg, where diffusion effects would not be expected to be of much importance, has found that the sputtering rate increases as the diameter of the wire decreases. His results are illustrated in Fig. 266. As the diameter of the wire increases the observed sputtering rate approximates to that observed for a plane surface. These results were interpreted to mean that the probability of sputtering increased with angle of incidence of the incident ions. As the diameter of the wire increases, a greater fraction of the ions strike the wire almost normally. It is evident, however, that more direct experiments are needed on the effect of angle of incidence of the ions in order to establish the validity of this interpretation.

† *Zeits. f. Phys.* **40** (1927), 886.

§ *Ann. der Physik*, **80** (1926), 672.

|| Loc. cit.

‡ *Phys. Zeits.* **34** (1933), 582.

9.29. Sputtering of alloys. A certain amount of work has been carried out on the sputtering of alloys,[†] and it seems that alloys sputter in much the same way as the pure metals would individually. Thus in an alloy of copper and gold, the gold sputters more readily than the copper.

9.3. Theories of cathode sputtering

Several theories have been proposed to account for cathode sputtering and each seems to contain at least part of the truth. It seems probable that the actual process of sputtering is not a simple one and may in fact be a combination of a number of different processes.

In the first place some of the sputtering undoubtedly arises from chemical effects. Güntherschulze[‡] has shown that the phenomena occurring in this type of sputtering are often qualitatively different from those that arise in the more usual sputtering processes. For example, in sputtering of certain materials in hydrogen, when hydride formation is possible no sputtered material at all is observed on the walls of the discharge tube in the neighbourhood of the cathode, whereas in the usual type of sputtering the sputtered deposit is most intense near the cathode. He concluded that hydrides formed at the cathode diffuse into the discharge in a gaseous state and are then decomposed into the metals and hydrogen. Evidently decomposition of the hydride does not take place at the part of the discharge near the cathode where the walls are clear. A further discussion of this type of sputtering is beyond the scope of this book. It is discussed by Glockler and Lind in their book *Electrochemistry of Gases and other Dielectrics* (John Wiley & Sons), Chap. XIX.

One of the earlier views of sputtering supposed it to arise from a physical disruption of the metal arising from the expansion of occluded gases under the influence of ion bombardment. But sputtering occurs also with metals at very high temperature and with liquids, where there is little adsorbed gas, so that this could at best be a partial explanation.

On the basis of their study of sputtering of thorium from the surface of a thoriated tungsten wire, Kingdon and Langmuir[§] developed the momentum interchange theory. According to this theory, ion bombardment first causes thorium atoms to be driven into the tungsten surface, thus creating a large number of depressions of atomic dimensions in the surface. After a time a second ion is reflected back by the thorium atom in the depression and on its way out may still possess sufficient energy to dislodge a second thorium atom. The thorium atom will be

[†] Asada and Quasebarth, *Zeits. f. phys. Chem. A*, **143** (1929), 435.

[‡] *Zeits. f. Phys.* **36** (1926), 563.

[§] *Phys. Rev.* **20** (1922), 108; **21** (1923), 210; **22** (1923), 148.

sputtered if the energy it receives in this second collision is greater than the atomic heat of evaporation—18.8 eV in this case.

If the collisions are elastic the maximum energy E , received by the cathode atom at the impact, is given by

$$E = 4E_0 mm'/(m' + m)^2,$$

where E_0 is the energy of the incident ion and m, m' are the masses of an atom of the cathode material and of the incident ion respectively. It is clear that this theory predicts the existence of a definite threshold energy of the incident ion for sputtering to occur, since it is necessary to communicate to a cathode atom an energy at least equal to the heat of evaporation. In their experiments Kingdon and Langmuir found evidence for the existence of a definite threshold—although, as we have seen (§ 9.21), later work seems to have thrown some doubt on this—and they found reasonable agreement between their calculations and observations for light ions, except for He^+ . The agreement was not good for heavy ions.

Lamar and Compton† have extended the momentum transfer theory to calculate the rate of sputtering in addition to the threshold for sputtering. They assumed the atoms to behave like elastic spheres in collision and were able to set reasonable upper and lower limits to the sputtering rate.

It is difficult, however, to reconcile the momentum transfer theory with the results of the experiments of Seeliger and Sommermeyer‡ described above which indicate no relationship between the direction of motion of the sputtered atoms and the direction of the incident ions. On the other hand, the experiments of Fetz‡ on the importance of angle of incidence of the ions on the total amount of sputtering would be explicable on a momentum transfer theory.

The most widely accepted theory of cathode sputtering is the evaporation theory, which has been developed particularly by Hippel and Blechschmidt§ and more recently by Townes.|| According to this theory an ion delivers its energy almost instantaneously to a small hemispherical region which becomes heated to such a high temperature that some of the atoms receive a sufficiently high energy to leave the metal. It is assumed that the energy transfer from the ion to the metal occurs so quickly that there is little chance of the heat being radiated fast enough

† *Science*, **80** (1934), 541.

§ *Ann. der Physik*, **81** (1926), 1043; **86** (1928), 1006.

|| *Phys. Rev.* **65** (1944), 319.

‡ *Loc. cit.*

to prevent a very high local temperature being obtained. We follow here the treatment given by Townes.

The impact of an ion, of energy E_0 ergs, on the surface at time $t = 0$ can be regarded as generating instantaneously an amount E_0/J calories of heat throughout a small spherical region of radius r_0 , J being the mechanical equivalent of heat. The temperature T at a subsequent time t at a distance r ($> r_0$) from the point of impact may then be calculated, by the standard methods of the theory of conduction of heat, in terms of the density ρ , specific heat c , and thermal conductivity σ of the cathode material to give

$$T = (E_0/8J)(\rho c/\pi^3 \sigma^3 t^3)^{\frac{1}{2}} \exp\{-r^2 \rho c/4\sigma t\} + T_0, \quad (3)$$

where T_0 , the temperature before impact, may be neglected in what follows. This formula is valid provided $t > t_0$, where $t_0 = \rho c r_0^2/\sigma$ and may be regarded as a time of collision. According to it a very high temperature will be generated over a spherical region, with radius a few times that of an atom, for a time a little greater than 10^{-16} sec. We may use (3) to estimate the vapour pressure at this high temperature and hence the total number of molecules evaporated by the impact.

When the vapour pressure is p the number ν of atoms of the cathode material evaporated per unit area of surface per second is given by

$$\nu = fp/mv, \quad (4)$$

where m is the mass of a molecule, f the fraction of molecules which stick to the surface on striking it, and v , the average velocity of the molecules in the vapour phase, is given by

$$v = (2\kappa T/m)^{\frac{1}{2}}. \quad (5)$$

The vapour pressure p , in mm. Hg, may be represented, at temperature T , by

$$p = \exp(b - a/\kappa T), \quad (6)$$

where a is the heat of evaporation of a molecule from the surface.

The total number of molecules ϑ evaporated by the impact is now given approximately by $\nu_m \Delta t \Delta s$, where ν_m is the maximum rate of evaporation per unit area given by (3), (4), and (6), Δt is the time required for the temperature to fall to such a value that the evaporation rate is reduced to $\frac{1}{2}\nu_m$, and Δs is the area over which the rate of evaporation is not less than $\frac{1}{2}\nu_m$. This gives

$$\vartheta = \{A f E_0^{\frac{1}{2}}/a^2 (m^3 \sigma^5 \rho c t_0)^{\frac{1}{2}}\} \exp\{b - B(\sigma^2 t_0/\rho c)^{\frac{1}{2}}(a/E_0)\}, \quad (7)$$

where a and E are expressed in eV and $A = 5.86 \times 10^{-32}$, $B = 6.96 \times 10^{24}$.

The difficulty in applying this expression lies in the lack of knowledge of the various constants. The quantities c and σ which appear in (7) may differ very considerably from those measured at ordinary temperatures. Townes estimated the rate of sputtering of barium by A^+ ions using the following values:

$$\rho c = 1 \text{ cal./degree cm.}^3, \quad \sigma = 0.5 \text{ cal./sec. cm.}^2 \text{ degree}, \quad t_0 = 3 \times 10^{-16} \text{ sec.},$$

$$a = 3.8 \text{ eV}, \quad b = 43, \quad m = 10^{-22} \text{ gm.}, \quad f = 1.$$

He found that about 2 atoms should be sputtered off for each impact of an ion of 8 eV energy. This is much too high as is also the rate of increase of sputtering rate with energy. Hippel's rather crude evaporation theory predicted a linear relation between sputtering rate ϑ and ion energy which is closer to the observed behaviour, but Hippel made no estimate of the absolute value of ϑ .

The main purpose of Townes's calculations was to provide a theoretical description of the observations made by Rockwood† on the sputtering of the active material (barium or strontium) from the cathodes of commercial cold cathode gas tubes filled with neon at a pressure of 60 mm. Hg. In these experiments the sputtering rate was measured from the useful lifetime of the tube. To deal with this problem it was necessary to make allowance for the diffusion of sputtered material back to the cathode and for the energy distribution of the positive ions incident on the cathode.

Using standard diffusion theory Townes showed that, if ϑ is the net rate of loss from the cathode, ϑ_0 the true sputtering rate in the absence of diffusion, and l the mean free path of the sputtered atoms at the gas pressure concerned, then for a cathode and anode in the form of two parallel planes at distance d apart

$$\vartheta = \pi l \vartheta_0 / 2d, \quad (8)$$

and for a spherical cathode of radius r_1 , surrounded by a concentric spherical anode of radius r_2 ,

$$\vartheta = \pi l \vartheta_0 r_2 / \{r_1(r_2 - r_1)\}. \quad (9)$$

These formulae enabled a suitable correction for back diffusion to be made.

By approximate arguments based on the analogy of collisions between rigid spheres Townes was led to adopt for the number $n(E)$ of ions striking the cathode with energy between E and $E + dE$ an expression given by

$$\frac{dn}{dE} = \frac{n_0}{Fl_i} \exp\left(\frac{1}{2} - E/Fl_i\right) \left\{ \frac{1}{8} - \exp\left(\frac{1}{2} - E/Fl_i\right) + E/4Fl_i \right\}, \quad (10)$$

F being the field strength near the cathode and l_i the mean free path of the ions.

Applying (7), (9), and (10) to Rockwood's work, good agreement with the observed form of the variation of ϑ/I with tube current I is obtained, as may be seen by reference to Fig. 267. It must be admitted that the agreement looks impressive, but before regarding this as evidence in support of the evaporation theory one would like to see better agreement with experiment in the case of the simple process of sputtering in a good vacuum.

Compton and Langmuir‡ raise as an objection to the evaporation theory that at the local temperatures supposed to be reached in the sputtering process, the thermionic emission would be expected to be very

† A.I.E.E. Technical Report, May 1941, 4.

‡ *Rev. Mod. Phys.* 2 (1930), 123.

great, thus giving values of secondary electron emission by positive ion bombardment much greater than observed. In this connexion Kapitza† suggested that thermionic emission due to local heating was the dominant process in secondary electron emission by positive ions, and it is interesting that, from measurements of the energy distribution of the secondary electrons emitted following positive ion impact, Oliphant and Moon‡

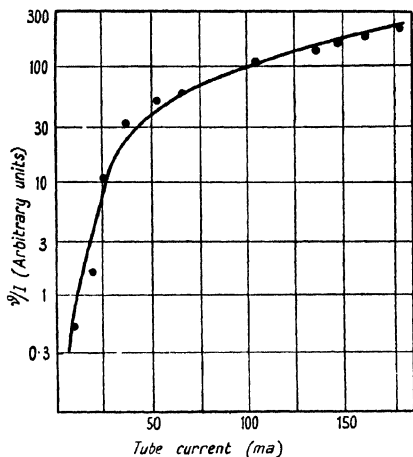


FIG. 267. Observed rate of sputtering per unit current from barium and strontium cathodes of commercial cold cathode neon-filled tubes (pressure = 6 cm. Hg) as a function of tube current. — calculated; experimental points. The rate of sputtering is taken as inversely proportional to the lifetime of the tube.

found a distribution such as would be expected for a thermionic emission at a temperature of 10,000° C. for Al, 30,000° C. for Ni, and 66,000° C. for Pt. This is the order in which sputtering occurs for these three metals. It may be, however, that this thermionic emission is limited to a small area and the current is kept small by space charge effects.

Useful evidence concerning the validity of the evaporation theory could be obtained from measurements of the velocity of the sputtered atoms just after leaving the cathode. Berkey and Mason§ determined the velocity of the vapour stream issuing from the cathode region of a vacuum arc between copper electrodes by measuring the momentum imparted to a small vane placed in front of the cathode. They obtained a velocity of 2×10^6 cm./sec. corresponding to a temperature of 500,000° C.,

† *Phil. Mag.* **45** (1923), 989.

‡ *Proc. Roy. Soc. A*, **127** (1930), 388.

§ *Phys. Rev.* **38** (1931), 943.

but Compton pointed out that this could have been due to ions recombining on the cathode surface and retaining a small fraction of their incident energy. On the other hand, Baum† estimated that silver atoms sputtered by hydrogen have a mean velocity of only 570 metres/sec., corresponding to a temperature of about 1,000° C., just above the melting-point of silver (961° C.).

All that can be said is that the evidence in favour of any of the theories of sputtering is inconclusive. Lamar and Compton‡ have suggested that the momentum interchange theory may be most important for ions of small mass, while the evaporation theory applies to heavy ions. Whatever the explanation, it is clear that more experimental information is needed on this as in all other fields concerning the collision of positive ions with solid surfaces.

10. The collisions of neutral molecules with solid surfaces under gas-kinetic conditions

A neutral molecule impinging on a solid surface with an energy comparable with that of the surface atoms may rebound with or without a change of energy or it may lose so much energy that it is captured or adsorbed, on the surface. These phenomena, while being of considerable importance in practice, are not susceptible of easy experimental investigation. The most fundamental and direct method is to study the effect of a surface on a beam of molecular rays, and a substantial contribution to knowledge of the interaction of molecules with a surface has been gained in this way. The information gained from such studies has been mainly, but not exclusively, concerned with processes in which no energy interchange with the solid occurs, i.e. with diffraction and selective adsorption. On the other hand, the chief additional source of information, the study of accommodation coefficients, is concerned with energy exchanges between the solid and gas molecule which do not lead to capture of the molecule. The complementary information obtained from these two experimental sources may be supplemented by a quantal theory of the various collision rates so that a useful body of information is available.

10.1. *Specular and diffuse reflection of molecules from surfaces*

Two conditions need to be satisfied in order that specular reflection of a molecular beam from a surface shall occur:

(a) The average magnitude of the deviation of the surface from a perfect plane, resolved in the direction of incidence, must be small

† *Zeits. f. Phys.* **40** (1927), 686.

‡ Loc. cit.

compared with the wave-length. This is the usual condition for true reflection of any waves from a surface.

(b) The average time a molecule spends on the surface must be small. If this is not satisfied the conditions under which re-evaporation of a molecule from the surface will occur will bear no relation to those which prevailed at condensation. They will be determined by the last stages in the history of the molecule on the surface.

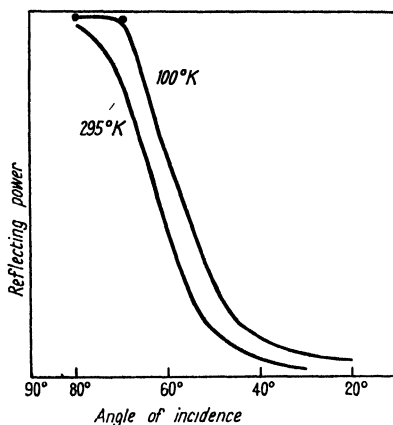


FIG. 268. Variation with angle of incidence of the intensity of reflection of molecular beams of helium from a cleavage plane of a LiF crystal at two different temperatures.

The cleaved surface of a crystal provides the most perfect natural reflecting surface. The inequalities present will be largely due to the temperature motion of the crystal atoms or ions of average magnitude d , of order 10^{-8} cm. at ordinary temperatures. The condition (a) then requires, for specular reflection at an angle θ ,

$$d \cos \theta \ll \lambda. \quad (11)$$

For helium atoms with kinetic energy corresponding to room temperature the wave-length λ is approximately 10^{-8} cm., so that the condition (11) should be satisfied if θ is greater than 60° or so. Estermann and Stern† have verified this by measuring the intensity of reflection of molecular rays of helium and of hydrogen from cleavage planes of LiF and NaCl crystals. A hot wire gauge detector (see Chap. VII, § 5.11) was used to measure the beam intensity. Their results for helium reflected from LiF are illustrated in Fig. 268. It will be seen that at ordinary temperatures

† Ibid. 61 (1930), 95.

the reflecting power falls to a quite low value for $\theta < 50^\circ$. At a lower temperature the reflecting power is increased, as would be expected from the decrease in the amplitude of the heat vibrations which determine d .

It is clear from these experiments that the condition (b) must also have been satisfied—the helium atoms or hydrogen molecules could not

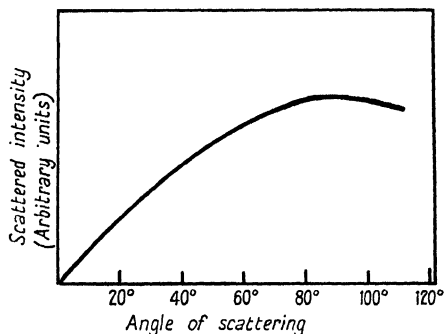


FIG. 269. Variation with angle of scattering of the intensity of reflection of Li atoms scattered from the cleavage plane of a LiF crystal. The angle of incidence was 15° .

have spent an appreciable time on the surface. For other atoms it has been found, however, that even though the condition (11) is satisfied, specular reflection does not occur. Thus Taylor† investigated the reflection of molecular rays of lithium, potassium, and caesium also from cleavage planes of LiF and NaCl crystals, using the surface ionization detector (Chap. VII, § 5.11). He found no evidence for any true reflection. This is clear by reference to Fig. 269, which illustrates the variation of the intensity of Li atoms scattered at various angles ϕ to the surface when the beam was incident at an angle of 15° , for which condition (11) is satisfied. It will be seen that this intensity distribution is quite closely proportional to $\sin \phi$, which would be the case if the surface behaved rather like a black body in optics, the direction of scattering bearing no relation to that of incidence. The absence of true reflection is made even more evident by noting that, if even 1/1,000 of the incident atoms were so reflected, the intensity at 15° would have been considerably greater than was observed.

Similar results were obtained at other angles of incidence and with other atoms. In these cases condition (b) is not satisfied, the atoms spending an appreciable time on the surface. This is associated with the

† *Phys. Rev.* **35** (1930), 375.

formation of an adsorbed layer. Estimates of the time τ of adsorption of a single atom may be made from measurement of the equilibrium surface concentration n /unit area of adsorbed atoms when the surface is bombarded by ν atoms/unit area/sec. for $n = \tau\nu$. Values of τ of the order 10^{-5} sec. are obtained in this way. We shall return to the discussion of this kind of adsorption in § 10.3 after first discussing reflection and diffraction which occur when both conditions (a) and (b) are satisfied.

10.2. Reflection and diffraction of molecular rays from crystal surfaces

10.21. Diffraction by a cross-grating. It is to be expected that a crystal surface which specularly reflects molecular rays of a particular kind will also diffract the rays. As the penetration into a surface of molecules with gas-kinetic energies is very small it will only be surface atoms of the crystal which will take part in the diffraction process. The surface of a simple cubic crystal should therefore act as a cross-grating, consisting of parallel coplanar equidistant rows of diffracting centres at distance a apart, equal to the distance between successive rows (see Fig. 270).

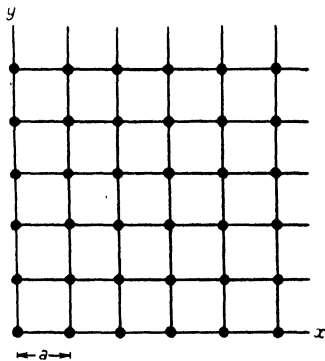


FIG. 270. Scattering centres in a cross-grating.

Suppose the z -axis is taken perpendicular to the surface, the x -axis parallel to the rows of diffracting centres, and the direction of the incident beam makes angles $(\alpha_0, \beta_0, \gamma_0)$ with the coordinate axes. Then the diffracted beams will make angles (α, β, γ) with these axes, given by

$$\begin{aligned}\cos \alpha - \cos \alpha_0 &= n_1 \lambda / a, \\ \cos \beta - \cos \beta_0 &= n_2 \lambda / a,\end{aligned}\tag{12}$$

where λ is the wave-length and n_1 and n_2 are any integers, positive or negative. Since fixed values of α, β respectively define right circular cones with the x - and y -axes as axes respectively, the directions of the diffracted rays may be defined as the intersections of appropriate α and β cones. In most experiments $\beta_0 = 0$. Fig. 271 illustrates the $(0, 0)$ and $(0, \pm 1)$ order diffracted rays for a case of this sort. In all circumstances the $(0, 0)$ ray is the reflected ray. It is noteworthy that no diffracted beam will be formed for which

$$90^\circ - \beta < \alpha_0\tag{13}$$

as $\cos^2 \alpha + \cos^2 \beta \nless 1$.

With molecular rays there is the complication that the beam is not monochromatic. However, the reflected ray and the $(0, \pm 1)$ diffracted rays will all lie on the cone of semi-vertical angle α_0 about the x -axis (the α cone). It is therefore convenient to examine the variation of intensity along a circular section of the cone such as AB in Fig. 271. The position on this section may be denoted by the azimuthal angle ψ

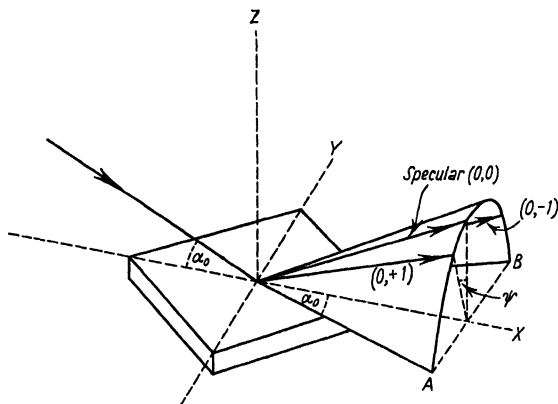


FIG. 271. Diffraction of a molecular beam by a cross-grating, showing the positions of the $(0, 0)$ specularly reflected and the $(0, \pm 1)$ diffracted rays.

shown in Fig. 271, $\psi = 0$ corresponding to the reflected ray. According to the cross-grating theory the intensity should vary with ψ as indicated in Fig. 272, the first-order diffraction peaks being broadened by the Maxwellian velocity distribution of the incident atoms.

10.22. Experimental study of diffraction. The first experimental confirmation that molecular rays could be diffracted by the cleavage plane of a crystal as from a cross-grating was provided by Stern† in 1929. He studied the diffraction of helium atoms from LiF. The above theory was found to apply provided the diffracting centres were taken to be the F^- and not the Li^+ ions. This work was extended by Estermann and Stern‡ and by Estermann, Frisch, and Stern§ who studied beams of hydrogen molecules as well as helium atoms. At much the same time Johnson|| exhibited the diffraction of atomic hydrogen from the same crystal using an MoO_3 target detector on which the first-order diffraction could be seen as a whole. The most complete investigations have been

† *Naturwiss.* **17** (1929), 391.

§ *Ibid.* **73** (1931), 348.

‡ *Zeits. f. Phys.* **61** (1930), 95.

|| *Phys. Rev.* **35** (1930), 1299.

those of Frisch and Stern† which brought to light the existence of remarkable anomalies in the diffraction and reflection phenomena which have proved of considerable importance for the study of the interaction between atoms and solid surfaces. As in the earliest work Frisch and Stern devoted most attention to studying the diffraction of He atoms from the cleavage plane of LiF crystals.

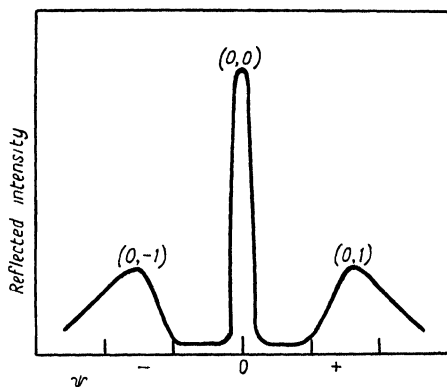


Fig. 272. Expected variation of intensity of reflected beam as a function of ψ .

The first part of the work was a continuation of earlier work using the geometrical arrangement illustrated in Fig. 271 in which the source and detector were fixed so that the direction of incidence and of the diffracted rays made equal angles with the plane of the crystal. The crystal could be rotated about the principal axis Ox in its plane.

In the position $\psi = 0$ the reflected $(0, 0)$ beam entered the detector. As the crystal rotated the diffracted $(0, 1)$ rays of different wave-lengths successively entered giving rise to the intensity distribution expected on passing round a circular section of an α cone.

Fig. 273 illustrates a typical set of observations obtained in this way. The dotted curve gives the theoretically predicted distribution of intensity for the $(0, 1)$ diffracted beams, derived from the Maxwell velocity distribution. It will be seen that, while there is very good general agreement in position of the maximum and shape of the distribution, there are two irregularities for ψ about 20° and 26° which are reproduced in detail for the corresponding negative values of ψ . In order to investigate further the nature of these anomalies Frisch and Stern modified the design of their apparatus. In its original form it suffered

† *Zeits. f. Phys.* **84** (1933), 430.

particularly from the disadvantage that the plane of incidence relative to the crystal varied as the crystal rotated. The second set of experi-

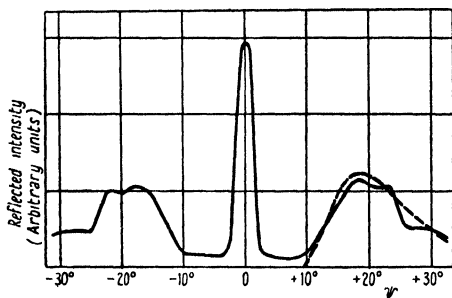


FIG. 273. Observed variation with ψ of reflected intensity for a beam of helium atoms incident on the cleavage plane of a LiF crystal. ----- theoretical intensity for (0, 1) diffraction.

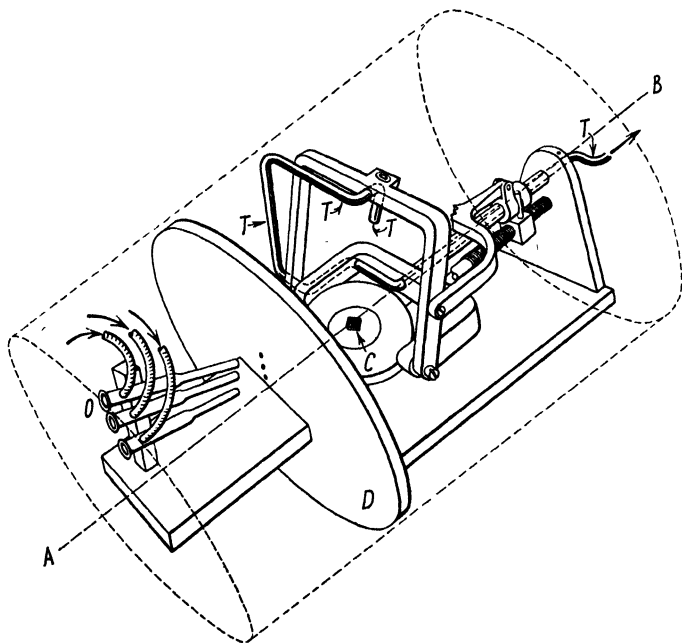


FIG. 274. Frisch and Stern's modified apparatus for studying diffraction of molecular beams.

ments was therefore performed with an apparatus of the form illustrated in Fig. 274.

In this apparatus the crystal was kept fixed throughout a series of observations, but it could be adjusted by rotation in its own plane *in vacuo*. The source was also kept fixed but, to obtain information about the effect of varying the angle of incidence, three alternative sources were included providing beams with angles of incidence of 78.4° , 71.5° , and 64.8° respectively. Two degrees of freedom were available for

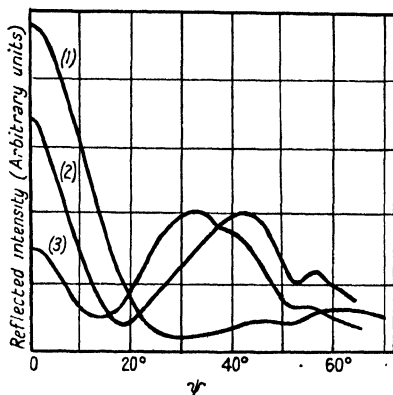


FIG. 275. Variation with ψ of diffracted intensity for a beam of helium atoms incident on the cleavage plane of a LiF crystal. The angle of incidence was 78.4° for curve 1, 71.5° for curve 2, 64.8° for curve 3.

moving the detector. It could be rotated about the principal axis Ox of the crystal plane (AB in Fig. 274) and the angle θ which its direction of detection made with this axis could also be varied. To observe the diffraction effects the detector was first rotated about the axis so that it lay in the plane of incidence. This was taken as the position $\psi = 0$, where ψ is the angle of rotation about Ox . Keeping ψ fixed the angle θ was then changed until the reflected beam entered the detector. θ was then fixed and the diffraction pattern observed by rotating the detector round the axis.

Fig. 274 illustrates the nature of the apparatus in some detail. It was enclosed in a metal cylinder divided into two sections by the circular disk D . On one side of the disk were the oven chambers O in which the molecular rays were generated, and on the other the diffraction chamber containing the crystal C and detecting tube T . Both sections were separately connected directly to steel vapour pumps.

Some of the diffraction patterns observed with this apparatus are illustrated in Fig. 275. Once more the anomalous minima are present,

although the (0, 1) maximum is in the correct position and the distribution of intensity is also generally correct.

As a further means of investigating the conditions determining the occurrence of the anomalous minima a detailed investigation was made of the variation of the reflected intensity with the angle η the plane of incidence makes with the principal axis Ox of the crystal. This was done by means of the apparatus illustrated in principle in Fig. 276.

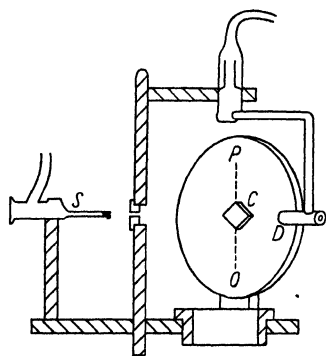


FIG. 276.

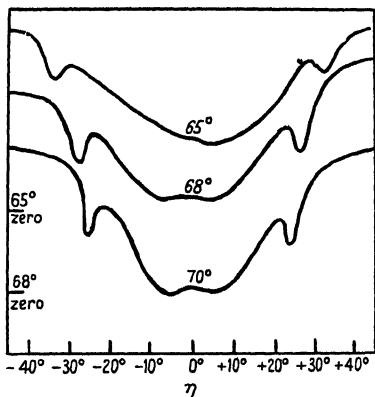


FIG. 277.

FIG. 276. Frisch and Stern's apparatus for studying the variation of the reflected intensity as a function of η , the angle the plane of incidence makes with a principal axis of the crystal.

FIG. 277. Variation of reflected intensity with η for a beam of helium atoms incident on the cleavage plane of a LiF crystal at angles of incidence of 65° , 68° , and 70° .

The source S was fixed, but the crystal C could be rotated about an axis OP perpendicular to the incident beam, so making it possible to vary the angle of incidence, as well as to rotate the crystal in its own plane. The detector D could also be rotated about the axis OP . The procedure consisted in fixing the angle of incidence and adjusting the crystal and detector to receive the reflected ray with the plane of incidence along Ox corresponding to $\eta = 0$. The variation of reflected intensity with η was then observed.

Typical results obtained in this way are illustrated in Fig. 277. Here again the appearance of well-defined minima appearing quite symmetrically on both sides of $\eta = 0$ is conspicuous.

Further studies were carried out to observe the effect of temperature, which was found to have little influence on the position of the anomalous minima, and to examine the relation of the minima to wave-length by

using incident beams made monochromatic by preliminary diffraction from another crystal. Similar anomalies were also found for He on NaF and H₂ on LiF.

From an analysis of the geometrical conditions under which the anomalous minima appeared Frisch† was able to show that they arose

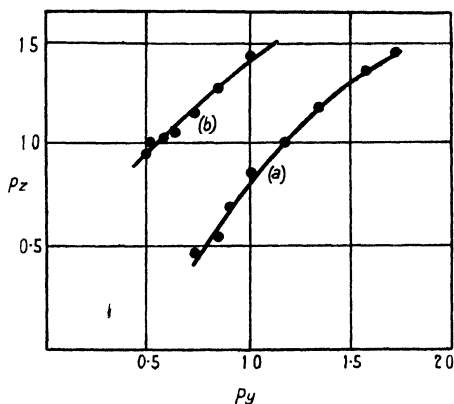


FIG. 278. Relation between momentum components p_z , p_y of the diffracted and specularly reflected molecular beams when anomalous minima occur.

when, for the diffracted or reflected beam under observation, the components p_z , p_y of momentum of the beam molecules along the Oz , Oy directions (Fig. 272) respectively bore a certain relation to each other. This is clear by reference to Fig. 278, in which p_z is plotted against p_y for beams exhibiting the anomalous minima, points derived from both diffraction and reflection experiments being included. The points lie on two curves (a) and (b) which may be represented respectively by

$$p_z^2 - 2p_y = -1.25, \quad (14)$$

$$p_z^2 - 2p_y = 0. \quad (15)$$

It was found from further experiments that a minimum also appeared in the intensity of the reflected beam, for variation of the angle of incidence in the xz -plane, when a similar relation existed between p_z and p_x . The effects are just as if the crystal absorbs selectively beams in which a definite relation between p_z and p_x or p_y is satisfied. We shall see in the next section that this is very nearly the case, the process being actually one of selective adsorption.

The molecular ray diffraction experiments have therefore not only

† *Zeits. f. Phys.* **84** (1933), 443.

established the validity of the cross-grating theory, confirming the assignment of the de Broglie wave-length to neutral molecules, but have also revealed a very interesting adsorption effect, which we shall now discuss.

10.23. Theoretical interpretation of diffraction anomalies—selective adsorption. The explanation of the anomalous effects observed in the diffraction and reflection of molecular rays was first given by Lennard-Jones and Devonshire.† They showed that, when relations such as (14) and (15) are satisfied, a transfer of energy from motion perpendicular to the surface to motion parallel to the surface may take place readily, leaving the atoms or molecules sliding freely over the surface while vibrating with finite amplitude in the normal direction, i.e. in an adsorbed state. Thus if the momentum conditions are satisfied by the incident beam this type of adsorption can occur instead of reflection or diffraction. Alternatively, if after collision the reflected or diffracted beam satisfies the conditions, it may also be adsorbed in this way instead of leaving the crystal. In either case there will be a diminution in intensity of the beam issuing from the crystal. The argument put forward by Lennard-Jones and Devonshire may be stated as follows.

With the same reference axes as in Fig. 271, the interaction energy $V(x, y, z)$ of a gas atom with the surface, in which the atoms are considered as at rest, may be expanded in a double Fourier series in x and y with the lattice spacing a as period. The first two terms in this expansion may be written

$$V = V_0(z) + V_1(z) \left(\cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a} \right). \quad (16)$$

In general the Fourier expansion will converge quite quickly so that, not only is the second term of (16) considerably smaller than the first, but all higher terms will be considerably smaller still.

If the second term of (16) is neglected the motion parallel to the surface is entirely free. If the x - and y -components of momentum of this motion are $k_1 \hbar$ and $k_2 \hbar$ respectively, the wave function for the motion, including that in the z direction, may be written

$$\Psi_{k_1 k_2} = \phi_{k_1 k_2}(z) \exp(i(k_1 x + k_2 y)), \quad (17)$$

where ϕ will satisfy the Schrödinger equation

$$\frac{d^2 \phi}{dz^2} + \left\{ \frac{8\pi^2 M}{h^2} (E - V_0) - k_1^2 - k_2^2 \right\} \phi = 0. \quad (18)$$

E is here the total energy of the atom, so that the energy E_z in the z -component is $E - \hbar^2(k_1^2 + k_2^2)/2M$, M being the mass of the atom. For a given value of the total energy E there will exist a number of different values of E_z as k_1 and k_2 are arbitrary real numbers. The values of E_z are limited by the quantum conditions imposed by the equation (18). All values of $E_z > 0$ are possible, but for $E_z < 0$ there will exist only a discrete set of allowed energy levels $-E_n$. These correspond to free

† *Nature*, **137** (1936), 1089; *Proc. Roy. Soc. A*, **156** (1936), 37.

motion over the surface associated with vibrations of finite amplitude normal to the surface. Thus, for a given total energy E the atom may either be moving with positive energy E_z so that it is not bound to the surface and at infinity possesses a z -component of momentum k_3 normal to the surface, or it may be bound with binding energy E_n to the surface. If $k_1\hbar$, $k_2\hbar$ are the x - and y -components of momentum in the first instance, $k'_1\hbar$, $k'_2\hbar$ in the second,

$$k_1^2 + k_2^2 + k_3^2 = k_1'^2 + k_2'^2 - 2ME_n/\hbar^2. \quad (19)$$

In the first case the wave function will be of the form (17) and in the second

$$\Psi_{k_1 k_2} = \phi_{k_1 k_2}(z) \exp\{i(k'_1 x + k'_2 y)\}. \quad (20)$$

In the approximation to which we have been working no transitions can take place between these two states of the same total energy. This can only occur if energy is transferred from one degree of freedom to another, whereas if V_1 in (16) is ignored there is no coupling between the different degrees of freedom. If we allow for the second term in (16) the situation is changed as it does represent coupling between the z and x , and z and y degrees of freedom. Nevertheless a strong selection rule will operate as may be seen as follows.

The probability of a transition will vanish, or at least be very small, if the average value of the coupling energy responsible, taken over the unperturbed wave functions of the initial and final state, vanishes. Suppose we consider a transition in which the energy in the x -degree of freedom changes from $k_1^2 \hbar^2 / 2M$ to $k_1'^2 \hbar^2 / 2M$. The appropriate average value of the coupling energy is

$$V_{1,if} = \int_0^\infty \int_0^a \int_0^a \Psi_{k_1 k_2} V_1(z) \left(\cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a} \right) \Psi_{k'_1 k'_2}^* dx dy dz. \quad (21)$$

Substituting for $\Psi_{k_1 k_2}$, $\Psi_{k'_1 k'_2}^*$ from (17) and (20) gives

$$V_{1,if} = \int_0^\infty \phi_{k_1 k_2}(z) V_1(z) \phi_{k'_1 k'_2}^*(z) dz \int_0^\infty \exp\{i(k_1 - k'_1)x\} \cos \frac{2\pi x}{a} dx. \quad (22)$$

The second integral vanishes unless

$$k_1 - k'_1 = \pm 2\pi/a, \quad (23)$$

giving the selection rule.

We see then from (19) and (23) that the chance of a transition from a free to a bound state, as far as motion normal to the crystal surface is concerned, will be relatively high when

$$k_3^2 + k_1^2 = (k_1 \pm 2\pi/a)^2 - 2ME_n/\hbar^2, \quad (24)$$

E_n being the binding energy of the atom when occupying an allowed energy level as far as motion normal to the surface is concerned.

If the transition is not reversed within a short time we would expect the emergent beam to be weak. Soon after the atom becomes bound to the surface it will lose energy either by exchange with the heat motion of the crystal or will have its motion changed by a collision with a crystal imperfection so that it is completely lost as far as reflection or diffraction is concerned. The identity of the relation (24) with that

derived empirically by Frisch (loc. cit.) from the diffraction experiments described above strongly suggests that this is what happens.

This phenomenon has been called selective adsorption by Lennard-Jones and Devonshire, and it may be used to determine values of E_n from observed data. Thus the two empirically deduced relations (14) and (15) of § 10.22 for reflection of helium atoms from LiF correspond to values of E_n of -57 and -129 cal./mole respectively. Less complete data for He on NaF gives two energies -80 and -193 cal./mole.

Using these energy values Lennard-Jones and Devonshire† were able to represent the interaction $V(x, y, z)$ in more detail. They represented V_0 by the form

$$V_0 = D[\exp\{-2(z-b)/d\} - 2\exp\{-(z-b)/d\}], \quad (25)$$

as in Chap. VII, § 12.6, D being the depth of the potential minimum at $z = b$ and d the range of the interaction. Assuming that the energy values derived from the diffraction experiments are for the two most firmly bound states, D and d may be determined. Thus for He and LiF it is found that $d = 0.9 \times 10^{-8}$ cm. and $D = 175$ cal./mol. V_1 was then chosen so that, for each value of x and y , the total interaction V remained of the form (25) but with the depth of the minimum varying from $D/(1-4\beta)$ over the centre of a lattice cell ($x = 0, y = 0$) to $D/(1+4\beta)$ over a lattice point. This was secured by writing

$$V_1 = -2\beta D \exp\{-2(z-b)/d\}. \quad (26)$$

β was chosen as 0.038 in order to give an interaction similar to that calculated by Lennard-Jones‡ for the fields of Ne near NaF and A near KCl. The equipotential contours illustrated in Fig. 279 give an idea of the nature of the field represented by (25), (26), and (16).

Having chosen suitable forms for V_0 and V_1 , the chance of selective adsorption, which depends on (22), may be calculated as well as the duration of the adsorbed state for a perfect crystal surface. The results obtained in this way§ for He on LiF are given in Table V. They refer, of course, only to a perfect crystal. The chance of selective adsorption involves averaging over the Maxwell distribution of velocities and does not refer to the chance when the condition (23) is precisely satisfied. It will be seen from the table that, for selective adsorption to be effective in reducing reflected intensity, a molecule on the surface must undergo a collision, either with the crystal lattice vibrations or crystal imperfections, in travelling a distance of order 10^{-5} cm. This does not seem unreasonable.

† *Proc. Roy. Soc. A*, **158** (1937), 242.

‡ *Trans. Far. Soc.* **28** (1932), 333.

§ Lennard-Jones and Devonshire, *Proc. Roy. Soc. A*, **158** (1937), 253.

Lennard-Jones and Devonshire† derived formulae for the intensities of the diffracted rays and discussed how it would be possible to obtain further information about the surface fields of crystals from diffraction experiments.

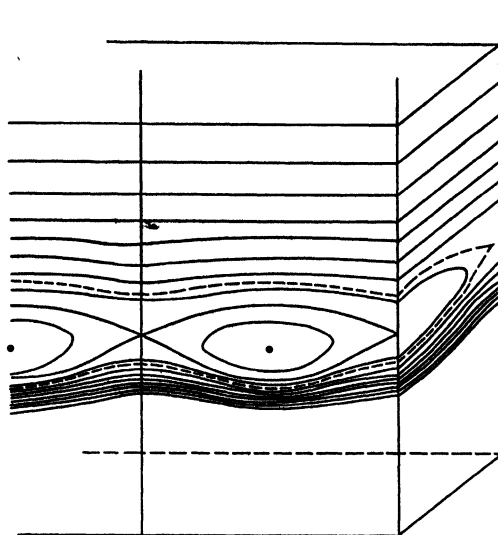


FIG. 279. Equipotential contours for the field between a helium atom and a LiF surface derived from a semi-empirical theory. The figure shows sections by the planes $x = a\pi$ and $y = 0$.

TABLE V

Selective Adsorption of He on LiF

T (° K.)	30	50	100	300
Chance of selective adsorption per impact	0.032	0.018	0.009	0.0025
Duration of adsorption (in 10^{-10} sec.)	6.27	3.47	2.22	2.12
Mean distance travelled over surface in adsorbed states (in 10^{-8} cm.)	3.32	2.08	1.69	2.58

10.3. Inelastic collisions of molecules with crystal surfaces

So far we have been concerned with collisions between gas molecules and the solid surface in which no exchange of energy between the

† Loc. cit.

molecule and the surface took place. In fact the chief mechanism of adsorption, in which no chemical forces are effective (van der Waals adsorption), is by an incident atom losing so much energy to the lattice vibration on collision with the surface that it is captured. The probability of capture of an atom from a molecular beam (in which there is a Maxwellian distribution of velocities) is called the coefficient C of condensation.

Adsorption by this mechanism is a result of a free-bound transition of the atom. Free-free transitions may take place also so that an atom colliding with the surface may leave the surface without adsorption occurring, but with a greater or smaller energy than before impact. Processes of this kind will occur when gas molecules are exposed to a hot metal surface.

For the theoretical treatment of these processes, allowance must be made in the interaction energy between the incident atom and the crystal surface for the heat motion of the surface atoms of the crystal which was neglected above in discussing elastic collisions. This may be done, to a first approximation, by neglecting V_1 and all higher terms in the Fourier expansion of V and replacing $V_0(z)$ by $V_0(z-Z)$, where z is now the distance of the atom from the undisturbed surface of the crystal and Z is the displacement of a surface atom of the crystal in the z direction due to the heat motion (cf. Chap. VII, § 12.6). Effects due to the lateral motion of either the crystal atoms or the incident atom are neglected.

It is possible to simplify the problem still further by writing

$$V_0(z-Z) \simeq V_0(z) + Z \left(\frac{dV_0}{dz} \right)_{z=0}. \quad (27)$$

This is because V_0 changes only by a small proportion in a distance equal to the amplitude of the heat motion.

With this approximation $Z dV_0/dz$ represents the coupling which leads to a finite probability of a transition in which energy exchange between the incident atoms and the crystal takes place. The probability of such a transition will be proportional as usual to

$$\left| \int \Psi_i Z \frac{dV_0}{dz} \Psi_f^* d\tau_a d\tau_c \right|^2, \quad (28)$$

in which Ψ_i and Ψ_f are the initial and final wave functions for the combined system in the absence of the coupling. They may be written as the products

$$\Psi_{i,f} = \phi_{i,f}(z) \chi_{i,f}(a_{jk}, b_{jk}). \quad (29)$$

$\phi_{i,f}$ refer to the wave functions for the motion of the atoms normal to the surface and satisfy the wave equation (18). $\chi_{i,f}$, the wave functions for the crystal motions,

will depend on the normal coordinates a_{jk} , b_{jk} of the lattice. The transition probability may be taken then as proportional to the product

$$\left| \int \chi_i Z \chi_f^* d\tau_c \right|^2 \left| \int \phi_i \frac{dV_0}{dz} \phi_f^* d\tau_a \right|^2. \quad (30)$$

The integral over the normal coordinates of the crystal, in terms of which Z may be expressed linearly,† can be evaluated by standard methods and with the form (25) for V_0 the second integral may be dealt with in much the same way as the similar integral in Chap. VII, § 12.6.†

This analysis is applicable whether ϕ_i or ϕ_f represent bound or free states of the atom.

10.31. Probability of condensation of atoms on a surface. The probability of condensation, for typical cases, has been calculated using the method outlined above, by Lennard-Jones and Devonshire.† Table VI gives the probability of condensation as a function of the energy of the incident atom. In obtaining these results the constants D and d in the interaction (25) were taken as 1,000 cal./mole and 10^{-8} cm. respectively and the mass of the incident molecule was taken as that of molecular deuterium.

The interesting feature of these results is that the probability of condensation per impact is quite small. It has a maximum of order 0.1 at a particular energy of impact, and increases with the temperature T of the crystal.

Using these values the coefficient of condensation, which is the average of the condensation probability over the Maxwellian distribution of energies of the incident molecules, may be calculated, typical results being given in Table VI.

There exists a statistical relation‡ between the coefficient of condensation C and the mean time τ which a molecule spends on the surface after capture before re-evaporating. Thus

$$C\tau = (h/\kappa T) \sum_s \exp(-E_s/\kappa T), \quad (31)$$

where the sum is taken over all bound states of motion of the molecule normal to the crystal surface with binding energy E_s . Table VII includes values obtained for τ using this relation.

It must be remembered in considering these results that it has been assumed that the adsorption is of van der Waals type. They do not apply when true chemical forces exist between the adsorbed and crystal atoms.

† Lennard-Jones and Strachan, *Proc. Roy. Soc. A*, **150** (1935), 442; Lennard-Jones and Devonshire, *ibid.* **156** (1936), 6; Strachan, *ibid.* **150** (1935), 456.

‡ Fowler, *Proc. Camb. Phil. Soc.* **31** (1935), 260.

TABLE VI

Probability of Condensation per Collision of Molecules of Mass $4M_H$ with a Crystal Surface (M_H = proton mass)

Incident energy of molecule (calories)	Crystal temperature (° K.)	
	30°	100°
	Probability of condensation	
3	0.074	0.097
6	0.086	0.114
12	0.090	0.117
18	0.092	0.120
24	0.094	0.126
36	0.100	0.120
48	0.088	0.099
60	0.065	0.069
84	0.038	0.040
96	0.015	0.015
10.8	0.003	0.003
Coefficient of condensation	1.16×0.081	1.16×0.091

TABLE VII

Times of Evaporation of Molecules of Mass $4M_H$ from a Crystal Surface on which they have been adsorbed (sec.)

Characteristic temperature (° K.)	Crystal temperature (° K.)			
	30° $\tau \times 10^5$	50° $\tau \times 10^8$	100° $\tau \times 10^{10}$	300° $\tau \times 10^{12}$
300	1.40	2.24	1.68	6.21
350	2.15	3.36	2.47	9.03
400	3.08	5.23	3.54	12.7
510	6.31	9.88	7.11	25.1

10.32. Free-free transitions—The accommodation coefficient. When a gas at a temperature T_2 is allowed to come into contact with a solid at a temperature $T_1 \neq T_2$ there is an interchange of energy between them. The rate of this interchange is defined by Knudsen's thermal accommodation coefficient α . A gas atom will strike the surface with an average energy E_2 determined by T_2 . If it came into complete thermal equilibrium with the solid before returning to the gas phase it would have a mean energy E_1 determined by T_1 . Instead it will leave the surface with mean energy E'_2 . Then α is defined by

$$\alpha = (E'_2 - E_2)/(E_1 - E_2), \quad (32)$$

or, for theoretical purposes, by

$$\alpha = \lim_{T_1 \rightarrow T_2} (E'_2 - E_2)/(E_1 - E_2). \quad (33)$$

It is easy to see how α is determined by the probability of energy interchange between the atom and the solid.

Let $P^+(E, E+h\nu) d\nu$ be the probability per collision that an atom incident with energy E will receive from the solid a quantum of heat vibration in the frequency range ν to $\nu+d\nu$. The fraction of atoms striking unit area of surface per second with energy between E and $E+dE$ is

$$E e^{-E/\kappa T_1} dE / \kappa^2 T_1^2. \quad (34)$$

Hence the total energy taken up from the solid per atom per second is, on the average,

$$\Delta E^+ = (1/\kappa^2 T_1^2) \int_0^{\nu_m} h\nu d\nu \int_0^\infty E P^+(E, E+h\nu) \exp(-E/\kappa T_1) dE, \quad (35)$$

ν_m being the maximum frequency of the solid.

Similarly the total energy given up to the solid per atom per second is, on the average,

$$\Delta E^- = (1/\kappa^2 T_2^2) \int_0^{\nu_m} h\nu d\nu \int_0^\infty (E+h\nu) P^-(E+h\nu, E) \exp\{-(E+h\nu)/\kappa T_2\} dE, \quad (36)$$

where $P^-(E+h\nu, E)$ is the probability per collision that an atom incident with energy $E+h\nu$ will give up energy $h\nu$ in exciting a quantum of heat vibration with frequency between ν and $\nu+d\nu$.

From the principle of detailed balancing

$$(E+h\nu) P^-(E+h\nu, E) = E e^{h\nu/\kappa T_1} P^+(E, E+h\nu), \quad (37)$$

giving

$$\begin{aligned} E'_2 - E_2 &= \Delta E^+ - \Delta E^- \\ &\simeq \frac{T_1 - T_2}{\kappa^3 T_2^4} \int_0^{\nu_m} (h\nu)^2 d\nu \int_0^\infty E P^+(E, E+h\nu) e^{-E/\kappa T_1} dE, \end{aligned} \quad (38)$$

if $T_1 - T_2$ is so small that

$$1 - \exp\{(h\nu/\kappa T_1) - (h\nu/\kappa T_2)\} \simeq h\nu\{(1/\kappa T_1) - (1/\kappa T_2)\}. \quad (39)$$

Hence, since

$$E_1 - E_2 = \kappa(T_1 - T_2)$$

$$\alpha = \lim_{T_1 \rightarrow T_2} \frac{E'_2 - E_2}{E_1 - E_2} = (\kappa^4 T_2^4)^{-1} \int_0^{\nu_m} (h\nu)^2 d\nu \int_0^\infty E P^+(E, E+h\nu) e^{-E/\kappa T_1} dE. \quad (40)$$

Hence, if P^+ can be calculated by methods outlined in § 10.34, α may be determined.

For obvious experimental reasons (see § 10.33) accommodation coefficients have been studied mainly for metal surfaces. Also, to ensure that the surface involved is really metallic and is not covered by adsorbed

layers, the choice of gases is limited largely to the rare gases, particularly helium and neon. Nevertheless the same methods may be employed as in dealing with the other surface problems in preceding sections. The aim is to analyse the available experimental data in terms of the theory to obtain information about the interaction between rare gases and a metal surface. Before discussing this we shall give a brief description of the scope and nature of the experimental work on the subject.

10.33. The measurement of accommodation coefficients.† If a fine wire is stretched along the axis of a cylindrical glass tube containing gas at such a low pressure p that the mean free path of the gas molecules is great compared with the radius of the tube, the accommodation coefficient may be measured in terms of the heat loss from the wire when it is maintained at a temperature T_2 above that, T_1 , of the glass tube.

All the gas molecules striking the wire can be regarded as at the temperature T_1 provided the diameter of the wire is small compared with that of the tube. For, when this is so, a molecule leaving the wire will make many collisions with the tube wall before returning to the wire. The number of molecules striking unit area of the wire per second is therefore $p/(2\pi M\kappa T_1)^{\frac{1}{2}}$, M being the mass of a molecule.

Suppose $f(v) dv$ to be the number of molecules per c.c. with velocities between v and $v+dv$. The total energy W_1 of all molecules reaching unit area of the wire per second is

$$\frac{M}{8} \int_0^{\infty} v^3 f(v) dv. \quad (41)$$

Assuming a Maxwellian distribution of velocities,

$$f(v) = 4n(M^3/8\pi\kappa_1^3 T_1^3)^{\frac{1}{2}} v^2 e^{-(Mv^2/2\kappa T_1)},$$

where n is the number of molecules per c.c.

Putting this relation in (41),

$$W_1 = n(2\kappa^3 T_1^3/\pi M)^{\frac{1}{2}} = n(\kappa T_1/2\pi M)^{\frac{1}{2}} 2\kappa T_1 = (p^2/2\pi M\kappa T_1)^{\frac{1}{2}} 2\kappa T_1. \quad (42)$$

The molecules leaving the wire will not be in thermal equilibrium with it at temperature T_2 but will have a mean energy corresponding to a temperature T'_2 . For small values of $T_2 - T_1$ their velocity distribution may be taken as approximately Maxwellian‡ if the gas is monatomic.

The total number leaving unit area per second may then be written

$$\int_0^{\infty} g v^3 e^{-Mv^2/2\kappa T'_2} dv = g \cdot 2\kappa^2 T'_2/M^2,$$

where g is a constant to be determined so that the number of molecules leaving is equal to the number arriving at unit area per second, i.e.

$$g \cdot 2\kappa^2 T'_2/M^2 = (p^2/2\pi M\kappa T_1)^{\frac{1}{2}}. \quad (43)$$

† See Roberts, *Some Problems in Adsorption*, C.U.P. (1939), Chap. I, and *Reports of Progress in Physics*, 7 (1940), 303.

‡ Knudsen, *Ann. der Physik*, 34 (1911), 593; 46 (1915), 641.

The total energy W_2 carried by the molecules leaving unit area of the surface per second is

$$\frac{gM}{2} \int_0^{\infty} v^5 e^{-Mv^2/2\kappa T_2} dv = (p^2/2\pi M\kappa T_1)^{\frac{1}{2}} 2\kappa T_2' \quad (44)$$

and the net loss of energy per unit area of the wire per second is

$$W = W_2 - W_1 = (p^2/2\pi M\kappa T_1)^{\frac{1}{2}} 2\kappa (T_2' - T_1). \quad (45)$$

From the definition (33) of the accommodation coefficient α , this may be rewritten

$$W = (p^2/2\pi M\kappa T_1)^{\frac{1}{2}} 2\alpha\kappa (T_2 - T_1). \quad (46)$$

In this expression all the quantities except α may be measured so that α may be determined. Thus T_2 is the temperature of the bath in which the glass tube is immersed, T_1 (usually taken to be about 20° greater than T_2) may be measured from the resistance of the wire and p by a McLeod gauge. W may be obtained from the electrical energy applied and the dimensions of the wire provided suitable corrections are made for end and radiation losses.

There is a further important point concerned in this measurement. It refers to the energy loss per unit apparent area of the wire and makes no allowance for the microscopic roughness of the surface. Because of this a fraction of gas molecules may make more than one collision with the surface before they finally leave it. If the true accommodation coefficient, for a perfectly smooth surface, is α and a molecule on the average strikes the surface in n different places before leaving it, then it may easily be shown† that the apparent accommodation coefficient α_1 , as measured, will be given by

$$\alpha_1 = 1 - (1 - \alpha)^n. \quad (47)$$

In the actual experiments it is not necessary to work at such low pressures that the mean free path is great compared with the tube diameter. If the free path l is only great compared with the diameter of the wire, the temperature difference between the wire and the gas is taken up within a distance of order l from the wire. In the region between this zone and the tube wall, the flow of heat follows by usual thermal conduction. Using the known value of the thermal conductivity of the gas it may then be verified that only a negligible temperature drop occurs outside the zone of radius l . The boundary of this zone can therefore be regarded, from the point of view of the preceding analysis, as equivalent to a solid wall at temperature T_1 .

The above analysis requires modification if polyatomic molecules are concerned. This is necessary to allow for the accommodation coefficients for vibrational and translational motion being different from that for translation. If the average rotational and vibrational energies per molecule at temperature T are $\frac{1}{2}f_r\kappa T$ and $\frac{1}{2}f_v\kappa T$ respectively and $\alpha_t, \alpha_r, \alpha_v$ are the respective translational, rotational, and vibrational accommodation coefficients, the expression (46) is replaced by

$$(p^2/2\pi M\kappa T_1)^{\frac{1}{2}} (4\alpha_t + f_r\alpha_r + f_v\alpha_v) \frac{1}{2}\kappa (T_2 - T_1). \quad (48)$$

A most important factor influencing the result of accommodation coefficient measurements is the state of the surface of the wire. Unless special precautions are taken to remove adsorbable impurities from the wire and to use gases free from even very small traces of such impurities.

† Roberts, *Proc. Roy. Soc. A*, **129** (1930), 146.

the value found for the accommodation coefficient is quite high. Thus, before the experiments of Roberts† in 1930, in which the most careful precautions were taken to avoid the presence of adsorbed layers, the accommodation coefficient of helium on tungsten was given as 0.3.‡ Roberts found that with a bare tungsten surface the value fell to 0.05.

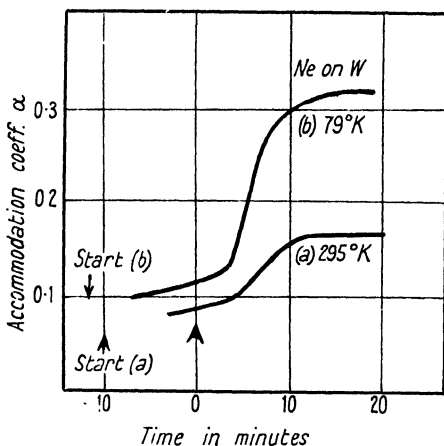


FIG. 280. Variation with time of apparent accommodation coefficient for neon on tungsten. At time $t = 0$ H_2 was admitted.

He also found a completely different temperature variation of the accommodation coefficient from that previously obtained.

As an illustration of the effect of adsorbed layers, Fig. 280 illustrates the variation with time of the apparent accommodation coefficient of neon on tungsten, obtained in certain experiments by Roberts.§ In this work the measurements were first taken for neon, which had been continuously circulated through charcoal tubes immersed in liquid air, and a tungsten wire which, after previous outgassing, had been flashed to $2,000^\circ$ to remove all adsorbed impurities. The measured values of α show a slow upward drift due to gradual accumulation on the wire of residual impurities. At a time indicated in Fig. 280, hydrogen, also purified by passage through liquid air cooled charcoal, was admitted to a partial pressure of 10^{-4} mm. The apparent accommodation coefficient immediately rose quite rapidly to a substantially greater saturation value. This indicated that hydrogen was adsorbed on the wire, forming

† Loc. cit.

‡ Soddy and Berry, *ibid.* **84** (1911), 576.

§ *Ibid.* **152** (1935), 445.

a practically complete monomolecular layer from which the larger accommodation coefficient was obtained. The accommodation coefficient has been used extensively by Roberts† as an indicator of adsorption phenomena.

Measurements of the accommodation coefficient have been made for pure helium on bare tungsten‡ and nickel surfaces§ and for pure neon on bare tungsten.|| These will be discussed in the next section. It will be found that even for pure neon, adsorption may occur on a bare metal wire at low temperatures so that there is little hope of extending the range of these measurements to heavier rare gases which are likely to be quite strongly adsorbed.

10.34. Analysis of observed data on accommodation coefficients. The first detailed quantal theory of the accommodation coefficient of an atom on a metal surface was given by Jackson and Mott†† following on preliminary work by Jackson.‡‡ They assumed a purely repulsive interaction V_0 between atom and metal given by

$$V_0 = -De^{-r/d}. \quad (49)$$

The calculation of the transition probability $P^+(E, E+h\nu)$ follows in exactly the same way as for the corresponding problem of the excitation of molecular vibration by atom impact in the gas phase (see Chap. VII, § 12.6). With this model they were able to obtain quite good agreement with the results of Roberts (§ 10.33) for helium on tungsten. The small value of the accommodation coefficient is essentially due to the same causes as the low probability of deactivation of vibrationally excited molecules by atom impact (Chap. VII, § 12.1). Their work was later refined by Jackson and Howarth,§§ who took into account the detailed distribution of normal modes within the crystal. A little later Landau|||| produced a purely classical theory from which he obtained the formula

$$\alpha = \frac{3}{8} \frac{1}{M_1 M^{\frac{1}{2}}} \left(\frac{8\pi\hbar^2 T}{\kappa d^2 \Theta^2} \right)^{\frac{1}{2}}, \quad (50)$$

in terms of the respective masses M , M_1 of a gas and of a solid atom and the characteristic temperature Θ of the solid. Finally, Devonshire††† calculated α with the form (25) for V_0 , allowing thereby for van der

† See *Some Problems in Adsorption*, Chap. VII.

‡ Roberts, *Proc. Roy. Soc. A*, **129** (1930), 146; **135** (1932), 192; Mann, *ibid.* **146** (1934), 776; Mann and Newall, *ibid.* **158** (1937), 397.

§ Raines, *Phys. Rev.* **56** (1939), 691.

|| *Proc. Roy. Soc. A*, **142** (1933), 518.

†† *Ibid.* **137** (1932), 703.

‡‡ *Proc. Camb. Phil. Soc.* **28** (1932), 136.

§§ *Proc. Roy. Soc. A*, **142** (1933), 447.

|||| *Phys. Zeits. Sowjetunion*, **8** (1935), 489.

††† *Proc. Roy. Soc. A*, **158** (1937), 269.

Waals attraction. He showed also that Landau's formula (50) is only valid, even if the attraction is negligible, provided

$$2\hbar^2/\pi^2 M \kappa d^2 \ll T \ll 0.006 \Theta^2 \pi^2 M \kappa d^2 / 2\hbar^2, \quad (51)$$

which, for helium on tungsten, requires T to lie between 10° and 24° K.

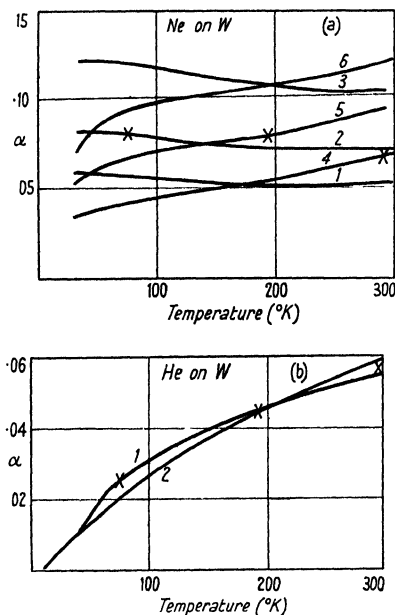


FIG. 281. (a) Variation with temperature of the accommodation coefficient α for neon on tungsten. The crosses are the experimental points obtained by Roberts. The curves were calculated by Devonshire with the following values of the interaction constants.

Curve	d cm.	D
1	1.41×10^{-8}	448 cal./mol.
2	1.33×10^{-8}	493 "
3	1.27×10^{-8}	553 "
4	1.00×10^{-8}	212 "
5	0.91×10^{-8}	252 "
6	0.86×10^{-8}	283 "

(b) Variation with temperature of α for helium on tungsten. The crosses were measured by Roberts. The curves were calculated by Devonshire with the following values of the interaction constants.

Curve 1: $d = 0.86 \times 10^{-8}$ cm.; $D = 60$ cal./mol. Roughness factor 1.1.

Curve 2: $d = 0.5 \times 10^{-8}$ cm.; $D = 0$. Roughness factor 1.06.

Fig. 281 illustrates the results of Devonshire's analysis of Roberts's results for neon and helium on tungsten. In each case a correcting factor slightly greater than unity is introduced to allow for the roughness

of the surface. It is clear that the theoretical values, with reasonable assumptions for D and d , are quite consistent with the observed magnitude and temperature variation of α . Thus for neon on tungsten the best agreement is obtained with $d = 1.33 \times 10^{-8}$ cm., $D = 493$ cals. The best choice for helium on tungsten is less definite, quite good agreement being obtained with both choices of constants illustrated in Fig. 281 (*b*). It is noteworthy what a large change of the constant d is required to compensate for the introduction of a quite small attraction ($D = 60$ cals.).

For helium on nickel† very good agreement, over the temperature range $369-90^\circ$, is obtained with Devonshire's theoretical values for $d = 1.33 \times 10^{-8}$ cm., $D = 428$ cals./mol., and a correcting factor of 1.04. The comparatively large attraction which this gives is perhaps a little surprising. It is of course assumed in all this analysis that no adsorbed layers are present. This is hardly consistent with the interaction found for neon and the lowest temperature. In this case the attraction is certainly large enough to lead to adsorption of neon atoms on the bare tungsten wire.

Apart from providing a most useful tool for the investigation of adsorption phenomena, the study of accommodation coefficients has furnished further evidence of the essential correctness of the theory of energy exchange between translation and vibrational motion of atoms, outlined in Chap. VII, §§ 12.1 and 12.6.

† Raines, loc. cit.

X

RECOMBINATION

1. Introduction

A KNOWLEDGE of the rate of recombination of positive ions with electrons or with negative ions is clearly of prime importance for any understanding of ionic phenomena. Thus the equilibrium concentration of ions built up in a large volume by any ionizing source is limited by the rate of recombination. A particular and important example is the ionization of the upper atmosphere due to solar ultra-violet radiation and other sources. Although the need for basic data on recombination is manifest and although the first experimental data on the subject date back to 1897, we are still far from possessing an adequate knowledge of the cross-sections for most of the two-body processes which lead to recombination. The severe experimental difficulties which are largely responsible for this arise from a number of reasons. Thus it is always difficult to measure rates of reaction between two systems neither of which can be maintained at a conveniently high concentration throughout the experiment. Added to this are the complexities arising from the strong Coulomb interaction between the ions which is particularly aggravating when the measurements have to be carried out for collisions between slowly moving ions, the important ones in most applications.

The only conditions under which both theory and experiment provide consistent and adequate information are those prevailing at pressures of a few mm. Hg or higher so that three-body recombination of positive and negative ions is predominant. For other, two-body, collisions leading to recombination between positive and negative ions there is no experimental information and only vague theoretical indications. Theory is more helpful in providing information about certain two-body recombination processes between positive ions and electrons, but it cannot give a complete account of all the possibilities which arise. Experimental evidence from a study of discharges confuses rather than clarifies the situation here. In view of these uncertainties and inadequacies it is perhaps not surprising that we are still far from sure of the nature of the processes which lead to effective recombination of electrons in the earth's ionosphere.

We shall commence by discussing recombination of positive and negative ions and, after a similar discussion for positive ions and electrons,

conclude with a brief outline of the problems presented in the interpretation of recombination in the different ionized layers of the upper atmosphere.

1.1 *The recombination coefficient*

Suppose that at any instant there are present in an ionized region n^+ positive ions and n^- negative ions/c.c. and that there is no source of ionization. Then, due to recombination,

$$\frac{dn^+}{dt} = \frac{dn^-}{dt} = -\alpha n^- n^+. \quad (1)$$

The quantity α is known as the recombination coefficient. It is given in terms of the recombination cross-section $Q_r(v)$ by the relation

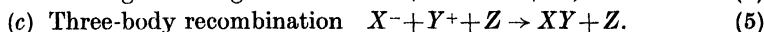
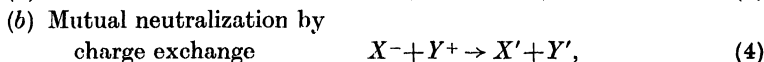
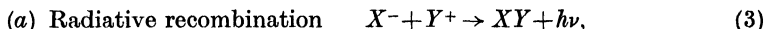
$$\alpha = \int_0^\infty v Q_r(v) f(v) dv, \quad (2)$$

where $f(v) dv$ is the fraction of encounters between positive and negative ions in which the relative velocity lies between v and $v+dv$. For most purposes α may be taken as $\bar{v} Q_r(\bar{v})$, where $\bar{v}$ is the mean value of v . In most applications it is more convenient to describe the rate of recombination in terms of the recombination coefficient rather than the corresponding cross-section.

2. Recombination between positive and negative ions

2.1. *Summary of possibilities*

Collisions between a positive ion Y^+ and a negative ion X^- which can lead to neutralization of charge may be summarized as follows.



Of these the first two are two-body processes and are therefore likely to be the only processes important at low pressures. The third is certainly the most important at pressures greater than a few mm. Hg.

2.2. *Radiative recombination*

A process such as (a) involves essentially a radiative transition between two electronic states of the molecule XY . The initial state must be one which, at infinite nuclear separation, dissociates into $X^- + Y^+$. The probability per collision may be estimated in the same way as was done for the chance of radiative capture of an electron by a positive ion in Chap. VI, § 2.1. It follows that the chance is unlikely to be greater

than 10^{-5} per collision, even for ions with room-temperature energy. The contribution to the recombination coefficient, at room temperatures, is therefore unlikely to be greater than $10^{-14}/\text{cm}^3/\text{sec}$.

2.3. Mutual neutralization

The process (b) is essentially a charge exchange collision (see Chap. VII, § 6.3; Chap. VIII, §§ 5.1, 6.21, 6.3). The electron may be captured into any state of the neutral atom X leaving a neutral atom Y in any state, provided energy is conserved. It is to be expected, however, that the probability will be a strong maximum for a particular pair of final states of X and Y .

Bates and Massey† have attempted to estimate the possible contribution to the recombination coefficient by applying the theory of the crossing of potential energy curves discussed in Chap. VII, § 10.31. Using the notation of that section, the interaction energy V_i between the initial pair of colliding systems, in a case such as (4), has an exceptionally large range due to the Coulomb interaction between the ions. The crossing-point at which $V_i - V_f = \Delta E$, the resonance defect, will be given closely by

$$R = -\epsilon^2/\Delta E, \quad (6)$$

the sign of ΔE in this case being taken as negative for a superelastic collision in which there is a gain in the energy of relative motion due to the impact. A real crossing-point exists therefore for any superelastic collision.

If I is the ionization energy of the atom Y , A the electron affinity of atom X and E_y , E_x the excitation energies of the respective atoms in their final states:

$$\Delta E = A - I + E_x + E_y. \quad (7)$$

For atoms such as oxygen there are a great number of excited states for which $|\Delta E|$ is quite small and the crossing-point occurs, according to (6), at a large value of R . At first sight this would appear to indicate that the cross-section might be as large as $\pi R^2 k'^2/k^2$, where k'^2/k^2 is the proportional increase in kinetic energy of relative motion,‡ but for reasons already mentioned in Chap. VII, § 10.31, this is not the case.

Referring to § 10.31 of Chap. VII it will be seen that the probability of the colliding systems finally separating beyond the crossing-point, with the charge transferred, depends on the magnitude of the transition potential $U(r)$. It has been pointed out in Chap. VII, § 10.31, that, for charge transfer, $U(r)$ falls off exponentially. For large values of R , $U(r)$

† *Phil. Trans. Roy. Soc. A*, **239** (1943), 269.

‡ The factor k'^2/k^2 arises because the cross-section is superelastic. $k\hbar$, $k'\hbar$ are the magnitudes of the initial and final momenta of relative motion.

will therefore be so small that the effective cross-section will be much less than $\pi R^2 k'^2/k^2$.

To take these effects into account Bates and Massey† studied in detail the case of atomic oxygen. Realizing at the outset that it was out of the question to attempt an accurate estimate of the probability for any particular transition, they contented themselves with examining the range of magnitude which the recombination coefficient might have due to different collisions of the type



To do this they wrote for $U(r)$ at the crossing-point

$$U = (\epsilon^2/a_0)\exp(-R/A) \quad (9)$$

and treated A as a variable parameter. Calculations were carried out for values of A ranging from a_0 to $8a_0$, the most probable values‡ lying between $2a_0$ and $4a_0$. Table I gives the results obtained for the mutual neutralization cross-section for impacts between O^- and O^+ ions with 1.7×10^{-2} eV relative energy (corresponding to a temperature of 250°K .), assuming different values of ΔE , and the two values $2a_0$ and $4a_0$ of the interaction parameter A . It will be seen that the maximum cross-section for a particular value of A does not occur at exact resonance

TABLE I

Calculated Cross-sections Q_m for Mutual Neutralization of O^+ and O^- for Different Values of ΔE and Two Values of the Interaction Parameter A

ΔE (eV)	0.50	0.75	0.90	1.0	1.5	2.0	3.0
$Q_m(\text{cm}^2) \begin{cases} A = 2a_0 \\ A = 4a_0 \end{cases}$	$\begin{matrix} \dots \\ 6 \times 10^{-18} \end{matrix}$	$\begin{matrix} < 10^{-19} \\ 9.7 \times 10^{-13} \end{matrix}$	$\begin{matrix} \dots \\ 2.1 \times 10^{-12} \\ (\text{max}) \end{matrix}$	$\begin{matrix} 6 \times 10^{-17} \\ 1.8 \times 10^{-13} \end{matrix}$	$\begin{matrix} 10^{-13} \\ < 10^{-10} \end{matrix}$	$\begin{matrix} 8.5 \times 10^{-13} \\ \dots \\ (\text{max}) \end{matrix}$	$\begin{matrix} < 10^{-10} \\ \dots \end{matrix}$

$\Delta E = 0$ but at a value of $|\Delta E|$ of the order of 1 eV. The sharpness of the maximum is also apparent, confirming the impossibility of accurate prediction. It is possible, however, to go a little farther by determining the actual values of ΔE which do arise in the particular collision we are considering.

Table II summarizes the different possible transitions with the corresponding values of ΔE . The uncertainty of 0.2 eV in the latter values arises from the inaccurately known electron affinity of atomic oxygen (see Chap. IV, § 6.3).

† Loc. cit.

‡ These may be obtained from a consideration of the wave functions for various electronic orbitals of the oxygen atom.

TABLE II.

Different Possible Final States arising from Mutual Neutralization of O^+ and O^- Ions with Corresponding Resonance Defects

<i>Terms</i>	<i>Configurations</i>	ΔE (eV)
$^3P + ^3P$	Both $(1s)^2(2s)^2(2p)^4$	11.35 ± 0.2
$^3P + ^1D$		9.39
$^1D + ^1D$		7.43
$^3P + ^1S$		7.18
$^1D + ^1S$		5.22
$^1S + ^1S$		3.01
$^3P + ^5S^0$	$(1s)^2(2s)^2(2p)^3 3s$	2.25
$^3P + ^3S^0$		1.87
$^3P + ^3P$		0.65
$^3P + ^3P$		0.40
$^1D + ^5S^0$		0.29
	$+ (1s)^2(2s)^2(2p)^4$	

From Table I it appears that the only important contribution is likely to be made by one of the five transitions in Table II for which ΔE is not greater than 2.25 eV. It is not unlikely that at least one of these transitions will be associated with a value of A , between $2a_0$ and $4a_0$, for which the cross-section is comparable with the maximum value possible for the particular value of ΔE concerned, i.e. between 10^{-12} and 10^{-13} cm.² It is most unlikely, however, that the cross-section could be much larger than this. Since the relative energy considered corresponds to a relative velocity of 5×10^4 cm./sec., the contribution to the recombination coefficient may well lie between 5×10^{-8} and 5×10^{-9} cm.³/sec., but is very unlikely to be much larger.

In the temperature range from 250° to 1,000° K. the recombination coefficient due to these processes is nearly proportional to v^{-1} .

No experimental evidence is available to test these theoretical conclusions and it is difficult to see how any direct evidence could be obtained.

2.4. *Three-body recombination—Theoretical considerations*

The surplus energy released by recombination is removed as radiation in a process such as (a) or is taken up as energy of excitation in the mutual neutralization process (b). An alternative possibility is that the energy is taken away by a third body as in (c). This will be important at pressures sufficiently high for the chance of a third atom or molecule to be in the neighbourhood of an interacting pair of ions to be large enough. At pressures of only a fraction of a mm. Hg recombination of positive and negative ions by this process makes by far the largest contribution to the recombination coefficient.

2.41. *J. J. Thomson's theory.* In 1924 J. J. Thomson† developed a theory of three-body recombination which has proved very successful, at least when the negative ions are of atomic mass and not electrons and the pressure is not too high.

According to this theory recombination occurs when either of two neighbouring ions of opposite sign lose sufficient kinetic energy by collision with a third body to describe a closed orbit relative to the other. The condition that two ions of mass M_1 , M_2 respectively, at distance r apart, should describe a closed orbit is that

$$\frac{1}{2} \frac{M_1 M_2}{M_1 + M_2} v^2 \leq \frac{\epsilon^2}{r}, \quad (10)$$

where v is the relative velocity of the ions when at the separation r . On the average at a temperature T each ion possesses the mean kinetic energy $\frac{3}{2}\kappa T$, so that the condition becomes, on the average,

$$\frac{3}{2}\kappa T \leq \epsilon^2/r. \quad (11)$$

Ions will therefore not recombine unless they approach each other, on the average, within a distance r_0 such that

$$r_0 = 2\epsilon^2/3\kappa T. \quad (12)$$

It is now assumed that, if either ion, when within a distance r_0 of the other, loses an amount of energy of order κT by collision with a third particle, recombination will occur. The recombination rate may therefore be determined by finding the number of such collisions, with gas atoms, effected by either ion when at a distance r_0 from the other.

Let s_1 be the chance that a positive ion makes a collision, involving appreciable energy loss, with a gas atom when within a distance r_0 from a negative ion, s_2 being the corresponding quantity for a negative ion. If n^- is the concentration of negative ions, the number of times per second that a positive ion approaches a negative ion within a distance r_0 is given, apart from a factor of order unity, by

$$\pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} n^-, \quad (13)$$

u_+ and u_- being the respective mean velocities of the ions. The chance that in such an encounter recombination will occur is $s_1 + s_2$ ‡ so that the chance per second that a positive ion will recombine is

$$\pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} n^- (s_1 + s_2). \quad (14)$$

† *Phil. Mag.* **47** (1924), 337.

‡ More accurately it is $s_1 + s_2 - s_1 s_2$, since the chance that both ions make effective collisions with the gas atoms when within a distance r_0 of each other has been included in both s_1 and s_2 .

We therefore have, if n^+ is the positive ion concentration,

$$\begin{aligned}\frac{dn^+}{dt} &= -\pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} (s_1 + s_2) n^- n^+, \\ &= -\alpha n^- n^+, \end{aligned}$$

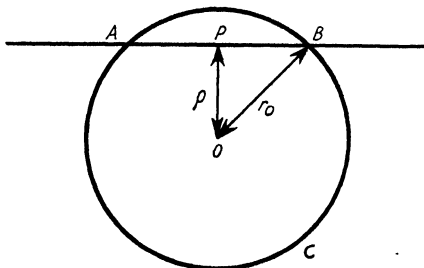


FIG. 282.

so that the recombination coefficient is given by

$$\alpha = \pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} (s_1 + s_2), \quad (15)$$

corresponding to a recombination cross-section

$$Q_r = \pi r_0^2 (s_1 + s_2). \quad (16)$$

It remains to calculate s_1 and s_2 .

Let l_1 be the mean free path for effective collisions (those involving appreciable energy loss) with gas atoms. Referring to Fig. 282, consider a positive ion which passes along the path AB relative to the negative ion at O , while within a distance r_0 from this ion, i.e. within the sphere ABC of centre O . The length of AB is $2(r_0^2 - \rho^2)^{\frac{1}{2}}$, where ρ is the distance OP . The chance that this positive ion will traverse the distance BA without making a collision is

$$\exp\{-2(r_0^2 - \rho^2)^{\frac{1}{2}}/l_1\}.$$

Averaging over all such paths as AB we have then

$$\begin{aligned}s_1 &= 1 - \frac{2}{r_0^2} \int_0^{r_0} \exp\{-2(r_0^2 - \rho^2)^{\frac{1}{2}}/l_1\} \rho \, d\rho \\ &= 1 + 2 \left\{ \frac{e^{-g_1}}{g_1^2} + \frac{e^{-g_1}}{g_1} - \frac{1}{g_1^2} \right\}, \end{aligned}$$

where

$$g_1 = 2r_0/l_1.$$

For low pressures, $g_1 \ll 1$ and $s_1 \simeq \frac{2}{3}r_0/l_1$ and for high pressures

$$g_1 \gg 1, \quad s_1 \simeq 1.$$

Substituting for s_1 and s_2 in (16) completes the derivation. For low pressures, l_1 and $l_2 \gg r_0$, we obtain then

$$Q_r = \frac{4\pi r_0^2}{3} \left(\frac{r_0}{l_1} + \frac{r_0}{l_2} \right). \quad (17)$$

Since l_1 and l_2 are inversely proportional to the gas pressure, Q_r and α are proportional to the pressure at low pressures.

At high pressures, on the other hand,

$$Q_r = 2\pi r_0^2, \quad (18)$$

pressure saturation occurs, and the recombination coefficient is independent of the pressure.

In the low-pressure region the three-body recombination coefficient is now given by

$$\alpha = \frac{64(2\pi)^{\frac{1}{2}}}{81} \frac{\epsilon^3}{(\kappa T)^{\frac{1}{2}}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{\frac{1}{2}} \left(\frac{1}{l_1} + \frac{1}{l_2} \right). \quad (19)$$

It therefore varies as $T^{-\frac{1}{2}}$ † and depends rather slightly on the masses of the ions through the factor $\left(\frac{M_1 + M_2}{M_1 M_2} \right)^{\frac{1}{2}}$. There will also be a small dependence on the nature of the ions through the free paths l_1 and l_2 .

At high pressures, according to this theory, α should reach a constant saturation value given by

$$\alpha = \frac{16(2\pi)^{\frac{1}{2}}}{9} \frac{\epsilon^4}{(\kappa T)^{\frac{1}{2}}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{\frac{1}{2}}. \quad (20)$$

As we shall see below, the theory is no longer reliable at high pressures and this expression is only valid at pressures in air between 700 and 1,000 mm. Hg.

There are two points which need further consideration. The first concerns the meaning of the free paths l_1 and l_2 . These refer to collisions in which the ion suffers an energy loss of order κT with a gas atom. Provided the masses of the ions and atoms are comparable this will occur in any collision in which there is an appreciable change in the direction of the relative velocity vector. To a sufficient approximation the cross-section for such collisions may be taken as the diffusion cross-section (Chap. VII, § 3.1) and the free paths calculated in the usual way from it. Thus, if n is the number of gas molecules per c.c. and Q_d is the diffusion cross-section, then $l = 1/nQ_d$. If the mass M of a gas atom is much greater than that m of an ion, this approximation is not correct. The fractional loss of energy per collision will be reduced by a factor of order m/M . The free path l to be taken must then be of order M/m

† This assumes l_1, l_2 do not vary with T .

times that derived from the diffusion cross-section. Furthermore, it has been assumed that a reduction of kinetic energy of either ion by collision will be equally effective in reducing the kinetic energy of relative motion of the two ions. This will only be so if the ions are of comparable mass. If one ion is much lighter than the other the only effective collisions will be those made by the light ion with the gas atoms. These reservations are not often important for recombination between ions but they are very important in extending the theory to estimate the rate of three-body recombination between positive ions and electrons (see § 3.5).

The second point concerns the assumption that recombination will occur if one of the ions makes an effective collision with a gas atom when within a distance r_0 of the other. No allowance is made, however, for the possibility of further collisions occurring while the ion is within the distance r_0 of the other. These collisions may well restore the original hyperbolic motion, and if the chance of their occurrence is high it is clear that the formula (16) will not give the correct result. We must therefore expect Thomson's theory to break down at high pressures. This is indeed the case, as will be shown in the next section. An alternative theory, due to Langevin,[†] may be used at high pressures.

2.42. Langevin's theory. According to this theory the ions are considered to drift towards each other under the influence of their Coulomb attraction. This drift is retarded by collisions with the gas atoms so that it takes place with a velocity proportional to the attracting force. Thus if k_1 and k_2 are the respective mobilities of the ions under the experimental conditions, the relative drift velocity when the ions are at a distance r apart will be

$$(k_1 + k_2)\epsilon^2/r^2. \quad (21)$$

Consider a spherical surface of radius r around a negative ion as centre. According to (21) the number of positive ions drifting radially inwards across this surface per second will be

$$4\pi n^+(k_1 + k_2)\epsilon^2, \quad (22)$$

n^+ being the concentration of positive ions/c.c. These positive ions will drift up to and hence neutralize the negative ion unless deflected by collisions with other ions. Ignoring this latter possibility the recombination coefficient α is given by

$$4\pi\epsilon^2(k_1 + k_2). \quad (23)$$

It follows that, under the assumed conditions, the recombination coefficient α varies with the pressure p in the same way as the mobility, i.e. it is proportional to $1/p$.

We shall see in the next section that the Langevin theory does give quite satisfactory results for the recombination of ions in air at pressures greater than 2 atmospheres. On the other hand, at pressures between 100 and 1,000 mm. Hg the Thomson theory proves very satisfactory and, although the region of applicability of the two theories does not overlap, taken together they give, with some

[†] *Ann. Chim. Phys.* **28** (1903), 289, 433.

interpolation, a good representation of the recombination over a very wide pressure range.

2.5. *Experimental study of three-body recombination of ions*

The first experimental work on the recombination of ions at atmospheric pressure dates back to 1897, when Rutherford and J. J. Thomson† showed that the rate of decay of ion density after the ionizing agency is cut off followed the quadratic law (1). Since these early experiments there has been very little change of principle in the methods used for measuring recombination coefficients but very substantial improvements in technique. The most recent work, that of Sayers,‡ has brought to light certain causes of error in earlier investigations, and has given very satisfactory information about the recombination coefficient in air at pressures between 100 and 1,500 mm. Hg. Reliable information is also available in the pressure range from 4,000 to 22,000 mm. Hg due to the work of Mächler.§ Combination of the two sets of observations with the predictions of the Thomson and Langevin theories gives a complete description of three-body recombination.

2.51. *The low-pressure range.* Sayers employed the principle used in Rutherford's pioneer work. The gas between two collecting electrodes was ionized by a short flash of X-rays and the ionization persisting at a time t after the flash measured by collecting the charges at the electrodes to which a sufficiently high potential difference was applied. The ionization chamber was constructed so that modern methods of purification under high vacuum conditions could be applied. All the metal parts, the end-plates, and the electrodes were of nickel. The collecting electrode was provided with a guard ring on which it was mounted with quartz supports, while the end-plates were held rigid and parallel by quartz spacers. The whole was fitted in a pyrex cylinder (9×20 cm. approx.). To prevent stray fields, due to charging up of the glass, from affecting the field between the electrodes a cylinder of nickel gauze was fitted between the glass and the ionization chamber. Surface contamination was removed from the metal parts before assembly, and after assembly the whole region within the glass envelope was highly evacuated, and heated to 500° C. for a few hours in an oven. Finally the metal parts were brought to red heat by an induction heater.

The apparent recombination coefficient α_a is given by

$$\alpha_a = \frac{d}{dt} \left(\frac{1}{n} \right), \quad (24)$$

† *Phil. Mag.* **44** (1897), 422.

§ *Phys. Zeits.* **37** (1936), 211.

‡ *Proc. Roy. Soc. A*, **169** (1938), 83.

where n is the ion concentration. A study of the variation of α_a under different conditions is important in leading to the choice of the true value of α due to three-body recombination. α_a varies with the time the observation is taken after the X-ray flash has ceased and also with the duration of the flash. Fig. 283 exhibits the former variation. At first α_a decreases with the time after the cessation of the X-ray

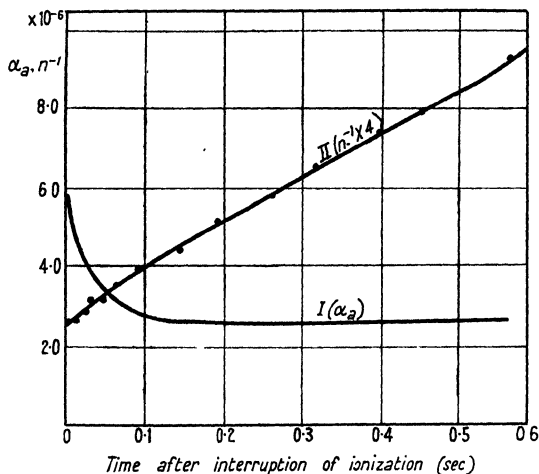


FIG. 283. Illustrating the variation of apparent recombination coefficient α_a with time after the ionizing X-radiation has been cut off. I gives the apparent recombination coefficient α_a derived by graphical differentiation of curve II for n^{-1} which has been obtained from the directly observed values of ion concentration.

flash, but after a tenth of a second it settles down to a completely steady value. If the duration of the flash is increased and the experiment repeated, a similar variation of α_a with time after the cessation of the flash is obtained but a smaller steady value is reached. The longer the flash the smaller the steady value becomes. Thus the apparent steady value of α changed from 2.65 to 2.3 cm.³ sec.⁻¹ when the initial ion concentration n_0 produced by the flash was increased from 1.5 to 4.1×10^6 /c.c. Similar results were found by Marshall, Luhr, and Gardner.† The interpretation of these effects is clear.

The initial ionization produced by the flash is rather concentrated along the track of the X-ray beam. The actual ion concentration which determines the rate of recombination is therefore greater than it would be if the ionization were uniformly distributed throughout the region

† *Phys. Rev.* **53** (1938), 75.

between the plates. The effective recombination coefficient may be determined from (24) by assuming uniform distribution of ionization. After this occurs the recombination coefficient should remain constant. The fact that it does so in the experiment shows that effects due to the presence of concentrated regions of ionization are no longer present. It remains to explain the increase in the steady value with duration of

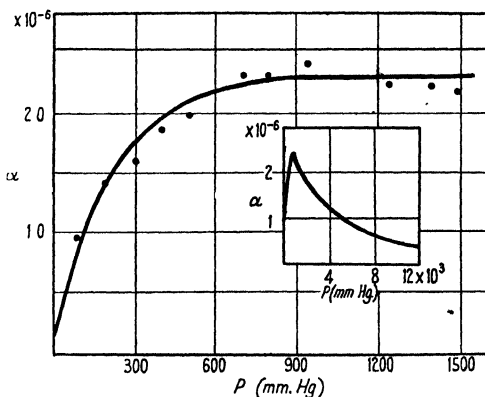


FIG. 284. Three-body recombination coefficient for ions in air as a function of pressure.

— predicted by J. J. Thomson's theory; • experimental points.

Inset. High-pressure region including measurements of Mächler.

the flash. This may be attributed to changes in the chemical composition of the air, such as the formation of ozone, by the X-radiation. Abnormally heavy ions, with low rate of recombination, might well be formed in this way. In support of this explanation it has been found that the effect is particularly marked in pure oxygen and absent in nitrogen or helium in which X-rays do not form complex molecules.

In view of these considerations the correct value to take for α is the steady value attained in the limiting case of very short irradiation. At the lower pressures a correction has to be made due to the loss of ions by diffusion to the plates. If d is the distance between the plates, D the diffusion coefficient of the ions, the correction to be applied to the observed value of α may be easily shown to be $\frac{3}{2}D/nd^2$. Taking D as $0.047 \text{ cm.}^2/\text{sec.}$ at N.T.P. the correction at 100 mm. pressure amounts to about 40 per cent. under the experimental conditions ($d = 1.5 \text{ cm.}$, $n = 10^6 \text{ ions/c.c.}$). The size of this correction shows that it is not possible in this type of experiment to obtain reliable data at much lower pressures.

Fig. 284 illustrates the comparison of the data obtained by Sayers for

air with the predictions of Thomson's theory (see (15) and (18)). The agreement is very close up to pressures of 1,000 mm. but there is a tendency for the observed values to decrease again at higher pressures.

2.52. The high-pressure region. Measurements of the recombination coefficient extending up to pressures of 22,000 mm. of air and CO_2 have been made by Mächler. As source of ionization he used 40 mg. of radium and his experiments were carried out with ion concentrations in the range $(0.4\text{--}8.0) \times 10^5$ ions per c.c.

His results for the variation of α with pressure for air are shown in Fig. 284 (inset). For the pressure range 11,000–22,000 mm. Hg the product αp for recombination in air at 18°C . remains constant. For air at 52°C . the product αp does not reach a constant value until a pressure in excess of about 15,000 mm. Hg. This behaviour is in good agreement with that to be expected from Langevin's theory. For CO_2 , on the other hand, αp passes through a maximum at a pressure of about 8,000 mm. Hg and falls slowly for further increase of pressure.

2.53. The ionization balance in the lower atmosphere. At the pressures prevailing in the lower atmosphere three-body recombination is the most important process which leads to loss of ions. Hence if q is the rate of formation of ions/c.c. at a given height and n_0 is the equilibrium ion concentration at that point, the equilibrium conditions require

$$q = \alpha n_0^2. \quad (25)$$

q has been measured at various heights by Regener and Pfotzer,† using sounding balloons, while Gish and Sherman‡ have measured the electrical conductivity at different heights using automatic recording apparatus during the stratosphere flight of *Explorer II* at South Dakota. Both sets of observations were made at approximately the same latitude. The conductivity σ is given in terms of the ion concentration by the relation

$$\sigma = e\mu n_0, \quad (26)$$

where μ is the ion mobility at the temperature and pressure concerned. It follows then from (25) and (26) that the conductivity may be calculated from known values of q , μ , and α . Comparison of the values obtained in this way with Gish and Sherman's observations reveals very good agreement over the entire height range of the measurements (3–17 km.). This provides additional confirmation of the accuracy of the measured recombination coefficients.

2.6. Concluding remarks on ion-ion recombination

The three-body recombination coefficient in air is given at temperature T and pressure p (< 300 mm. Hg) by

$$\alpha = 8 \times 10^{-3} p / T^{\frac{1}{2}}, \quad \text{where } p \text{ is in mm. Hg.} \quad (27)$$

The theoretical considerations of § 2.3 have indicated that the contribution from the two-body mutual neutralization process (8) is not greater than 10^{-8} cm.³/sec. so that three-body recombination is probably predominant at ordinary temperatures down to a pressure of 1 mm. Hg. The total recombination coefficient will therefore only become effectively independent of the pressure at pressures somewhat less than this.

† *Phys. Zeits.* **35** (1934), 779.

‡ *Bull. Int. Ass. Terr. Mag. Elect.* **10** (1936), 382.

3. Recombination between positive ions and electrons

3.1. Summary of possibilities

Corresponding to the processes summarized in § 2.1 we may summarize the processes which can lead to recombination of positive ions with electrons.

$$(a) \text{ Radiative recombination} \quad A^+ + e \rightarrow A' + h\nu. \quad (28)$$

$$(b) \text{ Dielectronic recombination} \quad A^+ + e \rightarrow A'' \text{ (doubly excited atom)}$$

$$\text{followed by} \quad A'' \begin{cases} \rightarrow A^+ + e, \\ \rightarrow A' + h\nu. \end{cases} \quad (29)$$

$$(c) \text{ Dissociative recombination} \quad AB^+ + e \rightarrow A' + B'. \quad (30)$$

$$(d) \text{ Three-body recombination} \quad A^+ + e + X \rightarrow A + X. \quad (31)$$

Just as in § 2.1, these processes differ essentially in the way the surplus energy, due to the recombination, is disposed of. We cannot, of course, be sure that they include all the possibilities.

3.2. Radiative recombination

This has already been discussed in Chapter VI. Referring to Table I of that chapter it will be seen that the contribution to the recombination cross-section due to these processes is only $3 \times 10^{-19} \text{ cm}^2$ for electrons with room-temperature energies. The corresponding recombination coefficient is thus only $3 \times 10^{-12} \text{ cm}^3/\text{sec}$.

3.3. Dielectronic recombination

In this process the surplus energy released by the recombination of the electron to some excited state is supposed, in the first instance, to be taken up by a second atomic electron which is also raised to an excited state. The doubly excited atom so formed is energetically unstable, and if the surplus energy is not disposed of in some other way will revert to the initial conditions ejecting one electron and leaving the other bound in its initial state. There is a chance, however, that before this happens, the doubly excited atom will undergo a radiative transition, thereby dropping to a stable, singly excited state.

The contribution from a process of this sort, first suggested by Sayers, has been estimated theoretically by Massey and Bates.† They found that the recombination coefficient arising from this process in a gas at temperature T is given by

$$(\hbar^2/2\pi m \kappa T)^{\frac{1}{2}} \sum_s (w_s/2w_2) \tau_s^{-1} \exp(-E_s/\kappa T).$$

E_s is the energy excess of a term of a doubly excited configuration of the

† *Reports on Progress in Physics*, ix (1942), 62.

atom concerned above that of the ground level of the corresponding positive ion. τ_s is the lifetime of the term towards a radiative transition to a stable level. w_s is the statistical weight of the doubly excited term and w_2 that of the ground level of the ion.

Substituting numerical values, taking T as 300° K. and τ as 10^{-8} sec., gives

$$\alpha \simeq 10^{-11} \sum (w_s/2w_2) \exp(-E_s/\kappa T).$$

Since the statistical weights are of order unity it is clear that an important contribution can only arise from this process if E_s is comparable with κT . For atomic oxygen, a case of special interest in connexion with the earth's upper atmosphere (see § 4), a study of the likely distribution of excited levels shows that the contribution is not likely to be greater than 10^{-12} cm.³/sec.

3.4. Dissociative recombination

If the positive ion is polyatomic the surplus energy due to recombination may be transferred to energy of molecular vibration leading to dissociation of the molecule, into fragments which may or may not be in their ground electronic states. This process is similar to the corresponding process of negative ion formation (dissociative attachment) discussed in Chap. IV, §§ 4.31, 6.32. In these cases the surplus energy released by electron attachment leads to molecular dissociation, as, for example, with oxygen (see Chap. IV, § 6.32)



It is clearly out of the question to measure the cross-section for the corresponding dissociative recombination



and it is not at present possible to make any reliable estimates even of the order of magnitude of the cross-section either directly from theory or by arguments based on the known order of magnitude for the reaction (32). The size of the cross-section will depend very markedly on the distribution of the potential energy curves for the various electronic states of O_2^+ and O_2 relative to each other. For the negative ion reaction (32) the potential curves of O_2^- and O_2 are involved and these are likely to be related in an entirely different manner.

The only evidence at present available about reactions such as (33) comes from some investigations by Mohler and Boeckner of the photo-ionization of caesium. It was found by Mohler, Foote, and Chenault† that ionization could be produced by irradiation of caesium vapour by lines of the principal series of the caesium

† *Phys. Rev.* **27** (1926), 37.

spectrum. These quanta are clearly not energetic enough to produce photo-ionization by direct absorption.

An alternative possibility, that caesium atoms excited by light absorption are subsequently ionized in collision with a normal atom, may well be the explanation of the ionization currents observed due to lines arising from transitions $m^2P-6^2S_{\frac{1}{2}}$ with m greater than about 15. Absorption of such lines will lead to caesium atoms excited to within a few hundredths of an electron volt of ionization. These atoms will readily be ionized in collision with normal atoms. However, the effect is observed even for $m = 8$. The energy required to ionize Cs (8^2P) atoms is 0.2 eV, which is so high that the chance of ionization occurring in a gas-kinetic collision is far too small.

For such cases the only remaining possibility is that a reaction



which is the inverse of dissociative recombination, is responsible. This explanation is consistent with the observation that the photo-ionization current is reduced by the addition of foreign gas which presumably acts by deactivating excited caesium atoms as in the quenching of resonance radiation.

Assuming the correctness of the interpretation in these terms Mohler and Boeckner† were able, by studying the photo-ionization currents produced in caesium, to estimate the product τQ of the radiative lifetime τ of a caesium atom in a particular excited state and the cross-section Q for the atom to leave the excited state by the process (34). For the lowest excited states investigated, 8^2P and 9^2P respectively, τQ was found to be 2.1×10^{-22} and 4.7×10^{-20} cm.² sec. respectively. Taking for τ a rough estimated value 10^{-6} sec. gives for Q the values 2.1×10^{-16} and 4.7×10^{-14} cm.² respectively. Up to $m = 12$ the observed values of τQ increase gradually, but for higher values of m they increase very rapidly showing, in all probability, that some additional process is becoming effective.

These indirectly obtained values of the cross-section for the process (34) can only be regarded as providing a rough indication. Owing to complete lack of knowledge of the properties of the potential energy curves for Cs_2^+ it is not possible to determine the energy of the ejected electron in (34). Without this knowledge it is not possible to derive the cross-section for the inverse dissociative recombination process for electrons at room temperature from Mohler and Boeckner's results. All that can be said is that the cross-section may be of the order of the gas-kinetic, giving a recombination coefficient between 10^{-8} and 10^{-9} cm.³/sec.

3.5. Three-body recombination

The formulae (15) and (18) for the three-body recombination of positive and negative ions may be extended to apply to electrons if the following modifications are introduced.

When an electron and positive ion are within the critical distance r_0 apart, the only collision which will be effective in reducing the relative velocity of the two charges will be one in which the electron loses energy. The cross-section for recombination becomes then $s_2 \pi r^2$, where s_2 will be given by the same formula as in § 2.41 but the free path l_2 is no

† *Bur. of Stand. J. of Res.* 5 (1930), 51, 399, 831.

longer nearly equal to the gas-kinetic free path. As discussed in § 2.41, for a collision to be effective in producing recombination it must result in the ion losing a large fraction of its energy. An electron of mass m loses only a fraction of order $2m/M$ of its energy in a collision with a gas atom of mass M , the effective cross-section for which is Q_d , the diffusion cross-section defined in Chap. I, § 5.1. Hence in the expression for s_2 , l_2 is to be taken as approximately $M/2mNQ_d$, N being the number of gas atoms/c.c.

Hence for three-body collisions involving rare gas atoms the cross-section for three-body recombination of electrons is given approximately by

$$Q_r = \frac{8\pi}{3} \frac{r_0^3 m}{lM}, \quad (35)$$

where l is of the same order as the gas-kinetic mean free path ($1/NQ_d$), provided

$$Ml/2m \gg r_0. \quad (36)$$

The recombination coefficient, under the same conditions, will be

$$\alpha = (8\kappa T/\pi m)^{1/2} 8\pi r_0^3 m/3Ml. \quad (37)$$

Comparing this with the corresponding expression (19) for ion-ion recombination when $l \gg r_0$, it will be seen that

$$\alpha \text{ (ion-ion)} \simeq (2M/m)^{1/2} \alpha \text{ (ion-electron)}. \quad (38)$$

These considerations apply only when the third bodies are atoms. If they are molecules, allowance must be made for the loss of energy by an electron in exciting inner molecular motion (see Chap. IV, § 7). The fractional loss of energy λ by an electron on impact may be appreciably higher than $2m/M$ and the formula (37) must be modified by replacing $2m/M$ by λ .

Substituting numerical values, the contributions to the electron recombination coefficient due to three-body recombination given in Table III are obtained. The values used for l are those discussed in Chap. I, § 8 (He and A) and in Chap. IV, § 7. For air and hydrogen the values used for λ are those given in Chap. IV, Table VI. The small recombination coefficient for argon is due to the Ramsauer effect, while the large values for air and hydrogen arise from the possibility of electron energy loss by the excitation of molecular vibration.

At sufficiently high pressures, for which $r_0 \simeq l$, the electron recombination coefficient will saturate. Estimates of the saturation pressures are given in Table III.

At ordinary pressures it is clear that three-body recombination of electrons to positive ions by the Thomson process takes place very

TABLE III

Three-body Recombination Coefficients for Electrons in Different Gases

Gas	α at N.T.P. cm. ³ /sec.	Estimated saturation pressure (mm. Hg)
Helium . . .	6.8×10^{-9}	2.8×10^4
Argon . . .	6.8×10^{-11}	2.8×10^5
Air . . .	1.7×10^{-7}	10^4
Hydrogen . . .	1.6×10^{-7}	10^4

slowly. It is important to remember, however, that we have ignored the effect of pressure on the rate of radiative recombination. In Chap. VI, § 2, this has been calculated on the assumption that even the most highly excited atomic states are completely unperturbed by the presence of neighbouring atoms. This cannot be true in fact, but so far no attempt has been made to allow for such effects as far as their influence on the rate of recombination is concerned.

A further possibility which has been ignored is the effect of neighbouring charges on either the rate of radiation or of three-body recombination. In a dense discharge plasma the long-range interaction between neighbouring charges may be quite important. It will certainly perturb the outer electronic orbits into which recombination can occur, but it will also provide an alternative means by which an electron may lose energy when within the critical distance r_0 of a positive ion. Again it is difficult to allow properly for either of these effects particularly because one must also allow for the neighbouring electrons being effective in the opposite way, by ionizing an atom in a highly excited state into which recombination has occurred.

In view of the difficulty of interpreting observed data or electron recombination in a dense plasma, discussed in the next section, it is important to remember the effects which have been ignored in summarizing the possibilities.

3.6. *Experiments on recombination in dense plasmas*

The only attempts which have been made to obtain direct information on the rate of recombination of electrons and positive ions have been concerned with the study of the decay of electron density in the positive column of an arc discharge after the exciting energy has been cut off. This rate of decay is determined not only by recombination within the column but also by the drift of ions to the walls of the discharge tube. In order that the latter effect, which gives a contribution proportional

to the ion concentration n , should not be much greater than that from volume recombination, which is proportional to n^2 , it is necessary to work with high ion densities of order 10^{12} – 10^{13} /c.c. This has the disadvantage that the influences of neighbouring charges on the recombination of any pair may well be considerable. There is also the complication that ion production does not cease immediately the exciting voltage is cut off. The temperature of the electrons in the plasma certainly falls but not so rapidly as to render immediately negligible the ionization by electron impact, particularly when metastable atoms are present.

So far recombination in argon,† caesium,‡ mercury,§ and helium|| has been studied. In all these cases, in which the negatively charged particles are almost certain to be mainly electrons, an effective recombination coefficient of between 2 and 4×10^{-10} cm.³/sec. was found. Before discussing the difficulties faced in attempting to interpret this result we shall describe a typical experiment, that of Mohler for caesium.

In these experiments the discharge tube consisted of a bulb of 500 c.c. capacity with the cathode and anode in diametrically opposite side tubes. It was necessary to choose a large bulb to increase the importance of volume as against wall recombination. A 10-volt D.C. discharge through caesium vapour at pressures ranging from 8 to 300×10^{-3} mm. Hg could be operated in the bulb. The discharge was short-circuited and restarted at suitable intervals by a commutator. Observations of the afterglow were made at various times during the intervals when the exciting voltage was off.

The decay of electron density in the afterglow was investigated in three ways—by visual intensity, spectrophotometric, and probe measurements.

For the visual intensity measurements a stroboscopic arrangement, employing a sectored disk mounted on the same shaft as the commutator, was used to view the afterglow as it appeared at known time-intervals after the discharge was short-circuited. With the commutator running at 1,200 revs. per minute each flash contributing to the stroboscopic image lasted 7×10^{-4} sec. The intensity was measured by a simple photometer using as comparison source a headlight lamp with yellow filter to match the pale yellow colour of the afterglow.

If the afterglow arises entirely from radiative recombination its intensity I must be proportional to n_e^2 , where n_e is the electron concentra-

† Kenty, *Phys. Rev.* **32** (1928), 624.

‡ Mohler, *Bur. of Stand. J. of Res.* **19** (1937), 447.

§ Mohler, *ibid.* 559.

|| Sayers, *Nature* (1947); Biondi and Brown, *Phys. Rev.* **75** (1949), 1700.

tion. If α is the effective recombination coefficient and n_1, n_2 the electron concentrations at times t_1 and t_2 , then

$$\frac{1}{n_2} - \frac{1}{n_1} = \alpha(t_2 - t_1), \quad (39)$$

so that, writing $I = kn_e^2$,

$$I_1^{-\frac{1}{2}} - I_2^{-\frac{1}{2}} = k^{-\frac{1}{2}}\alpha(t_2 - t_1). \quad (40)$$

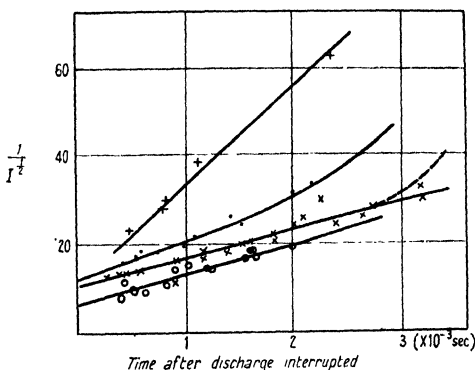


FIG. 285. Variation of $I^{-\frac{1}{2}}$ with time for an afterglow in caesium vapour of intensity I .

○, ×, *, + experimental points obtained at caesium pressure of 290, 46–110, 21, and 8×10^{-3} mm. Hg respectively.

Fig. 285 illustrates results obtained for the variation of $I^{-\frac{1}{2}}$ with time for various caesium vapour pressures. Although the variation is linear over a considerable time, the slopes of the curves in Fig. 285 increase with caesium pressure up to about 4.6×10^{-2} mm. Hg. This is probably due to decrease in the contribution from wall recombination. At pressures between 4.6 and 11.0×10^{-2} mm. Hg the initial slope of the curves remains constant, indicating that in this range we are dealing with true volume recombination, independent of pressure. The initial slope increases again at still higher pressures which might be due to increase of the volume recombination coefficient with pressure, but as the afterglow was not uniformly distributed through the bulb at these pressures this conclusion is uncertain.

In Fig. 285, for times greater than 3 milliseconds, a marked upward curvature is apparent. This is what would be expected when the electron density n_e has fallen so low that the diffusion 'correction', which is of the order $D/n_e r^2$ (see § 2.51), where r is the radius of the bulb and D the coefficient of diffusion of the electrons and ions, becomes dominant.

This raises some doubt as to the interpretation of the change in initial slope of the curves in Fig. 285 at low pressures. If this were due to diffusion becoming important the curves would not be expected to remain linear as they do.

Assuming, however, that the interpretation of the curves in Fig. 285 is correct it is possible to obtain an estimate of α . To do this k is obtained by extrapolation of the curves of Fig. 285 to $t = 0$ and the initial electron density n_0 taken as that prevailing in the steady discharge. In the pressure range $4.6\text{--}11.0 \times 10^{-2}$ mm. Hg, n_0 as determined by a probe measurement had a mean value of $1.9 \times 10^{12}/\text{c.c.}$ The corresponding value found for α is $3.5 \times 10^{-10} \text{ cm.}^3/\text{sec.}$

The spectrophotometric measurements were designed to measure the electron concentration in the afterglow by a comparison of the intensity of recombination spectrum appearing in it with the same spectrum in the steady discharge. The measurements made by Mohler and Boeckner for the latter conditions have already been discussed in Chap. VI, § 2.6. The formula (8) given there for the intensity involves not only the electron concentration but also the electron temperature. In the afterglow the electron temperature is considerably less than that in a steady discharge and gradually decreases with time since cut-off. Measurements were therefore made of the electron temperature T_e at two intervals after cut-off, using the same technique as that for the steady discharge—from the variation of the intensity of the recombination spectrum with wave-length (see Chap. VI, § 2.6). The absolute intensity at the series limit was also measured at the same time-intervals. Assuming these intensities to be proportional to $n_e T^{-\frac{1}{2}}$ it was then possible to determine n_e at the two time-intervals by comparison with the corresponding measurements in the steady discharge. Using the formula (39) α could then be found. Two such determinations were made. In one, at a pressure of 6.8×10^{-2} mm. Hg, the time-intervals were 0.87 and 1.63 milliseconds after cut-off. The electron temperature was found to have fallen to $1,300^\circ \text{ K.}$ and $1,200^\circ \text{ K.}$ respectively from the value $2,700^\circ \text{ K.}$ for the steady discharge. From this α came out to be $5.5 \times 10^{-10} \text{ cm.}^3/\text{sec.}$ A similar measurement at a higher pressure, 8.5×10^{-2} mm. Hg, gave $4.3 \times 10^{-10} \text{ cm.}^3/\text{sec.}$

The third method was based on purely electrical measurements. The current diffusing to the walls, in the afterglow, was measured by a disk probe 3 cm. in diameter and the electron concentration within the afterglow by a wire probe, 0.5 mm. in diameter, extending radially with exposed surface 6 cm. long.

It proved to be difficult to obtain reproducible results when the probes were used in the conventional way (positive to wall or space), so that all measurements were made with the probe potentials negative to a wall or space respectively. The true current to the wall was obtained by extrapolation of the current to the disk probe to give that when the disk was at wall potential. A similar extrapolation for the wire probe gave the positive ion current to it when at space potential, but it was still necessary, in this unconventional use of a probe, to obtain the relation between this current and ion concentration. To do this Mohler assumed that the relation would be independent of pressure and ion concentration and carried out measurements, with both probes, at such low caesium pressures that volume recombination could be ignored. In these circumstances, and assuming that in the afterglow ion production is negligible, the change Δn in ion concentration in a time-interval Δt could be deduced from the disk current measurements. The corresponding change Δi_+ in ion current to the wire probe at space potential may then be related to Δn . This procedure is very dubious as it now appears that positive ion collection by a probe in a plasma is a complex process and it is not legitimate to suppose that the relation between ion density and probe current at space potential is independent of ion concentration and gas pressure.

However, by making these assumptions, Mohler obtained curves giving the variation of dn/dt with ion concentration of which those shown in Fig. 286 are typical. Subtraction of the contribution from wall loss, measured by the disk probe, gave curves of the correct quadratic form, corresponding to volume recombination, at pressures $< 3 \times 10^{-2}$ mm. Hg. Over this pressure range a value of 3.4×10^{-10} cm.³/sec. was found. At higher pressures the variation with n was not sufficiently close to quadratic to give consistent results. However, the values found by the visual method in the pressure range 4.6 to 11.0×10^{-2} mm. Hg are not inconsistent, for, according to the electrical measurements, loss to the walls contributed between 0.4 and 0.3 of the total rate of loss of ions. Allowing for this the visual method gives 3.6×10^{-10} cm.³/sec. for α .

In a subsequent investigation using a mercury-cathode arc discharge Mohler† measured α for a mercury afterglow by the electrical method. The only difference in technique from that used in the caesium experiments was the method used to relate the positive ion current collected by the wire probe to the ion concentration. This was done by performing a few measurements, under suitable conditions, with a further small

† *Bur. of Stand. J. of Res.* **19** (1937), 559.

wire probe used in the conventional way (i.e. positive to space). From these measurements the electron density was derived and related to the positive ion current at space potential collected by the large wire probe under the same conditions. The value 2.3×10^{-10} cm.³/sec. was obtained for α at a pressure of 0.27 mm. Hg. It was not possible to decide whether α depended on the pressure.

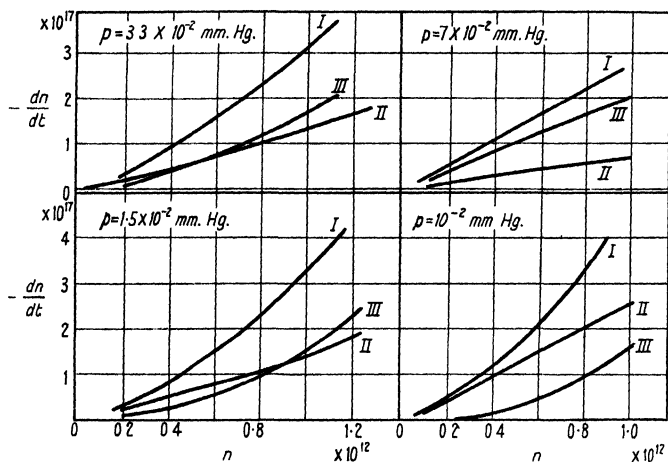


Fig. 286. Observed rate of change dn/dt of ion concentration (n) in a caesium afterglow as a function of n .

- I. Total rate of change.
- II. Contribution from wall loss measured from the current to a wall probe.
- III. Difference between I and II representing loss by recombination.

So far no satisfactory interpretation of these afterglow experiments has been provided. It is clear by reference to §§ 3.2, 3.3, and 3.5 that none of the processes (28), (29), and (31) are capable of providing such large recombination coefficients. Neither dissociative recombination (30) nor effects due to negative ions are likely to be important in the gases investigated. It has been pointed out, however (§ 3.5), that, at the gas pressures and ion densities prevailing in the afterglow experiments, radiative recombination particularly to highly excited states may be modified very considerably. In fact Mohler and Boeckner, in the course of their experiments on the intensity of the caesium recombination spectrum excited in a steady discharge, found evidence of an enhancement at pressures above 9×10^{-3} mm. Hg and also for a quenching effect at high ion densities. On the other hand, preliminary experiments by Sayers on recombination in a helium afterglow, which lead to a value of α of the

same order as that found by Kenty and by Mohler, reveal no pressure variations. This may not mean that multi-body effects are absent but that they are saturated.

It is of considerable importance to decide to what extent afterglow recombination is determined by the pressure and ion density conditions concerned. Otherwise it is not possible to know how far the results may be extrapolated to low pressures and ion densities. As there is no other evidence which suggests that the theoretical estimates of the various two-body recombination processes are in error, it is best to assume at this stage that the afterglow results are not capable of extrapolation to conditions in which three-body effects are negligible. In support of this is the small amount of observational evidence, discussed in Chap. VI, § 2.6, which favours the theoretical calculation of the radiative recombination coefficient under such conditions. On the other hand, the further study of afterglow recombination clearly remains a most important task.

In this connexion it is of interest to notice the possibility of using micro-wave technique for the determination of α . We have described in Chap. VII, § 6.22, how the mobility of helium ions in helium has been measured by observing the rate of decrease of electron density in helium, ionized by a micro-wave pulse, after the pulse is cut off and the ions have come to thermal equilibrium with the gas. The method consisted in measuring at different times the change, due to the ionization, of resonant wave-length of a micro-wave cavity enclosing the helium container. In most of this work the main loss of electrons was by diffusion to the walls, but at 20 mm. pressure recombination was more important. A value of 2×10^{-8} cm.³/sec. was found for the recombination coefficient α at this pressure. This is as difficult to understand as the results obtained by Mohler and others. Thus, referring to Table III, the expected value for α in helium is about 100 times smaller. Although the electron densities employed were about 100 times smaller than in Mohler's experiments, they were still not sufficiently low to rule out the possibility of effects due to interaction between the recombining pair and neighbouring charges. (See Appendix I.)

4. Recombination in the earth's ionosphere†

In the high atmosphere of the earth there exist quite well-defined layers of ionization. The most important of these are the *H* and *F* regions which, at night, are located at altitudes near 120 km. and between 200 and 300 km. respectively. During the day the *F* region divides into two, the *F*₁ near 220 km. and the *F*₂ at 300 km. and above. Below the *E* region a less well defined bank of ionization also

† Bates and Massey, *Proc. Roy. Soc. A*, **192** (1947), 1.

exists which is referred to as the *D* layer. It is normally only weakly ionized, but may be enhanced considerably during periods of solar activity. A considerable body of information is now available concerning the *E* and *F* layers. Table IV summarizes the present knowledge of the normal daytime properties of these layers. Variations, of different degrees of regularity, are observed in these properties, but we are not concerned here with these.

The information presented in Table IV has been obtained from the work of many investigators using radio and other methods.† It is not our intention to discuss how the information has been obtained, but to consider the interpretation of the observed recombination rates.

TABLE IV
Normal Daytime Properties of Ionospheric Layers

E layer

Altitude	= 120 km.
Scale height	= 10 km.
Gas density	= 6×10^{12} particles/cm. ³
Electron density	= 1.5×10^8 /cm. ³
Recombination coefficient	= 1×10^{-8} cm. ³ /sec.
Total rate of electron production	= 6×10^8 /cm. ² column/sec.

F₁ layer

Altitude	= 220 km.
Scale height	= 30 km.
Gas density	= 1×10^{11} particles/cm. ³
Electron density	= 2.5×10^6 /cm. ³
Recombination coefficient	= 4×10^{-9} cm. ³ /sec.
Total rate of electron production	= 2×10^8 /cm. ² column/sec.

F₂ layer

Altitude	= 300 km.
Scale height	= 70 km.
Gas density	= 2×10^{10} particles/cm. ³
Electron density	= 1×10^6 /cm. ³
Recombination coefficient	= 8×10^{-11} cm. ³ /sec.
Total rate of electron production	= 1.5×10^8 /cm. ² column/sec.

These rates refer to the loss of electrons according to the equation

$$\frac{dn_e}{dt} = q - \alpha n_e^2, \quad (41)$$

where n_e is the electron concentration and q the rate of electron production. Our problem is to interpret the observed values of α . In the *E* region, as noted in Table IV, α as defined by (41) is found to be independent of gas pressure and electron density so that a true recombination law is obeyed. The value found for α during the day, 10^{-8} cm.³/sec., is very high. Reference to § 3 shows that all the possibilities discussed there are excluded except dissociative recombination (30). As there may be negative ions present, either O^- , O_2^- , or both, since both are known to be

† For references see Bates and Massey, *Proc. Roy. Soc. A*, **187** (1946), 261; Bates, *Occasional Notes R.A.S.*

stable (see Chap. IV, § 6.3), we must also consider whether the observed variation of electron density may not take place via attachment to neutral atoms or molecules with subsequent recombination between the negative ions so formed and positive ions.

As our information on the rate of dissociative recombination is rather nebulous it is necessary to examine the possible influence of negative ions before falling back on the former as the interpretation most likely to be correct.

If the concentrations of electrons, negative ions, positive ions, and neutral atoms are n_e , n^- , n^+ , and n respectively, then we have

$$\frac{dn_e}{dt} = \mu n - \eta n_e n + \rho n^- + \kappa n^- n, \quad (42)$$

$$\frac{dn^-}{dt} = \eta n_e n - \rho n^- - \alpha_i n^- n^+ - \kappa n^- n, \quad (43)$$

$$n^+ = n^- + n_e. \quad (44)$$

In these equations the various terms have the following significance. μn is the rate of production of electrons by photo-ionization, $\eta n_e n$ is the rate at which electrons attach to neutral molecules to form negative ions, $\kappa n^- n$ is the rate at which electrons are detached from negative ions by such processes as



ρn^- is the rate of detachment of electrons from negative ions by absorption of radiation. α_i is the recombination coefficient between positive and negative ions, that between electrons and positive ions being ignored.

The only important attachment process at the pressure prevailing in the *E* region is the radiative one discussed in Chap. VI, § 2. The process discussed in Chap. IV, § 6.34, which is important at ordinary pressures will be quite negligible at pressures only 10^{-6} – 10^{-7} times as large. The value of ηn for this region, estimated by using the theoretical results of Chap. VI, § 2.5, and the data of Table IV (including the assumption that the oxygen in the *E* region is mainly in the atomic

TABLE V
Comparison of Recombination, Attachment, and Photodetachment Rates in the Ionosphere

Layer	Rate of recombination per electron sec. ⁻¹ (= αn_e)	Rate of attachment per electron sec. ⁻¹ (= ηn)		Rate of photodetachment per negative ion sec. ⁻¹ (= ρ)	
		(a)	(b)	(a)	(b)
70-km. level		10		≈ 0.5	
<i>E</i>	1.5×10^{-3} (obs.)	2×10^{-3}	6×10^{-2}	0.35	0.85
<i>F</i> ₁	1.0×10^{-3} (obs.)	4×10^{-5}	5×10^{-4}	0.35	0.85
<i>F</i> ₂	8×10^{-5} (obs.)	7×10^{-6}	5×10^{-5}	0.35	0.85

form†), is given in Table V. Two values are given corresponding to the uncertainty discussed in Chap. VI, § 2.5, which relates to the probable existence of a stable excited state of O⁻. One value has been calculated on the assumption of the calculated polarizability of atomic oxygen (curve *A* in Fig. 159, Chap. VI), and the

† Chapman, *Proc. Roy. Soc. A*, **132** (1931), 353; Wulf and Deming, *Terr. Magn. Atmos. Elect.* **43** (1938), 283.

other on the assumption of a larger polarizability which is just sufficient to introduce a stable excited state of O^- (curve *B* in Fig. 159, Chap. VI).

As radiative detachment is the inverse process the estimation of ρ offers no difficulty if the usual assumption that the sun radiates as a black body at $6,000^\circ K$. is made. The values found are given in Table V.

Comparison of the values of ηn and ρ with the observed value of αn_e shows that the radiative detachment rate per negative ion (ρ) is much faster than either of the other two rates. It is also probable that the attachment rate per electron is considerably faster than that of recombination. During the daytime the ratio λ of the concentration of negative ions to electrons will be $\gtrsim \eta n/\rho$, i.e. $\gtrsim \frac{1}{2}$. We may also assume, as a sufficient approximation, that while electron production and recombination proceeds the negative ions and electrons remain in a dynamical equilibrium with

$$\lambda \simeq \eta n/(\rho + \kappa n), \quad (46)$$

the contribution to detachment from such processes as (45) being also included.

Now by adding (42) and (43) and using (44) we have

$$\frac{dn^+}{dt} = \mu n - \alpha_i n^- n^+. \quad (47)$$

But, if $n^- = \lambda n_e$, $n^+ = (1 + \lambda)n_e$, so that

$$\frac{dn_e}{dt} = \frac{\mu n}{1 + \lambda} - \lambda \alpha_i n_e^2. \quad (48)$$

The effective electron recombination coefficient α defined from (41) is thus

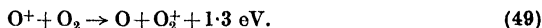
$$\lambda \alpha_i.$$

We have shown that λ must be $< \frac{1}{2}$, but actually it must be considerably smaller if α is to be independent of pressure. Referring to (46), this cannot be so unless κn is considerably greater than ρ , say $\kappa n = 4\rho$ at least to give constancy of α within the observed accuracy. This makes $\lambda < 1/10$, so α_i would have to be $> 10^{-7}$ cm.³/sec. At the pressure in the *E* layer three-body ion-ion recombination is quite unimportant. Thus (27) gives, using the data of Table IV, only 10^{-11} cm.³/sec. The only remaining possibility is that of mutual neutralization. This has been discussed in § 2.3 and it was shown to be most unlikely that the contribution from this process could exceed 10^{-8} cm.³/sec.

The interpretation of the recombination in the *E* layer in terms of ion-ion recombination is therefore highly unsatisfactory though not completely impossible. Moreover, it is found to be completely untenable in the *F* layers. In Table V the estimated magnitudes of ηn , ρ , and αn_e for these layers are given. Since for F_1 $\eta n/\rho \gtrsim 6 \times 10^{-4}$, λ must be even smaller than this. The ion-ion recombination required to give the observed value, 4×10^{-9} cm.³/sec., of α for this region would be as large as 10^{-6} cm.³/sec., which is completely impossible apart from any theoretical estimates. A two-body recombination coefficient as large as this would have become apparent in a departure from linearity of the variation with pressure of the recombination coefficient observed by Sayers for ions in air at 100 mm. pressure (see Fig. 284). For the F_2 layer the situation is similar.

In view of the failure of the explanation of the observed electron recombination in the *E* and *F* layers in terms of negative ions it is necessary to return to the consideration of dissociative recombination. Even if the rate of this process is fast enough it is applicable only to recombination with molecular ions. There is little doubt that, in all the layers, O^+ ions are formed. If there is no way in which they

are neutralized via molecular recombination, it is necessary to seek a further recombination process. Otherwise the concentration of atomic ions would build up relative to that of the molecular ions so that the recombination coefficient would fall to the value appropriate to atomic ions, in conflict with observation. A possible way out of this difficulty is gained by considering the E region in particular. This layer is not far from the transition region above which oxygen is predominantly atomic and below predominantly molecular. Oxygen molecules are therefore likely to be present in appreciable proportion in the region. Even if O^+ ions are formed initially they will be converted into O_2^+ ions through the charge exchange process (see Chap. VII, § 6.3, and Chap. VIII, § 5.1)



As this is an exothermic reaction, the ionization potential of O_2 (12.2 volts) being less than that of O (13.5 volts), it can proceed between ions and atoms of gas-kinetic energies. If this process occurs fast enough compared with the rate of dissociative recombination the ions will be predominantly molecular at all times and the observed conditions of pressure-independent recombination coefficient will be realized. In fact the problem of removal of atomic ions in the E region may not arise as there is some reason to believe that O_2^+ and not O^+ ions are primarily formed in this layer. There is no doubt, however, that in the F layers a considerable proportion of the ions initially formed are atomic. The dissociative recombination theory may still be applied if a molecule XY is present in sufficient fractional concentration to convert the atomic into molecular ions by an exothermic charge exchange process such as (49). This molecule must have a lower ionization potential than that of atomic oxygen. In the F_1 layer, where the recombination coefficient is independent of pressure the concentration of the molecule XY and the cross-section for the process



must be large enough for the rate of recombination to be determined by the rate of



rather than that of (50). Taking the cross-section for (50) as 10^{-17} cm^2 as a very rough estimate and the data of Table IV for the neutral particle concentration, the lifetime of an O^+ ion, at the level of the F_1 layer, before conversion into XY^+ , comes out to be $10/f \text{ sec.}$, f being the fractional concentration of XY molecules at that level. Using the data of Table IV for the recombination coefficient and electron concentration the lifetime of an XY^+ ion before recombination must be $1/\alpha n_e = 10^3 \text{ sec.}$ In order that this should be shorter than the lifetime of an O^+ ion f need only be greater than 10^{-2} . The theory would then be self-consistent with only a small relative proportion of XY molecules present.

On the other hand, the fractional concentration of XY molecules is very likely to fall off with height so that in the F_2 layer the rate of the reaction (50) may be reduced to such a low value that it is the process essentially determining the rate of disappearance of electrons. In these circumstances the recombination coefficient defined by (41) will be given by

$$\alpha n_e^2 = \beta n_0^+ n_{xy}, \quad (52)$$

where $\beta = \bar{v} Q_{\text{ex}}$, $\bar{v}$ being the mean relative velocity of an O^+ ion and an XY molecule and Q_{ex} is the effective cross-section for the reaction. n_{xy} is the concentration of

neutral molecules XY and n_0^+ that of O^+ ions. As the ions will now be mainly atomic, n_0^+ will be nearly equal to n_e and

$$\alpha \simeq \beta n_{xy}/n_e. \quad (53)$$

This gives an effective recombination coefficient proportional to the concentration of molecules XY and also to $1/n_e$, just as if the electrons disappeared by attachment to neutral molecules. Such behaviour of α is not in conflict with experimental data for the F_2 layer. There is no evidence suggesting that α is independent of pressure there. On the contrary the problem of the origin of the layer is simplified if α has the form (53) there. The F_2 layer could then arise, as a consequence of a decrease of the effective recombination coefficient with height according to some such law† as (53), from the same ionization process as the F_1 . It is also consistent with the great upward extension of the F_2 layer.

In the absence of any quantitative information on the rates either of dissociative recombination or of the charge exchange reaction (50) the molecular recombination theory cannot be regarded as established. It does possess a certain plausibility, particularly as it does not seem unlikely that molecules such as O_2 and NO , which would play the part of XY in (50), may be present in sufficient proportion in the F regions. If it should nevertheless prove incorrect it is difficult to see what further alternative could be invoked. At first sight it might appear that the same processes which give rise to the apparent recombination coefficient (of order 10^{-10} cm.³/sec.) in the afterglow of a discharge plasma, whatever they may be, may be responsible for the recombination in the F_2 layer, for which the electron recombination coefficient is of the same order. It seems very unlikely, however, that one can extrapolate data obtained at pressures of order 10^{-2} mm. Hg and electron concentrations of 10^{12} – 10^{13} /c.c. to apply at pressures a thousand times and concentrations a million times smaller, particularly as there seems to be no theoretical explanation of the afterglow results on the basis of any two-body process. In any case, if this were so for the F_2 layer there would still remain the problems presented by the E and F_1 layers.

At the 70-km. level, well below the E layer, the pressure is so high that the above considerations are markedly changed. Oxygen will be almost exclusively in the molecular state. Attachment will take place mainly by the process discussed in Chap. IV, § 6.34, leading to O_2^- ions. Table V gives estimated values of the attachment rate per electron and detachment rate per negative ion in these circumstances. It will be seen that the negative ion to electron ratio λ is likely to be as large as 20, in marked contrast to the upper layers. The effective recombination coefficient α is likely to be given now by $\lambda\alpha_i$, where α_i is the ion-ion recombination coefficient given by the Thomson three-body process. The contribution to α_i from this process may be obtained from the formula (27) if use is made of the known concentration of neutral molecules at the 75 km. level (2×10^{15} /c.c.). It comes out to be only 3×10^{-10} cm.³/sec. The contribution to α_i from mutual neutralization processes (§ 2.3) may well be 100 times larger, giving an effective recombination coefficient of the order 10^{-6} cm.³/sec., proportional to the pressure, through its dependence on λ .

† First suggested by Bradbury, *Terr. Mag. Atmos. Elec.* **43** (1938), 55.

APPENDIX I

SOME NOTES ON RECENT ADVANCES

The Theory of Scattering of Electrons by Atoms—Use of the Variation Method†

THE variation methods which have been developed during the past few years have recently been applied to the elastic scattering of electrons by hydrogen atoms. Huang‡ investigated the effect of polarization on the scattering of slow electrons in this way while Massey and Moiseiwitsch§ were able to allow for both polarization and exchange effects (see Chap. III, §§ 2.5 and 3.6).

The variation method may also be applied to inelastic collisions.||

The Fine Structure of X-ray Absorption Edges in Molecular Gases (Chap. IV, § 2.2)

The fine structure of the *K* absorption limit of germanium in GeH_4 , Ge_2H_6 , GeCl_4 , and GeBr_4 has recently been investigated by Glaser†† using a high resolution double crystal spectrometer. It seems clear from his observations in GeCl_4 that the theory of Hartree, Kronig, and Petersen‡‡ does not agree so well with experiment as Fig. 9 would indicate. With the high resolution many further maxima were found than in the earlier work.

Theories of Secondary Electron Emission

Further attention has recently been given to the free electron theory of secondary electron emission of Kadyshovich. A simpler formulation of this theory by Baroody§§ has confirmed the conclusions from the earlier calculations that a free electron theory can account successfully for a large part of the observed phenomena.

It has been shown that both the free electron theory of Kadyshovich and the Fröhlich–Wooldridge theory lead to a general relationship of the form

$$\delta/\delta_{\max} = f(E_p/E_{p\max})$$

between the secondary electron coefficient δ and the primary electron energy E_p .||| $E_{p\max}$ is here the electron energy at which δ has its maximum value, $\delta_{\max}$.

Brophy††† has also measured δ – E_p curves for liquid bismuth, gallium, lead, and mercury and has found them to be indistinguishable from the corresponding curves for the solid metals.

Microwave Investigations of the Decay of Electron Density in Discharge Afterglows

The microwave method for investigating the rate of decay of electron density in the afterglow of an electrodeless discharge which is described in Chap. VII, § 6.22 has been applied to many gases with very interesting results.

† Hulthen, *K. Fysogr. Sällsk. Lund. Förk* (1944), No. 21; Kohn, *Phys. Rev.* **74** (1948), 1763.

‡ *Ibid.* **76** (1949), 477.

§ *Ibid.* **78** (1950), 180; *Proc. Roy. Soc. A*, **205** (1951), 483.

|| Moiseiwitsch, *Phys. Rev.* **82** (1951), 753.

†† *Ibid.* **82** (1951), 616.

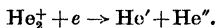
§§ *Phys. Rev.* **78** (1950), 780.

††† *Ibid.* **83** (1951), 534.

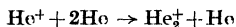
‡‡ *Physica*, **1** (1934), 895.

||| Brophy, *ibid.* **82** (1951), 757.

Most attention has been concentrated on the study of helium afterglows. The first measurements were those of Biondi and Brown† described in Chap. VII which although directed in the first instance towards the measurement of the mobility of He^+ ions in helium, gave the value 1.7×10^{-8} c.c./sec. for the electron recombination coefficient. This is far greater than would be expected from radiative (Chap. X, § 3.2) or three-body (Chap. X, § 3.5) recombination. It was therefore suggested by Bates‡ that a considerable fraction of the positive ions in the afterglow under investigation were He_2^+ rather than He^+ so that dissociative recombination occurred according to the reaction



He pointed out that He_2^+ would be formed at such a rate from the three-body process



that one would expect the ions in the afterglow to be mainly He_2^+ . Shortly after it was shown experimentally§ by Boyd that even in an arc discharge in helium at a pressure of 0.01 mm. Hg with a discharge current of 100 mA, a major fraction of the positive ions in the positive column are He_2^+ . In a later note Bates|| was able to show on theoretical grounds that it is at least possible that the dissociative recombination coefficient is large enough. Although there have been attempts†† to decide from simultaneous observations of the wave-length and intensity of the spectrum lines emitted from the afterglow and of the electron density whether dissociative recombination is indeed the correct explanation, no decisive data have yet been obtained (see, however, Note on p. 649).

The observations of the importance of He_2^+ in helium discharge plasma has also directed attention once more to the discrepancies (Chap. VII, § 6.52) between theory and experiment concerning the mobility of He^+ ions in helium. It seems that the explanation of the discrepancy given by Meyerott‡‡ is indeed correct. The ions whose mobility was observed by Tyndall and Powell§§ were He_2^+ . Hornbeck and Wannier|||| have recently measured simultaneously, by a pulse technique, the mobilities of both He_2^+ and He^+ ions in helium. They obtain values of 18 and 9.4 cm.²/volt sec. at room temperature for He_2^+ and He^+ respectively. These are to be compared with the value 19.9 cm.²/volt sec. observed by Tyndall and Powell and the value 11 cm.²/volt sec. calculated for He^+ by Massey and Mohr.††† Hornbeck and Wannier have also carried out similar measurements for neon and argon and find that in both cases their measurements for Ne_2^+ and Ar_2^+ agree within experimental error with the values ascribed by Munson and Tyndall‡‡‡ to Ne^+ and Ar^+ . Holstein§§§ has calculated the mobilities of Ne^+ and Ar^+ in their parent gases and his results are in good agreement with Hornbeck's measurements.

A further interesting aspect of these investigations has resulted from the observation by Biondi||||| that there is an initial increase of electron concentration after the field maintaining the discharges is cut off. This lasts for about 10^{-3}

† *Phys. Rev.* **75** (1949), 1700.

§ *Proc. Phys. Soc. A*, **63** (1950), 543.

†† Johnson, McClure, and Holt, *Phys. Rev.* **80** (1950), 376; Bates, *ibid.* **82** (1951), 103; Biondi and Holstein, *ibid.* **82** (1951), 962.

‡‡ *Phys. Rev.* **66** (1944), 242.

§§ *Proc. Roy. Soc. A*, **134** (1931), 125.

††† *Proc. Roy. Soc. A*, **144** (1934), 188.

§§§ Conf. on Gaseous Electronics, New York, 1950.

||||| *Phys. Rev.* **82** (1951), 453.

‡ *Ibid.* **77** (1950), 718.

|| *Phys. Rev.* **78** (1950), 492.

|||| *Phys. Rev.* **82** (1951), 458.

††† *Ibid.* **177** (1941), 187.

seconds and must be ascribed to ionization due to impacts between metastable atoms. From an analysis of the initial rate of rise Biondi has derived values for the diffusion coefficient of metastable helium atoms in helium and for the cross-section for volume destruction of metastable atoms by collision with normal atoms. The values obtained agree quite closely with those measured by Ebbinghaus† using the method described in Chap. VII, § 9. Biondi has found the same effect in neon.

Microwave methods have also been applied to study the decay of the electron density in afterglows in argon,‡ caesium,§ mercury,|| hydrogen,†† nitrogen,‡‡ and oxygen§§ but, in most cases, the interpretation of the results is still far from clear. No adequate explanation of the fact that the recombination coefficients found in argon, caesium, and mercury are between 10 and 100 times greater than those measured by probe techniques (Chap. X, § 3.6) has yet been forthcoming.

Study of Charge Exchange

A systematic experimental study of charge exchange for ions with energies between 25 and 900 eV has been commenced by Hasted||| using an apparatus of the Wolf type (Chap. VIII, § 5.12). He finds that, provided the energy discrepancy, ΔE , involved in the process is quite definite and only atomic ions and atoms are concerned, the cross-section rises with increasing ion energy to a maximum when $a|\Delta E|/\hbar v \simeq 1$, v being the velocity of the incident ion and a a length between 5 and 10×10^{-8} cm. This is in agreement with the theoretical interpretation in terms of nearly adiabatic collisions (Chap. VIII, § 6.1). In other cases where these considerations do not seem to apply failure can probably be traced to inadequate knowledge of ΔE . A certain fraction of the incident ions may be in metastable excited states instead of the ground state and both ions and atoms resulting from the charge exchange may be formed in excited states.

† *Ann. der Physik*, **7** (1930), 267.

‡ Biondi and Brown, *Phys. Rev.* **76** (1949), 1697; Redfield and Holt, *ibid.* **82** (1951), 874.

§ Dandurand and Holt, *ibid.* **82** (1951), 278.

|| Dandurand and Holt, *ibid.* **82** (1951), 868.

†† Biondi and Brown, *loc. cit.*; Richardson and Holt, *ibid.* **81** (1951), 153.

‡‡ Biondi and Brown, *loc. cit.*

§§ Biondi and Brown, *loc. cit.*

||| *Proc. Roy. Soc. A*, **205** (1951), 421.

Note. Biondi (*Phys. Rev.* **83** (1951), 1078) has recently obtained strong experimental evidence that dissociative recombination is indeed the correct explanation of the high rate of electron recombination in helium. He measured the recombination coefficient of electrons in an afterglow in helium containing 0.1 per cent. of argon and found it to be less than 10^{-3} of that observed in pure helium. Mobility measurements indicated that the ions in this case were very largely A^+ which were presumably formed by ionization of argon atoms in collision with metastable helium atoms. The low partial pressure of argon prevented the A_2^+ concentration from rising to an appreciable value and HeA^+ molecular ions are probably unstable or very weakly bound. With only atomic ions present, dissociative recombination is excluded and in its absence only a very low recombination coefficient was found.

APPENDIX II

MOLECULES INVESTIGATED BY MASS SPECTROGRAPH METHOD

H_2 (5,23)	CS_2 (6,8)	C_4H_8 (26,27,28,34)
O_2 (23)	CCl_4 (16)	C_4H_{10} (24,33,34,36)
N_2 (10)	$SiCl_4$ (39)	C_5H_{10} (34)
Br_2 (12)	CCl_2F_2 (16)	C_5H_{12} (34,36)
I_2 (1)	$AsCl_3$ (14)	C_6H_6 (14)
CO (23)	PCl_3 (14)	C_6H_{12} (14,34)
CO_2 (2,3,4,34)	$SbCl_3$ (14)	C_6H_{14} (34,36)
NO (10)	KI (35)	C_7H_{14} (34)
NO_2 (3)	NaI (35)	C_7H_{16} (34,36)
N_2O (3)	$CsCl$ (35)	C_8H_{16} (34)
CN_2 (14)	CH_2 (37)	C_8H_{18} (31,34)
NH_3 (22)	CH_4 (15,34,36)	C_9H_{20} (34)
N_2H_4 (11)	CD_4 (34)	$C_{10}H_{20}$ (34)
H_2O (22)	C_2H_2 (10,14,34)	$C_{10}H_{22}$ (34)
B_2H_6 (21)	C_2H_4 (14,34)	CH_3OH (20)
HCN (14)	C_2H_6 (17,24,34,36)	C_2H_5OH (20)
HCl (13)	C_3H_4 (19)	CH_3Cl (9)
C_5H_5N (14)	C_3H_6 (19,26,34)	$(CH_3)_3CCl$ (25)
SO_2 (7)	C_3H_8 (19,26,34,36)	$(CH_3)(CH_2)_2Cl$ (25)
		$CHBrF_2$ (18)

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APPENDIX III

MATERIALS FOR WHICH DATA ON SECONDARY ELECTRON EMISSION COEFFICIENTS FOR POSITIVE ION BOMBARDMENT ARE AVAILABLE

In each case the name of the ion is placed before that of the target material

(Hg^+ , Li)⁽¹¹⁾; (H^+ , Be)⁽²⁴⁾; (H^+ , C)^(9,24); (Hg^+ , Na)⁽¹¹⁾; (Ne^+ , Mg)⁽²⁰⁾; (A^+ , Mg)^(18,20,23); (Hg^+ , Mg)⁽¹¹⁾; (O_2^+ , Mg)⁽²⁰⁾; (He^+ , Al)^(18,20); (Ne^+ , Al)^(18,20); (A^+ , Al)^(18,20,30); (Li^+ , Al)^(1,28); (K^+ , Al)^(1,3,16,4a); (Rb^+ , Al)^(1,3); (Cs^+ , Al)⁽³⁾; (H^+ , Al)^(8,25); (Hg^+ , Al)⁽¹¹⁾; (H_2^+ , Al)^(25,27); (O_2^+ , Al)⁽²⁰⁾; (He^+ , K)⁽²⁰⁾; (Ne^+ , K)⁽²⁰⁾; (A^+ , K)⁽²⁰⁾; (Hg^+ , K)⁽¹¹⁾; (Ne^+ , Ca)⁽¹⁸⁾; (A^+ , Ca)⁽¹⁸⁾; (He^+ , Fe)^(5,20); (Ne^+ , Fe)^(5,20); (A^+ , Fe)^(5,20,23); (Kr^+ , Fe)⁽⁵⁾; (H_2^+ , Fe)⁽²⁰⁾; (N_2^+ , Fe)⁽²⁰⁾; (O_2^+ , Fe)^(19,20); (He^+ , Ni)^(5,25,29); (Ne^+ , Ni)^(4,5,29); (Na^+ , Ni)^(3a); (A^+ , Ni)^(10,23,26,29,5); (Kr^+ , Ni)⁽⁵⁾; (K^+ , Ni)^(3,3a,4a); (Rb^+ , Ni)⁽³⁾; (Cs^+ , Ni)^(3,3a,6); (H^+ , Ni)⁽²⁴⁾; (Hg^+ , Ni)^(7,11); (H_2^+ , Ni)^(12,29); (D_2^+ , Ni)⁽²⁹⁾; (He^+ , Cu)^(20,10a); (Ne^+ , Cu)^(17,20,22,10a); (A^+ , Cu)^(14,20,10a); (Kr^+ , Cu)^(20,22); (Xe^+ , Cu)⁽²⁰⁾; (K^+ , Cu)⁽¹⁶⁾; (H^+ , Cu)^(8,24,25); (Hg^+ , Cu)⁽¹¹⁾; (H_2^+ , Cu)^(20,25,27,10a); (N_2^+ , Cu)⁽²⁰⁾; (O_2^+ , Cu)^(19,20); (He^+ , Zn)⁽²⁰⁾; (Ne^+ , Zn)⁽²⁰⁾; (A^+ , Zn)⁽²⁰⁾; (H_2^+ , Zn)⁽²⁰⁾; (O_2^+ , Zn)⁽²⁰⁾; (He^+ , Mo)^(4a); (Na^+ , Mo)^(3a); (A^+ , Mo)⁽³⁰⁾; (K^+ , Mo)^(3,3a); (Rb^+ , Mo)⁽³⁾; (Cs^+ , Mo)^(3,3a); (H^+ , Mo)⁽²⁵⁾; (Hg^+ , Mo)⁽¹¹⁾; (H_2^+ , Mo)⁽²⁵⁾; (He^+ , Ag)⁽²⁰⁾; (Ne^+ , Ag)⁽²⁰⁾; (A^+ , Ag)⁽²⁰⁾; (Kr^+ , Ag)⁽²⁰⁾; (Xe^+ , Ag)⁽²⁰⁾; (Hg^+ , Ag)⁽¹¹⁾; (H_2^+ , Ag)^(20,27); (N_2^+ , Ag)⁽²⁰⁾; (O_2^+ , Ag)⁽²⁰⁾; (Hg^+ , Sn)⁽¹¹⁾; (He^+ , Sb)⁽²⁰⁾; (Ne^+ , Sb)⁽²⁰⁾; (A^+ , Sb)⁽²⁰⁾; (H_2^+ , Sb)⁽²⁰⁾; (N_2^+ , Sb)⁽²⁰⁾; (O_2^+ , Sb)⁽²⁰⁾; (A^+ , Ba)⁽²³⁾; (He^+ , W)⁽⁵⁾; (Ne^+ , W)⁽⁵⁾; (Kr^+ , W)⁽⁵⁾; (Cs^+ , W)^(13,21); (Hg^+ , W)⁽¹¹⁾; (He^+ , Pt)⁽²⁰⁾; (Ne^+ , Pt)⁽²⁰⁾; (A^+ , Pt)⁽²⁰⁾; (Li^+ , Pt)⁽¹⁾; (K^+ , Pt)^(1,16,4a); (Rb^+ , Pt)⁽¹⁾; (H^+ , Pt)⁽²⁴⁾; (H_2^+ , Pt)⁽²⁰⁾; (N_2^+ , Pt)⁽²⁰⁾; (O_2^+ , Pt)⁽²⁰⁾; (H^+ , Au)^(2,8); (He^+ , Pb)⁽²⁰⁾; (Ne^+ , Pb)⁽²⁰⁾; (A^+ , Pb)⁽²⁰⁾; (H^+ , Pb)⁽²⁵⁾; (H_2^+ , Pb)^(20,25); (N_2^+ , Pb)⁽²⁰⁾; (O_2^+ , Pb)⁽²⁰⁾; (He^+ , Bi)⁽²⁰⁾; (Ne^+ , Bi)⁽²⁰⁾; (A^+ , Bi)⁽²⁰⁾; (H_2^+ , Bi)⁽²⁰⁾; (N_2^+ , Bi)⁽²⁰⁾; (O_2^+ , Bi)⁽²⁰⁾; (A^+ , MgH)⁽¹⁸⁾; (H_2^+ , MgH)⁽¹⁸⁾; (A^+ , MgO)⁽¹⁸⁾; (H_2^+ , Al_2O_3)⁽¹⁸⁾; (N_2^+ , Al_2O_3)⁽¹⁸⁾; (O_2^+ , Al_2O_3)⁽¹⁸⁾; (H_2^+ , CaH)⁽¹⁸⁾; (He^+ , brass)^(10a); (Ne^+ , brass)^(10a); (A^+ , brass)^(10a); (H^+ , brass)⁽⁹⁾; (H_2^+ , brass)^(10a); (A^+ , Cs-AgO)⁽²⁶⁾; (Cs^+ , W-H layer)⁽²¹⁾; (Cs^+ , W-O layer)⁽²¹⁾; (Cs^+ , W-K layer)⁽²¹⁾; (Cs^+ , W-Cs)⁽²¹⁾.

Methods employed: (I) Direct measurement (refs. 1, 2, 3, 4a, 5, 6, 7, 8, 9, 10, 11, 12, 13, 16, 21, 24, 25, 27, 28, 29).

(II) Güntherschulze's calorimetric method (18, 19, 20).

(III) Measurement of Townsend's second coefficient (14, 15, 17, 22, 23, 26).

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APPENDIX IV

USEFUL PHYSICAL CONSTANTS AND CONVERSION TABLE

Velocity of light, c	$= 2.9978 \times 10^{10}$ cm. sec. ⁻¹
Electronic charge, e	$= 4.8024 \times 10^{-10}$ e.s.u.
	$= 1.6020 \times 10^{-20}$ e.m.u.
Mass of the electron, m	$= 9.1055 \times 10^{-28}$ gm.
Specific charge of the electron, e/m	$= 1.7594 \times 10^7$ e.m.u./gm.
Mass of the proton, M_p	$= 1.6725 \times 10^{-24}$ gm.
Ratio, M_p/m	$= 1836.6$.
Planck's constant, h	$= 6.624 \times 10^{-27}$ erg sec.
Radius of first Bohr orbit	
$=$ atomic unit of length, a_0	$= 0.5292 \times 10^{-8}$ cm.
Fine structure constant, α	$= 7.2978 \times 10^{-3}$.
Ionization potential of H atom	
$= \frac{1}{2}$ atomic unit of energy	$= 13.54$ eV.
Ionization potential of He atom	$= 24.46$ eV.
Energy equivalent to 1 eV	$= 1.6020 \times 10^{-12}$ erg.
Temperature such that κT is 1 eV	$= 1.161 \times 10^4$ °K.
Wave-length λ of electron of energy V eV	$= (153.5/V)^{\frac{1}{2}} \times 10^{-8}$ cm.
Quantum energy of photon of wave-length λ in eV	$= \frac{1.2395}{\lambda} \times 10^4$ eV (λ in Å).
Boltzmann's constant, κ	$= 1.3803 \times 10^{-16}$ erg deg. ⁻¹
Avogadro's number, N_0	$= 6.0251 \times 10^{23}$ mole ⁻¹ .
Loschmidt's number, n_0	$= 2.6873 \times 10^{19}$ cm. ⁻³ (at N.T.P.).
$\frac{3}{2}\kappa T$ at 0° C.	$= 5.657 \times 10^{-14}$ erg.
No. of electronic charges equivalent to 1 Coulomb	$= 6.2422 \times 10^{18}$.
Cross-section, πa_0^2	$= 8.806 \times 10^{-17}$ cm. ²
Cross-section, a_0^2	$= 2.803 \times 10^{-17}$ cm. ²
Cross-section, 1 cm. ² /cm. ³ at 1 mm. Hg	$= 2.81 \times 10^{-17}$ cm. ²

Velocity v and Wave-length λ of Electrons and H, He, A, and Hg Atoms of Different Energy

Energy (eV)	Electron			H atom		He atom		A atom		Hg atom	
	$(1-\beta^2)^{-\frac{1}{2}}$	v (units 10^{10} cm./sec.)	λ (Å)	v (units 10^7 cm./sec.)	λ (Å)	v (units 10^7 cm./sec.)	λ (Å)	v (units 10^7 cm./sec.)	λ (Å)	v (units 10^7 cm./sec.)	λ (Å)
1	1.000002	0.005932	12.26	0.1386	0.286	0.06978	0.144	0.02203	0.0455	0.00982	0.0203
10	1.0000196	0.01876	3.878	0.4388	0.0905	0.2209	0.0455	0.06969	0.0144	0.03111	0.00640
100	1.0001957	0.05932	1.226	1.386	0.0286	0.6978	0.0144	0.2203	0.00455	0.09816	0.00203
1,000	1.001957	0.1873	0.3877	4.388	0.00905	2.209	0.00455	0.6969	0.00144	0.3111	0.00064
10,000	1.01957	0.5846	0.1220	13.86	0.00286	6.978	0.00144	2.203	0.000455	0.9816	0.00020
100,000	1.1957	1.644	0.03702	43.88	0.00091	22.09	0.000455	6.969	0.00014	3.111	0.000064

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PRINTED IN
GREAT BRITAIN
AT THE
UNIVERSITY PRESS
OXFORD
BY
CHARLES BATEY
PRINTER
TO THE
UNIVERSITY

