ELECTRON SCATTERING IN GASES

Gordon Owen Baines

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ELECTRON SCATTERING
IN GASES

being a thesis

presented by

Gordon O. Baines M.A.

to the University of St. Andrews in

application for the Degree of Ph.D.

DECLARATION.

I hereby declare that the following Thesis is based on the results of experiments and calculations carried out by me, that the Thesis is my own composition, and that it has not previously been presented for a Higher Degree.

The Research was carried out in the Physical Laboratory of the United College of the University of St. Andrews, under the direction of Professor H. Stanley Allen, F.R.S.

CERTIFICATE.

I certify that Gordon O. Baines, M.A., has spent the equivalent of nine terms at Research Work under my direction, and that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

CAREER.

I matriculated in the University of St. Andrews in October 1928, and obtained the degree of Master of Arts with First Class Honours in Mathematics and Natural Philosophy in June 1932.

In October 1932, I was admitted as a Research Student in the University, and commenced work on the research which is now being submitted as a Ph.D. Thesis.

In July 1932, I was awarded a Carnegie Research Scholarship, which was renewed for Session 1933-34. In July 1934, I was appointed to a Carnegie Senior Research Scholarship, tenable for one year.

INTRODUCTION.

Since the time when, in 1921 Ramsauer discovered the effect of the cross sections of certain atoms, for electron impact, decreasing with the energy of the colliding electrons at low energies, much work, both experimental and theoretical,has been done on the collisions of electrons with atoms. Interest in this line received a further stimulus when some nine years later, diffraction maxima and minima were discovered in the angular distribution curves for electrons scattered by atoms.

On the theoretical side, the new wave mechanics was found necessary to explain all the observed facts. The agreement obtained with experiment was found to be good, especially as more and more complicating factors were allowed for in the theory.

Most of the experimental work on the direct measurement of the cross sections of atoms has been confined to the case where all types of collisions are included. An electron may however make elastic or inelastic impacts with an atom. Practically the only knowledge so far of the elastic cross sections of gas atoms has been derived from a numerical integration of angular scattering curves; while for inelastic impacts, both collective and discrete, the majority of results have been obtained by indirect optical methods. In addition, most measurements of discrete inelastic cross sections by electrical methods, have been confined to electrons scattered through one definite angle, usually zero angle. Theory has shown, and it has been confirmed by experiment, that the excitation cross sections for such angles vary very differently with the energy from the cross sections obtained when all angles are included. It is therefore important to study the variations of the inelastic cross sections with energy for electrons deflected through large angles.

This thesis is divided into two parts; the first containing theoretical work and discussions; and the second the experimental work. Section 1 contains a discussion of the stationary states in an atom and the kinetic theory expression for the mean free path of an electron in a gas, leading up to the formula for the passag of a beam of electrons through a gas. In section 2, the previous methods of obtaining cross sections, both total and inelastic, are dealt with and the results discussed. An outline of the wave mechanical theory of collision processes is given in section 3, with indications of the agreement obtained with experiment by different methods. The results of some approximate theoretical calculations of phases and an angular scattering curve for krypton are given in section 4. The results of this section have already been published by Dr.F.L.Arnot and the author.

Section 5, the first of Part II, contains a description of a new apparatus designed to obtain measurements of the total , elastic and inelastic cross sections in gases. The method of using the apparatus and a number of tests of its working are described in section 6. The last section, 7, contains the results obtained with the apparatus for the total, elastic and inelastic cross sections of the mercury atom, along with the cross sections for the ionisation, 2^1P_1, 2^3P_1, 3^1D_2 states. It concludes with an interesting test of the working of the apparatus and a discussion of the possible errors of the method.

PART I. THEORY.

SECTION 1.

DISCUSSION OF COLLISIONS OF ELECTRONS AND ATOMS.

Before proceeding with a discussion of the types of collisions, something must be said about the structure of the atom.

What may be termed the accepted classical conception of an atom was that of a hard, smooth, elastic sphere. Now however, research has shown that this is by no means true. Instead the atom is known to have a very openwork structure of electric charges. Most of the mass of the atom is concentrated in the nucleus, which carries a net positive charge equal to the atomic number of the element. Round the nucleus revolve a number of electrons again equal in number to the atomic number of the element, so that the net charge of an atom, in its normal state, is zero. Each of these electrons revolves round the nucleus in a certain clearly defined orbit, each orbit having, corresponding to it, a certain definite amount of energy. The orbits, or levels, or stationary states as they are called, are quantised, in that there are only certain discrete amounts of energy allowed; a continuous variation of energy is not possible. These electrons round the nucleus are arranged in shells; for each shell there is a maximum number of electrons which it can contain. The electrons with which we shall be concerned mostly are those in the outermost shell; these are called the valency electrons, and are obviously the most loosely bound to the atom.

Consider one of the valency electrons moving in its normal or ground state round the nucleus, if a certain amount of energy is given to this electron it might be possible for it to move up into another orbit of higher energy. This is however only possible if the amount of energy given to the electron is a certain discrete value, equal to the difference in energy between the two levels, since there is not an infinity of levels corresponding to all levels but only quantised, distinct orbits. The energy given to the electron may come in various ways, either thermally or by impact with another atom or electron, or by impact of a quantum of light of the correct frequency. When an electron in an atom has been raised in any manner to a level above its normal state the atom is said to be in an excited state. The electron in the higher orbit in general falls back to a lower orbit in a very short time, usually of the order of 10^{-7} sec. The difference in energy between the two orbits has then to be given up, and it usually appears as radiation of a frequency ν given by Bohr's second postulate $W_1 - W_2 = h\nu$,

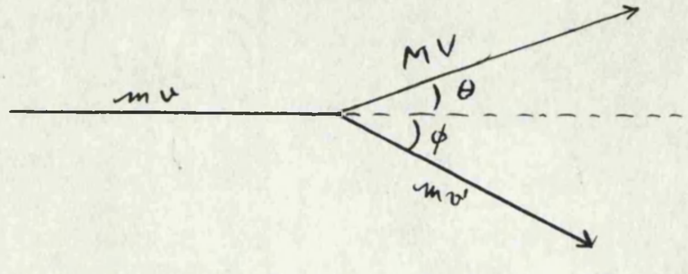
where $W_1 - W_2$ is the difference of energy and h is Planck's constant. Again, it is possible to raise the electron from its normal state to higher and higher levels till finally, it may be lifted right out of the atom altogether. The minimum amount of energy necessary to do this is again found to be a constant. When the electron, which is negatively charged, has been removed from the atom, the atom is left positively charged and is then called a positive ion. The process of removing an electron from an atom is called ionisation of the atom and the atom is said to be ionised.

This discussion is summarised very well by Darrow (1) in the statement that: "An atom or a molecule is capable of existing in any one of various distinct, discrete and definite stationary states or levels, for each of which its internal energy has a specific and distinctive value."

The first level above the normal or ground state which combines with the normal state, is usually called the resonance level, and the quantum or photon emitted by the atom on returning from this level to the normal state is called the resonance radiation. Occasionally all the excited states are spoken of as resonance levels, but usually this term only refers to the state of lowest energy above the ground state, which combines with it. This latter phrase is added because there are certain states, called metastable states, which can be excited by normal means but from which the atom cannot return by emission of a quantum of radiation. The only way in which an atom can leave a metastable state is by giving up its energy to another atom or electron in a collision, or by being excited by a further impact with an electron to a still higher state not metastable from which it can then return by emitting a photon. All atoms except hydrogen and helium have several ionisation levels as well as excitation levels. These various ionisation levels correspond to the removal of an electron from the different shells of the atom.

It has been said that an atom can be excited or ionised in a number of ways, one of which was by impact with an electron. This is the method which concerns us chiefly here. It has also been said that to excite an atom to a specific level requires a definite and specific amount of energy. Now an electron moving with a certain velocity has a definite kinetic energy. On colliding with an atom it may give up some of its energy to the atom and s raise an electron in the atom from one orbit to a higher on or even right out of the atom, so ionising it. The electro then goes on with decreased energy and possibly a change in direction also. Such a type of collision, where a transfer of energy takes place between the electron and the internal structure of the atom is called an inelastic collision. The other type of collision is also possible, in which the only transfer of energy between the electron and atom is that necessary for the conservation of energy and momentum. Such a collision is called an elastic collision. It should be noticed that a collision in which the incident electron is exchanged with an electron in the atom without any change of internal energy, is still an elastic collision.

In an elastic collision between an electron and an atom it is quite easily seen that the electron lo~~o~~ses very little energy on account of the very small mass of the electron in comparison with that of the atom. For suppose that an electron of mass 'm' moving with a velocity 'v', strikes an atom of mass 'M', assumed at rest, and that after the collision the electron and atom have velocities v' and V respectively, and their directions make angles ϕ and θ with the original path of the electron thus:-



Then, resolving momenta and taking the Kinetic Energy equation, we have -

$$mv = mv' \cos\phi + MV\cos\theta \qquad (1).$$

$$0 = mv' \sin\phi - MV\sin\theta \qquad (2):$$

From (1) we get -

$$m^2v^2 + M^2V^2\cos^2\theta - 2mMvV\cos\theta = m^2v'^2\cos^2\phi \qquad (4).$$

which with (2) gives

$$m^2v^2 + M^2V^2 - 2mMvV\cos\theta = m^2v'^2 \qquad (5).$$

(3) can be written as

$$m^2v^2 - mMV^2 = m^2v'^2. \qquad (6).$$

Thus we have, substracting (5) and (6) and cancelling M & V

$$(M+m)V = 2mv\cos\theta \qquad (7).$$

Thus

$$\tfrac{1}{2}MV^2 = \tfrac{1}{2}mv^2 \cdot \frac{4mM}{(m+M)^2}\cos^2\theta \qquad (8).$$

which is

$$E_M = E_e \cdot \frac{4mM}{(m+M)^2}\cos^2\theta \qquad (9).$$

where E_M is the kinetic energy of the atom, which is the loss in kinetic energy of the electron and E_e is the origina kinetic energy of the electron. Now in the case of hydrogen the lighest atom, m:M = 1:1835, so that equation (9) can be written as, taking the average value of $\cos^2\theta$ as $\frac{1}{2}$,

$$E_M = E_e \cdot 2m/M \qquad (10).$$

Again using the above ratio of m:M it is seen that the energy lost by the electron is only 1/918 of its initial energy in the case of an impact with a hydrogen atom, and in the case of any other atom the fraction will be much less.

For the case when the atom of mass M is moving, and m is much smaller than M, and the speed of the impacting particle is fairly large, K.T. Compton (2) has shown that the fraction f of the average energy of the electron lost at a collision is given by

$$f = 2m/M \cdot (1 - E_M/E_e) \qquad (11).$$

where E_M and E_e are the average energies of the atom and electron respectively. A further addition to this theory was made by Cravath (3) who extended the argument to the general case of particles with Maxwellian distributions of velocities, no stipulation being made as to the relative magnitudes of the masses. His result is

$$f = 8/3 \cdot mM/(m + M)^2 \cdot (1 - T_M/T_e). \qquad (12).$$

T_M and T_e are the absolute temperatures denoting the energies of the atoms and electrons respectively, while f is defined as above.

Both these expressions reduce to much the same thing for $m \leqslant M$ and $E_M < E_e$. It is therefore quite obvious that the result is unaltered, that the loss of energy by an electron in an elastic collision with an atom is very small.

In discussing the stationary states of an atom it was said that to each state there corresponded a definite energy. In measuring or referring to this energy, in general, no absolute value can be fixed; all that can be done is to refer the energy of the levels to the energy of one taken as standard. Usually the energies are referred to the normal state as zero; so that the energy which is used, is the difference between the energy of the state under consideration and the energy of the normal state. Sometimes the energies are referred to the energy of the state of ionisation as zero, since this is the way in which the energies result from spectroscopic data. In this method the lower states come out with a negative energy, so that the former method will be used here, in which they are positive.

Since an electron has a negative charge, energy can be imparted to it by letting it fall through an electrostatic field. If the electron starts from rest and falls through a difference of potential V, then the kinetic energy it will have acquired will be eV where e is the charge on the electron. However, if the mass of the electron is m and its velocity after falling through the field is v, then its kinetic energy is also $\frac{1}{2}mv^2$.

Thus

$$\begin{aligned} \tfrac{1}{2}mv^2 &= eV \qquad \text{V in electrostatic units} \\ &= eV/300, \text{ V in volts.} \qquad (13). \end{aligned}$$

From this equation it is easily seen that the energy of an electron can be expressed as the number of volts through which the electron would have had to fall from rest to have obtained the given energy. Thus the volt can be used as a unit of energy, the unit being called the electron volt. This unit is very commonly used in all work dealing with electrons and stationary states. The unit is equal to the energy acquired by an electron in falling from rest through a potential of one volt. Using the value of e given by Birge (4) i.e. $e = 4.770 \times 10^{-10}$ E.S.U. we see that one electron volt is equal to 1.590×10^{-12} ergs.

Again from equation (13) it is seen that the velocity of an electron having an energy of V equivalent electron volts is

$$v = \left[\frac{eV}{m \cdot 150}\right]^{1/2} \text{ cms. per sec.}$$

$$= 5.946 \times 10^{7} \times V^{\frac{1}{2}} \text{ cms. per sec.} \quad (14).$$

Thus the velocity of an electron in cms. per sec. is proportional to the square root of the potential through which the electron has fallen from rest. Therefore, in presenting results in which the electronic velocity is one of the variables, it is usual to use the square root of the potential through which the electron has fallen, for this variable, instead of the actual velocity of the electron in cms. per sec.

Returning to the discussion of the excitation of stationary states by electron impact, we know that the electrons must have a definite energy before they can excite a certain level, and now we have shown that we can express this energy as so many volts. Thus, as we increase the energy of the impacting electrons from zero, only

elastic impacts will occur till the energy of the electrons is sufficient to excite the resonance level. The potential, through which the electrons must have fallen from rest to have just sufficient energy to excite this level is called the resonance potential. Similarly, for the other stationary states, we have excitation potentials and ionisation potentials. Resonance, excit:
:ation and ionisation potentials are all included in the term critical potentials.

However, it is not necessary for the impacting electron to have an energy just equal to the energy of the state into which it is going to excite the atom; any energy greater than the excitation is allowed; the excess is then carried away by the colliding electron as kinetic energy. When ionisation takes place, the excess energy may be shared between the impacting electron and the ejected electron.

Since the energy of the electron which can excite a certain state can be expressed as so many electron volts, so it is often convenient to denote the energy of a state by the critical potential corresponding to it. Thus it is usual to speak of the resonance level in the mercury atom, as the 4.86 volt level, or state. In addition, since the life of an excited atom is very short and it returns to a lower state by the emission of the excitation energy as a quantum of radiation of frequency ν given by Bohr's relation, it is possible to determine the critical potentials accurately from spectroscopic data, since

$$E_1 - E_2 = h\nu . \qquad (15).$$

and ν can be determined with great accuracy spectroscopically. Therefore, since the difference of energy is eV/300 where V is the excitation potential in volts,

$$V = (300/e)\cdot h\nu . \qquad (16).$$

from which V can be found, knowing ν .

Thus each level can be denoted either by its critical potential referred to the normal state as zero, or by the frequency of the line emitted by the atom in falling from the excited state to the normal state.

Finally, mention should be made of the notation used by spectroscopists to denote the various levels. They use a symbol such as n^1S_o, which is derived from a knowledge of the quantum states of the atom. In this symbol, S denotes the aximuthal quantum number of the state, the subscript denotes the inner quantum number, the superscript denotes the multiplicity of the level and the spin quantum number, and the n depends on the total quantum number.

A diagrammatic representation of the lower stationary states of the mercury atom is given in Fig. I.

On the left of the figure the numbers are the energies

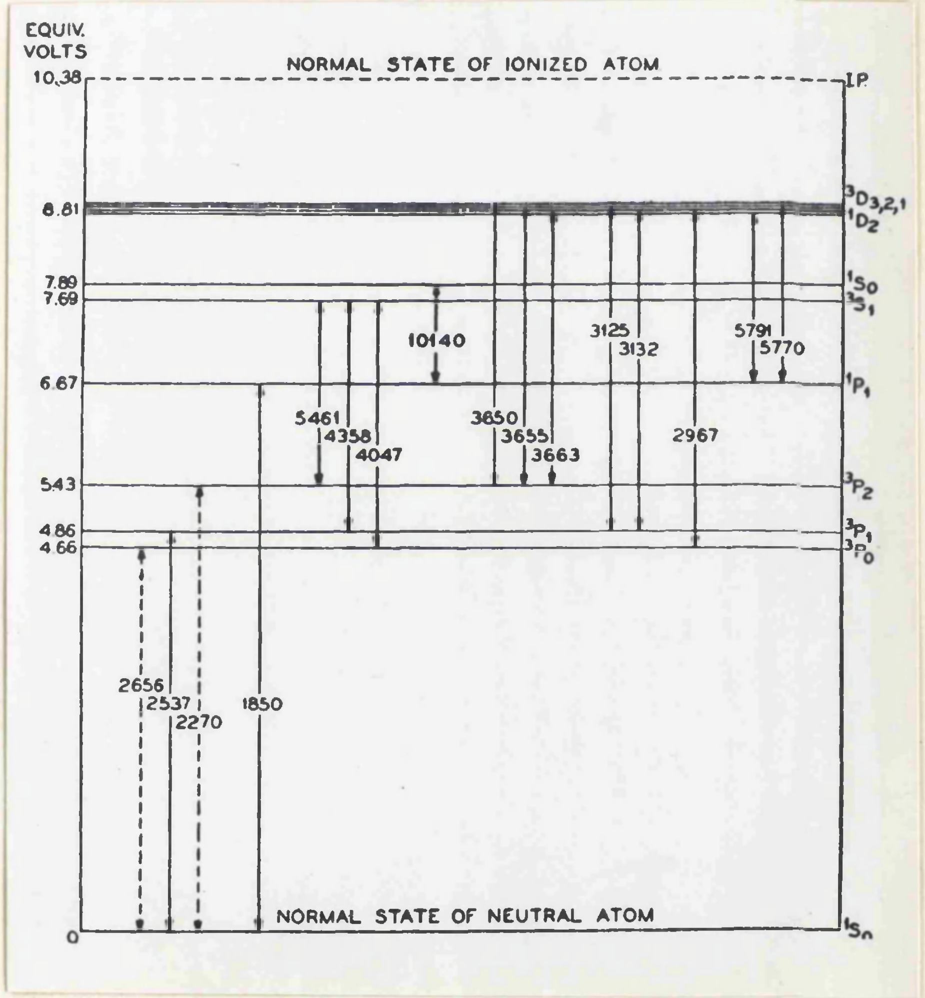

EQUIV. VOLTS
10.38
NORMAL STATE OF IONIZED ATOM
I.P.
8.81
$^3D_{3,2,1}$
$^1D_2$
7.89
7.69
$^1S_0$
$^3S_1$
10140
3125
3132
5791
5770
6.67
$^1P_1$
5461
4358
4047
3650
3655
3663
2967
5.43
$^3P_2$
4.86
4.66
$^3P_1$
$^3P_0$
2656
2537
2270
1850
0
NORMAL STATE OF NEUTRAL ATOM
$^1S_0$

Fig. 1.

of the different levels in equivalent volts. On the right are the spectroscopic symbols for the transition. The numbers on the arrows are the wavelengths of the lines emitted by the atom in passing spontaneously from the higher state to the lower. The two levels from which the dotted lines are drawn are metastable states.

CROSS SECTIONS AND MEAN FREE PATHS.

From the standpoint of the Kinetic Theory the ideas of a mean free path and an atomic radius are well known facts. The mean free path of any particle moving amongst other particles is defined as the average distance moved between collisions. It is here necessary to define a collision more precisely. For the case of smooth elastic spheres, that is the ideal gas, where only purely mechanical effects are considered, a collision takes place when two particles approach each other within a distance equal to the sum of their radii. This is the definition from the standpoint of the Kinetic Theory. However, an atom is known not to be a smooth, elastic sphere. In fact it more probably has an open-work structure consisting of a nucleus surrounded by electrons revolving in orbits round it. Therefore a more rigid definition of a collision is necessary, thus:- if the relative distance between two particles is at first decreased and then increased a collision is said to have occurred if any physical change can be detected during the process. This definition is seen to include all physical effects, electrical, magnetic or mechanical and so on. It thus includes such cases as where an electron is deflected by the field of an atom, even although the electron may not have approached sufficiently close as to come into contact with the atom.

Returning to a consideration of Kinetic Theory results, some useful information can be obtained about the motion of electrons in gases.

The mean free path λ_1 of particles of a type 1, moving among particles of a type 2, has been shown by the Kinetic Theory (5) to be given by

$$\lambda_1 = \frac{1}{\pi n_2 (r_1+r_2)^2 \left[1+ \frac{\overline{C_2}^2}{\overline{C_1}^2}\right]^{1/2}} \qquad (17)$$

where r_1 and r_2 are the respective radii of the hypothetical smooth elastic spheres, and n_2 is the number of particles of type 2 per unit volume. $\overline{C}_1$ and $\overline{C}_2$ are the respective root mean square velocities. If the atoms are all of one type this formula reduces to:-

$$\lambda_1 = \frac{1}{\sqrt{2}\cdot \pi n d^2} \qquad (18)$$

where d is the diameter of the atom.

For the case of electrons moving in a gas it is legitimate to neglect the radius r_1 of the electron in comparison with the radius of the atom, since the classical radius of the electron is of the order of 10^{-13} cms., while the average atomic radius is of the order of 10^{-8} cms. Again the root mean square velocity $\overline{C}_2$ of a gas atom at room temperatures expressed in equivalent volts is of the order of 1/30 volt, while the velocities of electrons used in experiments is seldom less than one volt, so that $(\bar{C}_2/\bar{C}_1)^2$ can also be neglected. Therefore for the mean free path of an electron in a gas we obtain;

$$\begin{aligned}\lambda_e &= \frac{1}{r^2 \pi n} \\ &= \frac{4}{\pi n d^2} \\ &= \underline{4\sqrt{2}}\,(\lambda_1)\end{aligned} \tag{19}$$

Thus the Kinetic Theory mean free path of an electron is $4\sqrt{2}$ times the mean free path of the atom amongst which it is moving. This argument assumes that the gas kinetic diameter of the atom or molecule and the diameter for electron impact are equal.

While the value of the electron mean free path obtaine from Kinetic Theory considerations cannot be rigidly accurate, since the assumption of a smooth, spherical, elastic sphere is not correct, yet it is justifiable to take this value of the mean free path as somewhere near the truth.

Continuing with the hard spherical atom of diameter d, $\frac{\pi d^2}{4}$ will represent its cross sectional area A, and thus

$$\frac{1}{\lambda_e} = \left(\frac{d^2}{4}\right) n = nA. \qquad (20).$$

Here nA is seen to be the product of the cross sectional area of a single atom and the number of atoms in a unit volume, that is nA is the total effective cross section of all the atoms in unit volume. That is, the reciprocal of the mean free path represents the total effective cross section.

From the most reliable values of Avogadro's number N, and the volume of the gramme molecule, as given by Birge, and the value of the gas kinetic cross section of mercury vapour atoms, obtained by viscosity measurements in the gas, and given in Landolt-Börnstein, it is possible to find a numerical value for the Kinetic Theory mean free path λ_e of electrons in mercury vapour.

Birge gives $N = \underline{6}\cdot064 \times 10^{23}$ mole^{-1} at 0°C and 760 mm. pressure and the volume V of the gram molecule as $22\cdot414 \times 10^3$ cc/mole at 0°C and 760 mm. pressure. Thus the value of n, the number of molecules in one cubic centimetre at one mm. pressure is given by

$$n = \frac{N}{V.760}$$
$$= \frac{6\cdot064 \times 10^{23}}{22\cdot414 \times 10^3 \times 760}$$
$$= 3.562 \times 10^{16}$$

The value given for the gas kinetic cross section A of mercury vapour is $10{\cdot}2 \times 10^{-16}$ cm^2.

Thus the value of the electronic mean free path is

$$\lambda_e = \frac{1}{nA} = \frac{1}{3.562 \times 10^{16} \times 10{\cdot}2 \times 10^{-16}}$$

$= 0{\cdot}02752$ cm. at 0°C and one mm. pressure. of mercury.

At room temperatures the vapour pressure of mercury is approximately 10^{-3} mm. of mercury; so that the value of λ_e at room temperatures becomes

$$\lambda_e = \frac{0{\cdot}02752}{10^{-3}} = 27{\cdot}52 \text{ cms.}$$

This value is very important since later on, in the experimental work it is applied to indicate what dimensions of apparatus and what gas pressure may be used so that the mean free path of the electrons in the gas in the apparatus, may be such that the probability of an electron making more than one collision in the apparatus shall remain quite small.

The gas kinetic cross sections for argon and helium are given by the same source as $6{\cdot}46 \times 10^{-16}$ cms.^{2} and $2{\cdot}83 \times 10^{-16}$ cms.^{2} respectively. From these figures the electron mean free paths for these gases are calculated to be 43.46 cms. and 99·19 cms. respectively for a pressure of 10^{-3} mm. of mercury.

Thus it is seen that for mercury the electronic mean

mean free path is much smaller than for the rare gas argon and helium, so that, for these latter gases, a much higher pressure than for mercury could be used without the probability of multiple collisions becoming appreciable.

PASSAGE OF AN ELECTRON BEAM THROUGH A GAS.

We will now proceed to consider the case of what happens to electrons moving in a gas. Suppose that we have a parallel beam of electrons of uniform velocity passing through a gas at a pressure of p mm. of mercury, where p is so low that in the region under consideration the probability that any one electron will make more than one collision is very small. Thus if an electron makes a collision and leaves the beam it is highly improbable that it will return to the beam, before the beam leaves the scattering region.

Considering a length dx of the beam, we see that the beam will loose intensity in this length dx due to collisions, the amount of this loss being -dI. This loss will obviously be proportional to the pressure p and to dx and to I the intensity, and to no other variable; so that , including a constant α it is possible to write

$$-dI = \alpha\, pIdx \qquad (21).$$

However the loss in intensity should obviously depend on the total effective cross section of the gas atoms through which the gas atoms are passing. Thus, by suitable arrangement, α is defined as the total effective cross section for interception of electrons by the gas atoms, or the absorption coefficient.

Integrating the above equation, we obtain:

$$\log_e I = -\alpha p x + \text{constant} \qquad (22).$$

If it is now assumed that at the point where the beam enters the gas $I = I_0$ and $x = 0$, then we obtain the result that:

$$I = I_0 e^{-\alpha x p} \qquad (23)$$

which gives the intensity I of a beam of electrons after passing a distance x through a gas at a pressure p.

To justify the definition of α as the total effective cross section, it is necessary to show the relation between α and the mean free path, λ_e.

From the equation $I = I_0 e^{-\alpha p x}$ by multiplying each side of it by ε the charge in the electron we see that I is the number of electron paths that have extended from $x = 0$ to $x = x$ uninterrupted. The number of these paths which stop between x and $x + dx$ is $-dI$ which from above is

$$-dI = p\alpha I dx = p\alpha I_0 e^{-\alpha p x} dx. \qquad (24).$$

Multiplying this equation by x gives the sum of the lengths of all these paths. If this equation is now integrated from $x = 0$ to $x = \infty$, the total length of all the paths of all electrons entering the gas at $x = 0$ is obtained. Dividing this by I_0 will then give the mean free path of an electron, λ_e, in the gas. Thus:-

$$\lambda_e = \frac{1}{I_0}\cdot\int_0^\infty x p\alpha I_0 e^{-\alpha p x} dx$$

$$= p\alpha\int_0^\infty x e^{-\alpha x p} dx$$

$$= p\alpha\left[\frac{x e^{-\alpha x p}}{-\alpha p}\right]_0^\infty - p\alpha\left[\frac{e^{-\alpha x p}}{\alpha^2 p^2}\right]_0^\infty$$

By integrating by parts.

$$= 0 + \frac{p\alpha}{p^2\alpha^2}$$

$$= \frac{1}{\alpha p} \qquad (25).$$

Comparing this with $\lambda_e = L/nA$ and knowing that p is proportional to n, we see that the definition of α as the total effective cross section is justified.

The dimensions of α are L^{-1}, that is L^2/L^3, i.e. cm.^{2}/cm.^{3}, which is the total area of all the molecules in one cubic centimetre. Usually α is reduced to its value at 0°C. and a pressure of one mm. of mercury.

α here is the total effective cross section but it is possible to find the cross section for other types of collisions. For example, we may measure the cross section for elastic impacts, or for inelastic impacts. In particular the cross sections may be found for ionisation or excitation to certain levels.

Again, the reciprocal of the mean free path is the number of collision made per unit path length, and it is therefore a measure of the probability of a collision. However the absorption coefficient α is the reciprocal of the mean free path apart from a constant, so that the absorption coefficient is also a measure of the probability of a collision. The probability of a collision is defined by Brode (6) to be the number of collisions made, per unit electron current, per unit path length, per unit pressure at $0^{o}C.$, which is seen to be exactly what α in equation (21) represents.

Thus in experimental work the curves for total effective cross sections really represent the probability of a collision apart possibly from some constant numerical factor. In order to find the probability that a collision shall be of a certain type, it is only necessary to divide the cross section for that type of collision, as determined experimentally, by the total cross section for all types of collisions.

Although an atom cannot have a sharp outer boundary and so that cross section cannot be ascribed to any particular part of the atom, yet it is often convenient to speak of the effective cross section of an atom for collision. For a single atom this cross section 'q' is given by $q = \alpha/n$ cm.^{2} where, as before, n is the number of atoms in unit volume at unit pressure (one mm. of mercury) at $0^{o}C$.

This gives $$q = 0{\cdot}2807 \times 10^{-16} \times \alpha . \text{cm}^2$$

The radius r of a circle of this area is then given by,

$$r = 0{\cdot}2989 \times 10^{-8} \times \tfrac{1}{2}. \text{ cm.} \qquad (26).$$

For values of α between 1 and 100, this value of r is seen to be in general agreement with values of r as found from kinetic theory measurements.

Methods of presenting the results for the probability of collision are somewhat various. Some authors use the effective cross section, q, of a single atom; others use q, divided by the gas kinetic cross section A, for the gas used in the experiment, or by some other arbitrary standard area. Others still, use the total effective cross section α , i.e. q x n. The first and the last of the above methods will be the ones used here. The cross section, q, of a single atom will be expressed in atomic units, that is in units of πa_0^2 , where a_0 is the radius of the first Bohr orbit in the hydrogen atom In dealing with the probabilities of specific types of collisions, the results are often expressed as a ratio to the probability of all collisions α . That is they thus represent directly the area of the atom that must be hit in order that a collision of the desired type shall be a certainty.

Returning to equation (7) we see that it can be written as

$$\log_e I/I_0 = -\alpha xp$$

or as $\log I = \log I_0 - \alpha px.$ (27).

Here I_0 is a constant and x can be kept constant, so that if p is varied, and the various values of $\log I/I_0$ or $\log I$ so obtained are plotted against the values of p, then the graph obtained should be a straight line, and its slope should give the value of α. Similarly p can be kept constant and x varied by suitable means; the slope of the resulting straight line again giving the value of α. Both the methods have been used experimentally by various workers to find values of α. The advantage of this method is that equation (23) can be written as

$$I = k\, I_0\, e^{-\alpha p x} \qquad (28)$$

where k is the fraction of the original beam that would reach the collector if there were no gas present in the apparatus. That is, the equation gives the practical state of affairs in the apparatus more accurately, since it allows for the spreading of the beam and any other such losses from it, otherwise than by impacts with gas atoms. On taking logs. as before, this becomes

$$\log I = \log k + \log I_0 - \alpha p x. \qquad (29).$$

$\log I_0$ and $\log k$ are both constants so that variation of x or p will still give a straight line but the slope of it will represent α more accurately than previously. This latter method has been used by many workers on this subject, and it is the intention of the author to use the principle of it in dealing with gases, such as helium, for which the pressure can be varied easily. The method will be to take two sets of observations for pressures p and p', then from equation (29) it is easily seen that:

$$\alpha = \frac{1}{x(p-p')} \cdot \left(\log \frac{I'}{I'_0} - \log \frac{I}{I_0} \right) \qquad (30).$$

Here it is at once seen that k has disappeared and with it all background scattering. α then represents the total cross section for impacts with the gas atoms only. In the experimental part of the thesis it will be explained why it was not possible to use this method in dealing with mercury vapour.

SECTION 2.

TOTAL EFFECTIVE CROSS SECTION MEASUREMENTS.

In the previous section an equation was derived for the passage of a beam of electrons through a gas. In this equation there was a certain constant α , variously described as the total effective cross section, or the absorption coefficient or the probability of collision. From Kinetic Theory considerations a numerical value was found for this constant. However, whenever attempts were made to find values for this constant experimentally for different gases, it was found that α was not a constant but that it varied with the velocity of the impacting electrons in the beam. The ways in which α varied for different gases and for different velocities were often very different. Much work has been done in determining this variation of α with velocity and gas, especially in the last ten years.

The earliest attempts to determine a value of α were made by Lenard in 1895 (7) and in 1903 (8). At first he used cathode rays of high energy, about 30 kilovolts. Later he used an apparatus in which the electrons were derived photoelectrically from a zinc plate Z by shining ultra violet light on it. By means of a potential applied between the plate and a grid immediately in front of it, the electrons were accelerated to the desired speed. The beam so obtained then passed through a field free space and into a collecting chamber E at the end. By measuring the current to this chamber and the total current leaving the plate, Lenard was able to find a value for α . His apparatus, which has since been used in modified forms by many workers, is shown in fig. (2). His measurements were for energies extending from 4 to 30,000 electron volts. The conclusions he reached from his results were that at high velocities, the cross section was only a few per cent of the kinetic theory value; as the energy of the electrons in the beam was decreased, Lenard found that the cross section increased steadily at first and then more slowly at low voltages, where also its value was of the same order as the kinetic theory value. He concluded that the cross section was approaching this value as a limit. Also, at high voltages, the cross section was found to be proportional to the atomic number of a monatomic gas and to the sum of the atomic numbers of the atoms of a polyatomic gas. In addition, at the same voltages, the cross section of a polyatomic molecule was found to be the sum of the cross sections of its constituent atoms.

Becker (9) and Silbermann in 1905 extended these researches and especially verified the fact that for fast electrons the cross section of polyatomic molecules is the sum of the cross sections of its atoms. They used a large number of organic compounds, some of whose molecules contained as many as twenty atoms and found that the relation held accurately.

None of these workers made accurate measurements at low voltages so that they were unable to disprove Lenard's assumption that the cross section tended to the kinetic theory value as a limit at these voltages.

The earliest detailed work at low voltages was done by Åkesson with the same type of apparatus as Lenard used. His results, although presented in a different way, showed that the cross section did not increase to a constant value as the energy of the electrons was decreased, but that for most atoms which he studied, maxima and minima appeared. He called this effect in his curves a selective absorption. Although he did not actually plot cross section curves he was able to make the statement that in a number of cases - "the slower electrons were more penetrating than the faster." Åkesson's work has since been verified by a number of other workers, using the same and other methods.

In this Lenard type of apparatus, as used by Mayer, Jones and others, only those electrons are lost from the

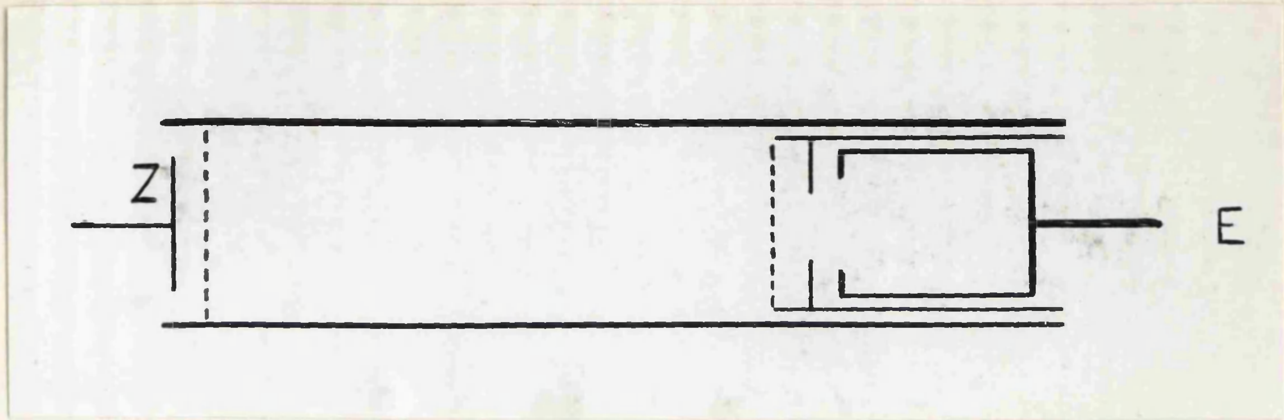


Fig. 2. Lenard's Apparatus.

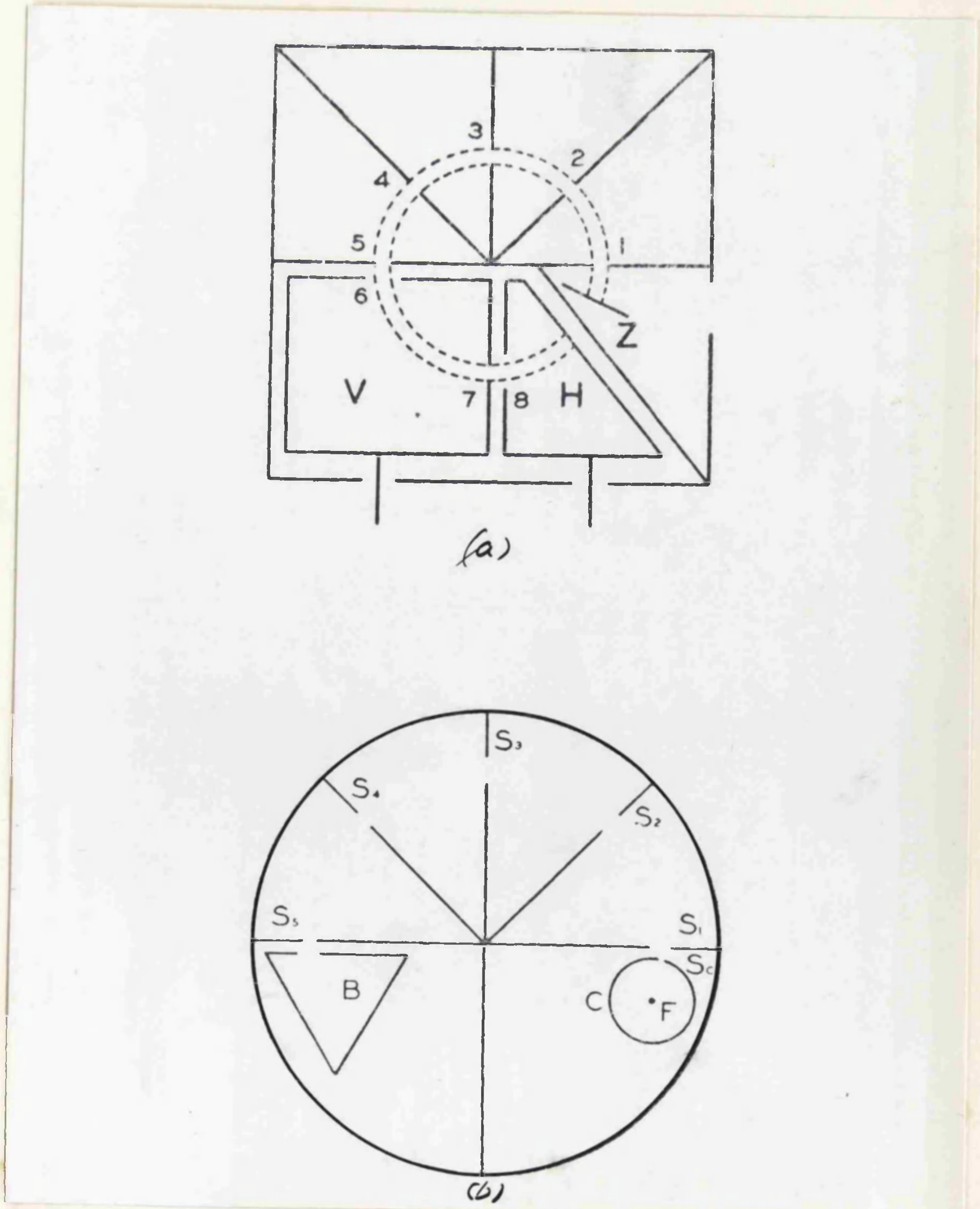


Fig. 3. (a) Ramsauer's Apparatus, (b). Brode's Apparatus.

beam and so contribute to the cross section, which have suffered an appreciable change in direction, say a deflection greater than 5°. Any electrons which make a collision and loose energy, but do not have their directions much altered, still pass on and are collected, and so do not contribute to the probability of a collision. Thus the probability as measured by this type of apparatus may not necessarily be the correct one.

In 1921, Ramsauer (10) working in Lenard's laboratory designed an apparatus which should give the cross section more accurately. His apparatus and a modification of it as used by Brode, are shown in Fig. (3). In the original apparatus, electrons were derived from a zinc plate Z by means of ultra violet light as in Lenard's apparatus. The desired velocity was then given to the beam by accelerating it up to the first slit 1. Then, by means of a magnetic field, normal to the plane of the paper, the beam was bent into a circular path, and passed through the slits 2 to 8. The magnetic field H necessary to bend a beam of electrons of velocity v into a circle of radius r is given by $H = \frac{mvc}{re}$ where e and m are the charge and mass of the electron respectively and c is the velocity of light.

The currents collected by the chambers labelled V and H are measured by galvanometers or electrometers, and from these the probability of collision can be calculated, since the total current leaving slit 5 is given by $V+H$, and the current leaving at slit 7 after passing through a distance x, is H. It will be seen that only those electrons can reach H which have suffered no collision in any form. For if at a collision, the electron changes its direction it is immediately lost from the beam, or if it changes energy without change of direction, it will be at once removed from the beam by the magnetic field, or if it attaches itself to an atom or molecule, the resulting ion will have a much larger mass than the electron and so will be removed from the beam. Again if the electron ionises the atom and so ejects an electron, the velocities of both electrons will be too small for them to remain in the beam, since the net energy available to them will be the original energy of the electron less the energy of ionisation. Also the velocity distribution of the electrons in the beam due to their varying initial velocity on leaving the plate, will be much narrower, since all electrons with velocities larger or smaller than a certain mean will be deflected out of the beam by the magnetic field and will be unable to enter the scattering region. On account of the gas pressure being so low that the mean free path of the electrons is large compared with the dimensions of the apparatus, no electron which has once left the beam can return to it, since this would require at least two collisions, which we have arranged to be very improbable.

In the modified form of the apparatus as used by Brode (11), the electrons are derived thermionically from a filament, and are accelarated to the desired velocity by a potential between the filament and a coaxial cylinder. The chamber V is dispensed with, the currents entering B and leaving S_c being the only ones measured. The current I_0 at the start of the path, is assumed proportional to the latter current G, so that $I_0 = kG$. I is the current recorded by B. The equation (28) of section (1) is then used to calculate the probability of collision.

An important advantage of this type of apparatus is that the velocity of the electrons in the beam can be determined accurately knowing the magnetic field necessary to bring them into the required circular path. If their velocity is taken as the accelerating potential applied between their source and the first slit, as is done in the case of experiments with the Lenard apparatus, there may be quite large errors present due to contact potentials and the potential drop along the filament due to the filament heating batteries.

A number of workers, among whom were Jones (12), Mayer (13) and Maxwell (14) have used a modified Lenard type of apparatus. The electrons are generally derived from a filament and the beam is defined by a succession of slits all in a straight line. Two chambers are provided, one for collecting the electrons which leave the beam in the length x, and the other for collecting all those electrons which have passed straight through the first chamber without making a collision. It will be seen that this type of apparatus takes no account of electrons which have suffered loss of energy only. It might therefore be expected that the two types of apparatus would give very different results for the probability of collision; the Lenard type giving the smaller probability since in it, fewer scattered electrons are collected. However, Jones (12) used both methods in an investigation of the cross section of mercury vapour. His results show that the difference in cross section as obtained by the two methods is fairly small, and that the Ramsauer method gives the smaller value, a rather surprising result. Comparing, however, the results obtained by Jones by the Lenard method with those obtained by Brode (11) by the Ramsauer method, the author finds that the agreement between the curves is almost perfect, so that it may be assumed that results obtained by either method will represent accurately the probability of collision.

Using his apparatus, Ramsauer (10) made a number of measurements for hydrogen, nitrogen, helium and argon at low velocities, below one volt, and found for argon a minimum value at about 0.75 volt. This work was extended and verified by Mayer using the Lenard type of apparatus, who found a maximum at about 12 volts. The result was also verified by Townsend and Bailey (15) by an entirely different method. Later Ramsauer (16) further extended his observations to the rare gases, and found that, in the case of argon, krypton and xenon, the probability showed a maximum at from 7 to 12 volts. This effect of slower electrons being more penetrating than faster ones is known as the Ramsauer effect. It will be noticed that Åkesson had, in point of fact, actually observed this effect some years before, although his results were so presented as not to demonstrate the fact clearly. Brode (6), in discussing Lenard's results, points out that the probability curve which he gives for argon shows a maximum at low voltages, although Lenard himself drew his argon curve parallel to his other curves so that it did not show the effect.

More recent work by Ramsauer and Kollath (17), which has been confirmed by Brode, and Normand (18), indicates that at still lower velocities the cross section rises again. The curves for argon, krypton, xenon and neon are shown in Fig. (4). At the maxima the values of the cross sections are much larger than the kinetic theory values, while at the minima they are much smaller. There is no indication

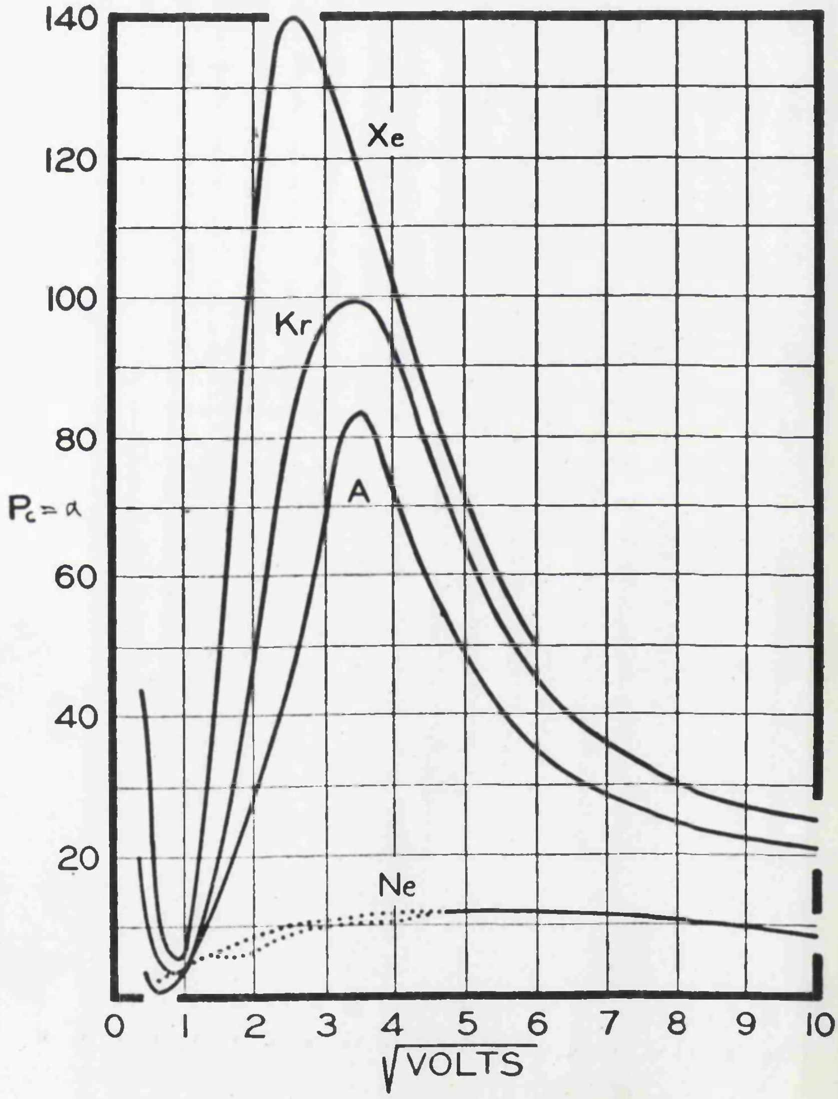


Fig. 4. Ramsauer and Kollath's Curves for Xe, Kr, Ar, and Ne.

that the cross section approaches the kinetic theory value as a limit, which was Lenard's original assumption.

Following on the discovery of the Ramsauer effect by Ramsauer and his co-workers, numerous other investigators have studied the effect in different gases and vapours, using both the methods outlined above. In addition to the rare gases, several other gases have been found to show the effect; the maxima in polyatomic gases usually appear at lower energies than for the rare gases. A notable polyatomic gas which shows the effect is methane, CH_4. The cross section-velocity curve as obtained by Brüche (19) for methane is very similar to the curve for xenon. The explanation seems to be that the four hydrogen atoms in the methane molecule may form a closed shell with the four valency electrons of the carbon atom, which shell is then similar to the outer shell of the rare gases.

Brode has further extended the subject to the study of the monatomic metal vapours; among them the cadmium, mercury and zinc group (20) has received special attention. In each of the curves obtained for these metals, there is a slight hump but no pronounced maximum as in the case of the rare gases. Brode's curves for these vapours are shown in Figure (5). The group of alkali metal vapours, sodium, pôtassium, rubidium and caesium has also been

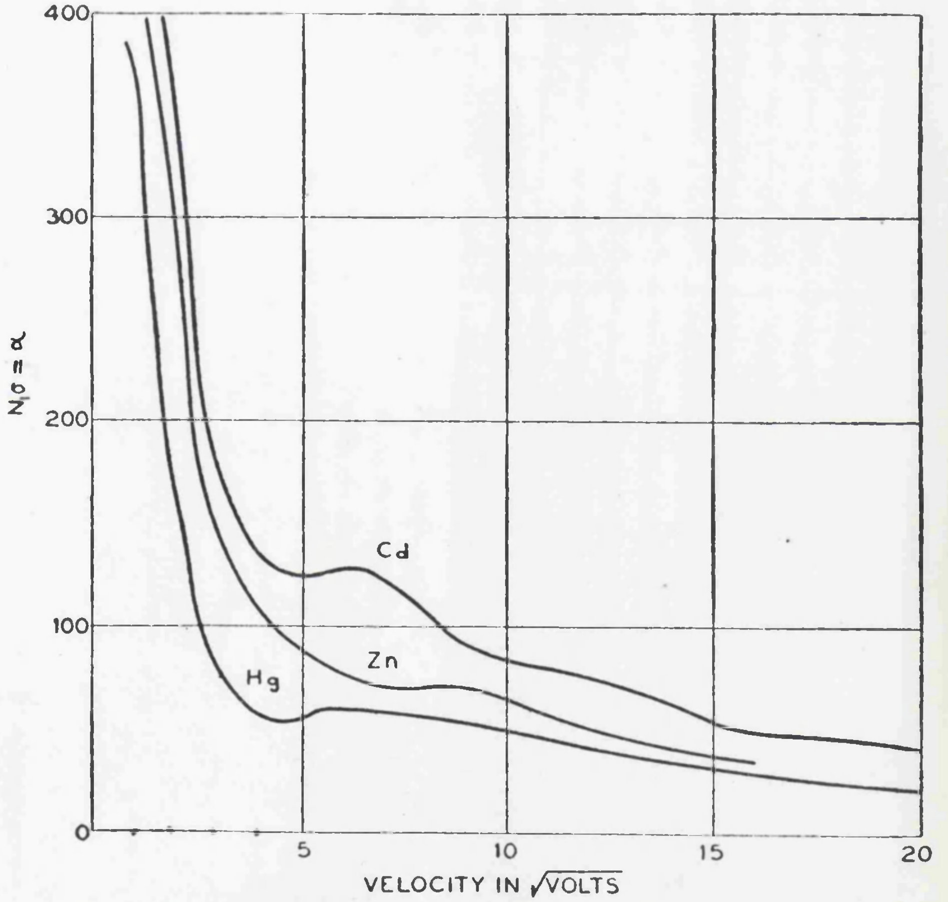


Fig. 5. Brode's curves for Hg., Cd., and Zn.

has also been studied by him (21). All these four curves show a sharp maximum at about 1 to 2 volts energy. The noteworthy feature of the cross sections of the elements of this group is their very large magnitude, especially at low voltages; the value being between 1000 and 2000 cm^2/cm^3 at about 2 volts energy, as compared with 300 in the case of mercury, and 10 in the case of argon. The cross section α given here is the cross section of all the molecules in one cubic centimetre at one mm. pressure and 0°C. Taking the number of the molecules in this volume at this temperature and pressure as $3 \cdot 5 \times 10^{-16}$ and α as 1050, the cross section q of a single molecule can be calculated to be 3×10^{-14} cms^2. and thus r the radius of the atom is approximately 10^{-7} cms. or 10 Angstroms, which is a surprisingly large figure.

From a comparison of the different curves for the various atoms, it is at once apparent that there is a distinct similarity in form between the curves for elements which are in the same group of the periodic table, for electrons of average and low velocities. The curves for the rare gases are similar to each other as are the curves for the alkali metals, and so on; but the curves for the rare gases are in no way similar to the curves for the alkali metal vapours. Since the members of a group have similar electronic structures, it seems likely that there is a relation between electronic structure and probability of collision. This postulate is further strengthened by the fact that the curve for methane is similar to that for the rare gases, since its structure can be considered as similar to that of the rare gases as explained above. The similarity is also found in the case of nitrogen, N_2, and carbon monoxide, CO, which can be considered as having similar electronic structures. The nitrogen molecule has fourteen external electrons, while the carbon monoxide molecule also has fourteen, six from the carbon atom and eight from the oxygen atom. Their cross section curves as determined by Normand (18) are almost identical. Brüche (22) has studied a large number of molecules with similar electronic structures and has found good agreement in the curves for such molecules.

The results of the above paragraph lead to the suggestion that the cross section for low velocity electrons is determined, for the most part, by the potential field of the external electrons of the atom or molecule. For molecules with similar outer shells of electrons, the cross section will be similar even although the nuclei may be very different.

At relatively large energies, above 100 volts, all the curves for the monatomic gases and vapours are decreasing uniformly. If a comparison is made of the values of the cross sections at a given velocity, they are found to be approximately inversely proportional to the ionisation potentials of the different elements. It is also known that the ionisation potentials are, approximately, periodic functions of the atomic numbers of the elements so that the cross sections at high velocities are also periodic functions of the atomic numbers of the elements.

For the very fast electrons recent experiments have proved Lenard's original conclusion, that the cross section is mainly determined by collisions with the nucleus at these velocities.

The causes and explanations of the Ramsauer effect will be discussed fully in a later section.

In addition to the direct experimental methods of obtaining the probability of collision, as described above, there is another less direct method. Numerous workers such as Arnot, Bullard and Massey, Tate and Palmer, Dymond and others, have made investigations of the distribution in direction, or angular scattering of electrons at collisions with atoms, using an apparatus consisting of an electron gun and a collecting chamber; the gun can be rotated about an axis through the electron beam and perpendicular to it. If the current recorded by the collector, when the angle between its direction of collection and the direction of the electron beam is θ , is $I(\theta)$ per unit solid angle, per unit electron current, per unit path length, per unit pressure at 0°C., which can be divided into the intensities scattered elastically and inelastically, I_e and I_i respectively, then the cross section or probability of collision is given by the integral over a complete sphere of the scattered intensity, i.e.

$$\alpha = \int_0^{\pi} I_i \, 2\pi \sin\theta \, d\theta + \int_{\delta}^{\pi} I_e \cdot 2\pi \sin\theta \, d\theta. \qquad (1).$$

The latter integral does not extend right to zero as the lower limit but only to a small angle δ , since if it were extended to zero it would include the part of the beam which had made no collisions. In practice and from the quantum theory, it is found that $I_e \sin\theta$ tends to zero with θ so that the integral can be extrapolated to zero as a lower limit without bringing in the original beam. Numerical integration of an angular scattering curve for a given velocity, will then give the cross section for that particular velocity.

The scattered intensity $I(\theta)$ is easily seen to have the dimensions of an area per unit volume, so that it is also a measure of a cross section. Thus it is defined as the differential cross section.

This method has been employed by a number of workers to find values for the total cross section and also for the cross section for specific types of collisions, in particular for elastic collisions, since the cross section for elastic collisions will be given by

$$\alpha_e = \int_{\delta}^{\pi} I_e \cdot 2\pi \sin\theta \, d\theta \qquad (2).$$

Results obtained by this method are in general not very reliable, and also little comparison with results by Ramsauer's method is possible since absolube values of the cross section can be rarely obtained from an angular scattering curve. The reason why the results are not reliable is that in practice it is seldom possible to obtain values of $I(\theta)$ over the whole angular range 0° to 180°. Thus it is necessary to extrapolate the experimental curves for $I(\theta)\sin\theta$ to the limits at both ends. This however may introduce considerable errors, since, in nearly all experimental curves, diffraction effects are present, so that maxima and minima may occur between the last experimental point and either end point. A uniform extrapolation might thus be much in error. Results have been obtained however, by this method which do show a qualitative agreement with results by the direct methods.

So far the direct methods have given values for the total effective cross sections, that is for all types of collisions at once, elastic and inelastic. The only results for the elastic collisions alone have been obtained by the above method of integration of angular scattering curves. For the probability of collision for certain specific types of inelastic impacts, namely excitation to a specified level or ionisation, curves have been obtained by indirect optical methods or by analysis of the positive ions produced in the latter case. For excitation, a very few curves have been obtained by direct electrical methods. A discussion of the previous work on the cross sections for excitation and ionisation now follows.

PROBABILITIES OF EXCITATION AND IONISATION.

In a study of the cross sections for excitation and ionisation by electron impact, there are two possible methods of approach. The first is to study what happens to the atoms at the collision, and the second is to study what happens to the electrons. For both excitation and ionisation it has been seen that energy is necessary for the process, which is obtained from the kinetic energy of the colliding electrons. After the collision, the electron moves off with its energy decreased by a definite amount if excitation has occurred, or by any amount greater than a certain minimum if ionisation has occurred. In the latter case, the impacting electron ionises the atom so using up a definite amount of energy, and in the process knocks an electron out of the atom. To this ejected electron it may give any fraction of its own remaining energy. Thus in the case of ionisation, the impinging electron may loose any amount of energy greater than a certain minimum.

From the above discussion it is seen that a study of the number of electrons which have lost certain definite amounts of energy in collisions, will lead to a knowledge of the probability of excitation to a certain level, or of ionisation.

An investigation of what happens to the atoms after a collision may also lead to a value of the probability of excitation or ionisation, not necessarily the same as from the previous method however. The reasons for this will be discussed later.

When ionisation takes place, the atom looses one or more electrons and so becomes a positive ion. By suitable application of a potential it can be drawn to a collector and so the number of positive ions can be recorded. Most writers define this number of positive ions formed in the gas per unit path length, per unit electron current, per unit pressure at 0°C., as the efficiency of ionisation. The probability of a collision resulting in ionisation, can then be found by dividing the efficiency by the total number of collisions; which latter figure can be calculated from the kinetic theory cross section or from the total cross section curves. It is also well known that an atom may be doubly or trebly ionised and so on, corresponding to the removal of two or more electrons from it. This if the probability of multiple ionisation to a degree n is represented by P_{ni} and the efficiency of ionisation, which is really the number of electronic charges recorded, by E_i then the relation between the P_{ni}'s and the E_i is

$$E_i = 1P_{1i} + 2P_{2i} + 3P_{3i} + \ldots\ldots$$

In recording the number of ions and defining the efficiency of ionisation, each multiply charged ion is counted as so many singly charged ions. Thus it is seen that the efficiency of ionisation or the probability calculated from it, may not be the same as the probability obtained by investigations of the number of electrons which have lost a certain amount of energy in ionising the atom in one particular way. In addition, an atom may be singly ionised in a number of different ways corresponding to the removal of electrons from different shells: the singly charged ion resulting is indistinguishable from any other singly charged ion, but the electron which has ionised the atom has lost an amount of energy corresponding to the way in which it has singly ionised the atom, since the ionisation potentials for electrons in different shells are not the same.

When atoms are excited by impacts of electrons there is no means by which the excited atoms can be drawn out of the gas and recorded, since they are not charged. The only way in which information can be obtained about the probability of excitation by studying the atoms, is to make use of the fact that an excited atom returns spontaneously to a lower state and, in so doing, emits the surplus energy as a quantum of radiation, of a definite frequency. By measuring the intensity of light emitted by the gas on being bombarded by electrons of a known energy, and by converting this intensity to the equivalent number of quanta, the number of atoms excited per unit path length, per unit electron current, per unit pressure at 0°C. may be calculated; which then gives a measure of the probability of excitation of the atoms to that state from which they descended in emitting the quantum of radiation. It is assumed here that the wave length measured is one corresponding to a transition from an excited state to the normal state. In dealing with this method a number of reservations are necessary.

Firstly the method assumes that no atoms have reached the given excited state except by a single impact of an electron with an atom in its normal state; and secondly it is assumed that no atom leaves the excited state except by falling into its normal state in one transition with emission of the desired quantum. Thirdly, it is assumed that none of the radiation emitted is absorbed in the gas before it reaches the instrument recording the intensity of radiation. If all these assumptions were true, it would then be reasonable to expect that the probability, obtained by this method, would be in agreement with the probability as obtained by observations on the electrons which have excited the desired state. None of the assumptions, however, can be taken as completely true. In the case of the first, atoms may have reached the given state by first being excited to a higher state and then falling to the given state emitting a quantum of another wavelength. Again, an ionised atom may have combined with a free electron, and then the resulting neutral, but excited, atom may have fallen to the given state. Finally the atom may have reached the given state by a collision of the second kind with another atom. A collision of the second kind may be defined here, as a collision in which an excited atom collides with another atom and passes on to it, some or all of its excitation energy, thereby raising the second atom to an excited level or increasing its kinetic energy, while the first atom falls to a lower excited state or its normal state without emitting a photon.

The second assumption as to all the atoms leaving the excited state by emission of the desired quantum may also be far from true. A collision of the second kind may cause the atom to leave the state without emission of the desired quantum; or the atom may be struck again by an electron and so raised to a higher state from which it may fall direct to the normal state. Finally, should the given excited state not be the one next to the normal state, metastable states excepted, the atom may first fall to a lower state and then to the normal state; thus not emitting the desired quantum.

Absorption of the radiation emitted in a transition may be quite strong in many cases such as the absorption of the 2537 line of mercury vapour in a hot mercury arc.

It is thus seen that results for the probability of excitation of a given state, as obtained from study of the intensity of the radiation emitted by the atoms in falling from that state to the normal, may be far from correct. Further it is apparent that only in exceptional cases can results be obtained by this optical method for the absolute probability of excitation of a certain state, since, for this to be possible, the effects discussed above must all be allowed for and, in general, only relative measurements of the intensity of a spectral line can be obtained. Relative measurements of the probability can however be obtained and these in themselves are very interesting and in most cases exhibit a certain similarity to the results obtained by the electrical method.

The general result by all methods is that the excitation function starts from the excitation potential and rises to a maximum at some higher value of the energy, and then falls steadily as the energy of the electrons is further increased.

Very few results have been obtained for excitation probabilities by the electrical method.

The earliest observations were made on the $2\,^{3}P_{3,2,1}$ states of mercury by Sponer (23) whose results were recalculated by Hertz (24). The method used was to analyse the electrons with a retarding field after they had passed through a region containing gas. As the energy of the primary electrons was varied, the variation of the probability of excitation to the given states, with velocity could be determined, by the change in current collected by the plate. The result of these observations was that the probability curve showed a maximum at about 6 volts. Sponer actually believed that on account of the velocity spread of the electrons in the beam, the result was inaccurate, and that the maximum should appear exactly at the excitation potential. Eldridge (25) also investigated the 4·9 volt state in mercury vapour and concluded that the probability rose to a maximum almost at the excitation potential and then fell as the energy was increased.

Both Eldridge, and Brattain (26) studied the 6·67 volt level in mercury vapour. The former concluded that the probability increased from a small value as the energy was increased to a few volts above the excitation potential Brattain with an improved form of apparatus, found that the probability showed a maximum about a tenth of a volt above the excitation potential. In his paper he suggests that the probability may not fall continuously after this maximum but that it may rise again to another maximum at a considerably higher voltage, as optical methods have suggested.

The only other notable work on probabilities of excitation by a direct electrical method has been done on the 2^3S_1 state of helium , whose energy is 19·77 volts, by Dymond (27) and Glockler (28). Dymond's method depended on finding the difference in current to a collector with and without a retarding potential slightly larger than the excitation potential. Glockler's results were derived from a study of the effect of the inelastic collisions on the current-voltage curves of his apparatus. Both workers concluded that the probability showed a maximum a few tenths of a volt above the excitation potential. The magnitudes of their maxima are not in very good agreement.

A somewhat less direct method has also been developed. It consists in spreading out the electron beam into an energy spectrum by means of an electrostatic or magnetic field. The states which have been excited can be determined from the positions of the different groups of electrons in the spectrum, and the probability of excitation of the state can be found from an integration of the area below each peak. By variation of the velocity, curves of the probability against velocity can be obtained. This method has been used by a number of workers, among them, Whitney (29) and Tate and Palmer (30) in mercury vapour, and Van Atta (31) and Hughes and McMillen (32) and Whiddington and Taylor (33) in the rare gases. In some cases the probability has been measured only for all the inelastic collisions and not for a definite state. In addition this latter method has only been applied to electrons scattered through one definite angle, or to those which have suffered loss of energy without change of direction. The results are therefore not strictly comparable with results where the electrons scattered through all angles are included. Finally in some cases the pressure of the gas has been so high that the electrons have made many collisions before reaching the collector. This will certainly effect the observed probability since an atom may reach the desired level by more than one transition caused by successive impacts with electrons.

The optical method of studying probabilities is to focus the light from a certain part of the path of the electron beam on to the slit of a spectrograph. The intensities of the different lines so obtained can be measured either with a microphotometer or by using a photoelectric cell. Thus the relative probabilities of the excitation of the different levels is obtained, or what Darrow (34) more accurately calls the probability of stimulation of a certain spectral line.

Numerous workers have used this method but few have been able to obtain an absolute value for the probability. For the 4·9 volt state in mercury, Bricout (35) has obtained an absolute value of $6cm^2/cm^3$ at the maximum. A considerable amount of work has been done by the optical method on mercury vapour, especially for the 2^3P_1 state, of energy 4·86 volts, by Schaffernicht (36) and others. The general conclusion is that the probability of excitation of this state has a sharp maximum at from 6 to 7 volts. Schaffernicht examined some seventy lines in the various spectra of mercury and found an agreement between his results for similar types of lines. For the triplet lines he found that a sharp maximum followed by a sharp fall was present at a very few volts above the excitation potentials, approximately between 9 and 12 volts, while for singlet lines there is a broad maximum, at about 30 volts, followed by a slow fall. In the case of intercombination lines, he finds that the character of the line is determined by the initial level of the transition. Certain lines give curves which show two maxima, one of the singlet type and one of the triplet type. The curves for lines belonging to similar series or arising from similar terms show a similarity.

Since results for the probability of excitation by electrical methods are very few, it is hardly possible to compare the results by the two methods; but it may be noticed that Sponer's conclusions for the 4·9 volt state of mercury are in fair agreement with the optical results, but that in the case of the 6·67 volt state there is practically no agreement. The optical method has failed to confirm the maximum found by Brattain close to the excitation potential.

In a determination of the efficiency of ionisation, as defined previously, the commonest method is one in which the positive ions formed by collisions, are drawn out of the gas and then recorded. A number of variations of the method have been used in which there are modifications to lessen the distortion of the beam and other sources of error, caused by the potential applied to the ions. One such is to use a magnetic field parallel to the beam; this has the effect of keeping any electrons scattered from the beam moving in spirals round it, and also of preventing the escape of secondary electrons from the plate which photoelectric action of radiation from the beam or collisions of metastable atoms with the plate might tend to release. The magnetic field has little effect on the heavier positive ions which can thus be drawn to the plate by a small applied potential.

Much work has been done by modifications of this method on a number of gases. For mercury vapour results have been obtained by Compton and Van Voorhis (37), Jones (38), Bleakney (39), Smith (40), and Hughes and Klein (41), for the efficiency of ionisation. The results are in general agreement, namely a steady rise from zero at the lowest ionisation potential to a broad maximum at between 80 and 120 volts, and then a slow uniform fall as the energy is increased.

In order to obtain measurements of the probability of ionisation in a particular manner, for example, single ionisation or double ionisation, it is necessary to make an analysis of the charge on the ions as they are drawn out of the collision region. This can be done either by a magnetic field or by an electrostatic field or by a combination of both. Bleakney has used a combination of both in his work on mercury vapour, and, by plotting the current to the analyser collector against the electrostatic field strength, has been able to obtain a curve showing each type of ionisation as a sharp peak. By measuring the area below each peak, and repeating the observations for a number of velocities, he was able to obtain curves representing the percentage of the different types of ionisation present at the different velocities. Finally by multiplying the total ionisation or efficiency of ionisation by each percentage in turn and dividing by the number of charges on the ion, he was able to obtain the probabilities of the different types of ionisation. In all this work the gas pressure was kept so low that the probability of an atom suffering more than one collision with an electron was very small. Each case of multiple ionisation was thus caused by a single electron knocking two or more electrons out of the atom in one collision.

In a study of the probability of single ionisation of the atom, no evidence can be obtained by the above method as to the manner in which the atom has been ionised; whether the ionisation is due to the removal of the least securely bound electron or whether an electron belonging to an inner shell has been removed. Naturally at low energies, the ionisation will be due mostly to the removal of the valency electron, since the impinging electron will not have sufficient energy to remove an inner electron for which the ionisation potentials are known to be greater than for the valency electron. In addition to the removal of an inner electron instead of the outer valency electron, it might also be possible for the impacting electron to excite the atom as well as ionise it, if it had sufficient energy. This could occur for all kinds of ionisation provided the total energy of the colliding electron was sufficiently large. No evidence of this effect could be found by the method of positive ion analysis.

Now, after ionisation has taken place, it should be possible to examine what has happened to the impinging electrons. However, after ionisation, there will also be present the ejected electrons, and the two types of electrons are obviously experimentally indistinguishable. Nevertheless, analysis of the velocity distribution of the electrons after collision should lead to some information as to the probability of ionisation of the atom to particular degrees and in particular manners. Knowing the ionisation potential for the removal of a valency electron, i.e. 10·38 volts in mercury vapour, it should be possible to study these electrons which have lost this amount of energy. However the electrons may have handed over some of their energy to the ejected electrons so that it would be necessary to include in the measurements all electrons which had energies up to half the available energy, that is up to half the original energy of the electrons in the beam less the ionisation energy. This could be done by a suitably arranged retarding potential. Some work by Eldridge (25) and by Langmuir and Jones (42) and by Hughes and McMillen (43) has indicated that it is more probable that the available energy will be almost entirely retained by one of the ejected or impacting electrons than that it should be evenly divided.

Langmuir and Jones' work has been done by collecting the positive ions from a gas at a relatively high pressure so that the effects of multiple ionisation should be taken into account. It should thus be possible to obtain a fairly accurate estimate of the probability of single ionisation from a method in which half the available electrons were collected, as outlined above; the electron which is removed being the valency electrom. However if excitation of the atom takes place at the same time as ionisation, this will not be detected by this method provided the remaining energy is greater than the retarding potential applied to analyse the electrons. So far as the author has been able to discover few, if any, observations have been made by this method yet. Some measurements have been made by Eldridge but they are confined to a region close to the ionisation potential. Results obtained by the author by an attempt to apply this method will be given in the experimental section.

SECTION 3.

WAVE MECHANICS OF COLLISION PROCESSES.

A theoretical derivation of the probabilities of collision is an exceedingly difficult problem since there are so many effects which must be taken into consideration and methods of allowing for them are in general very difficult to derive. It has been seen that the classical kinetic theory predicts a value of the cross section or probability, constant with velocity. Experiment has shown that this is incorrect, so that a new theory is necessary. Such a theory is the wave mechanics put forward by Heisenberg, Dirac and others about 1925. Under this theory a beam of electrons is regarded as a beam of waves. Experiment confirmed this idea and from the work of G.P. Thomson on the diffraction of electrons by crystal surfaces, it was verified that the wave length λ of the electron wave is given by $\lambda = \frac{h}{mv}$ where h is Planck's constant and mv is the momentum of the electron, m and v being its mass and velocity respectively. From a relation discussed previously, the wave length of the electron can be given in terms of the accelerating potential V, in volts, applied to it, as -

$$\lambda = h\sqrt{\frac{150}{emV}}$$

which gives $\lambda = 12.25 \times 10^{-8} \times V^{-1/2}$ cms. (1).

For ordinary values of V, say 0 - 100 volts, the wave length is seen to be approximately of the same order of magnitude as the diameter of an atom: so that, comparing the analogy of light waves falling on particles of a diameter approximately equal to their wave length, for which a wave length theory is necessary to explain the resulting effects, we see that it is reasonable to expect that a wave theory would also be necessary in the case of the electron to give a correct result.

Before any theoretical results can be obtained, we must have a knowledge of the potential field of the atom and the variations of this when the atom is in its different states, normal, excited and ionised.

The various effects which can take place at a collision between an electron and an atom, and which must be allowed for in any complete theory, are the variations of the potential field, as discussed above, and the effect on this field of the colliding electron, i.e. polarisation. Secondly the effect of the exchange of electrons between the beam and the atoms must be allowed for. This is especially difficult since electrons are completely indistinguishable from each other. An ejected electron cannot be distinguished from the one which ejected it, and the electron which leaves an atom in an excited state may not be the one which excited it to that state. It is quite conceivable and in some cases necessary to comply with quantum theory rules, that an electron colliding with an atom and exciting it to the $n^{th.}$ state, should itself go into the $n^{th.}$ level of the atom, at the same time handing over its excess energy to the electron in the ground state, which then flies out of the atom and behaves as if it were the original electron. As mentioned in Section (1), exchange effects can also be present in elastic scattering.

On account of the various complicating factors it is easily seen that an exact solution of the problem is seldom possible. For the most part the only solutions possible are approximate ones, the degree of approximation varying with the allowances that are made for the different complications. A discussion of the wave mechanics treat::ment of the problem will now be given, on the lines of that given by Mott and Massey (44).

In wave mechanics the amplitude and phase of the motion of a wave are represented by a function $\psi(x,y,z,t)$ usually complex, of position and time, called the wave function. In all the following discussion the time factor, which is usually of the type e^{-iat} where a is a constant, will be omitted. Also throughout the work it will be assumed that the velocity of the electrons under consid::eration is small compared to the velocity of light, so that no relativity correction is necessary. This will certainly be the case for the velocities in all the actual experiments considered, namely for velocities up to about 1000 volts. The wave function ψ is such that the square of its amplitude $|\psi|^2$ at any point at any time gives the probability of an electron being at that point at that time.

Suppose the electrons in a beam are accelerated from rest to a velocity v in cms. per sec., by the application of an electrostatic potential Φ, then the energy E of the electrons in the beam is given by the sum of their potential and kinetic energies, V and E_0 respectively. Here the kinetic energy is given by $E_0 = \frac{1}{2}mv^2$, and the potential energy by $V = -e\Phi$, where e is the charge on the electron.

Thus $$E = \tfrac{1}{2}mv^2 + V \qquad (2).$$

Therefore $$v = \sqrt{\frac{2}{m}(E - V)} \qquad (3).$$

But the wave length has been shown to be $\lambda = \frac{h}{mv}$

so that $$\lambda = h\left[2m(E - V)\right]^{-\frac{1}{2}} \qquad (4).$$

The wave equation for any monochromatic train of waves in a homogeneous medium is of the usual form

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \qquad (5).$$

With the above value of λ this becomes

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad (6).$$

which is Schrödinger's wave equation.

To solve any collision problem it is then necessary to solve this equation. In the application of this wave equation there are certain difficulties. The first is that, since, under the uncertainty principle, the product of the uncertainties in the momentum and position of a particle, at a given instant, is constant, it is not possible to determine the potential V exactly, since V is the change in the Kinetic energy of the particle which depends on its velocity. In practice, what is done, is that a likely value is assumed for V, and it is taken as satisfactory if, on substitution in the wave equation, it gives results in agreement with experiment. A further difficulty is that the wave equation has virtually been deduced from experimental observations in the case of slowly varying fields. To apply this equation to atomic fields which may be very large and may vary very rapidly, may not be justified. Agreement with experiment is again the only test of accuracy.

In considering the scattering of a beam of electrons by a field of force such as the potential field of an atom, we must find a solution of the wave equation which, at large distances from the scattering centre, represents the incident and the scattered waves. We will deal with elastic scattering only. Such a solution is $\psi = \psi_0 + \psi_1$ where ψ_0 is the incident wave and ψ_1 the scattered wave. The wave equation can be written as

$$(\nabla^2 + k^2)\psi = \frac{8\pi^2 m}{h^2} . V . \psi . \qquad (7)$$

where $k^2 = \frac{8\pi^2 mE}{h^2}$, and $k = \frac{2\pi mv}{h} = \frac{2\pi}{\lambda}$

In general it is convenient to choose the original wave as a plane monochromatic wave moving along the z axis. Its form is then given by $\psi_0 = e^{ikz}$.

The amplitude of the wave scattered through an angle θ at a distance r can then be represented by $r^{-1}f(\theta)e^{ikr}$. In order to find the scattered intensity, that is the number of electrons scattered into a given solid angle per unit time through an angle θ, we must find $f(\theta)$. We know that the probability of scattering is given by the square of the modulus of the scattered wave, which then is $|f(\theta)|^2$ so that the scattered intensity is given by

$$I(\theta) = |f(\theta)|^2 \qquad (8).$$

The solution of the wave equation that we require is then of the form

$$\psi \sim e^{ikz} + r^{-1} f(\theta) e^{ikr} \qquad (9).$$

If we consider the equation $(\nabla^2 + k^2)\psi = 0$ we see that e^{ikz} is a solution of it. Also a solution is -

$$\psi \sim P_n(\cos\theta) f_n(r) \tag{10}$$

where P_n is the nth. Legendre coefficient, and f_n is a solution of the differential equation -

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) + \left(k^2 - \frac{n(n+1)}{r^2}\right)f = 0. \tag{11}$$

Then if $f_n(r)$ is the particular solution of this equation which is bounded at the origin, then it can be shown that e^{ikz} can be expanded as

$$e^{ikz} = \sum_{n=0}^{\infty}(2n+1)\, i^n P_n(\cos\theta) f_n(r). \tag{12}$$

By a similar method it can be shown that the wave function representing the incident and scattered waves is -

$$\psi = \sum_{n=0}^{\infty}(2n+1)\, i^n e^{i\delta_n} L_n(r) P_n(\cos\theta), \tag{13}$$

where L_n is the solution which is finite at the origin of -

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right) + \left[k^2 - \frac{8\pi^2 m}{h^2}V - \frac{n(n+1)}{r^2}\right]L = 0 \tag{14}$$

and where the δ_n are constants depending on k and on V, which can in general only be determined by numerical integration. In a later section (4) an approximate method of determining these phase constants will be discussed and some results obtained by applying the method to krypton will be presented.

The solution of the above equation (14) which is finite at the origin can be shown to have the asymptotic form -

$$L_n \sim (kr)^{-1}\sin(kr-\tfrac{1}{2}n\pi+\delta_n) \qquad (15)$$

which can be written as

$$L_n \sim (2kri)^{-1}\left[e^{i(kr-\frac{1}{2}n\pi+\delta_n)} - e^{-i(kr-\frac{1}{2}n\pi+\delta_n)}\right] \qquad (16).$$

The corresponding form of $f_n(r)$ is similarly -

$$f_n \sim (kr)^{-1}\sin(kr-\tfrac{1}{2}n\pi)$$

which is -

$$f_n \sim (2kri)^{-1}\left[e^{i(kr-\frac{1}{2}n\pi)} - e^{-i(kr-\frac{1}{2}n\pi)}\right] \qquad (17).$$

By substracting equation (12) from equation (13) and dividing by $r^{-1}e^{ikr}$, and using (16) and (17) the required asymptotic form of the amplitude of the scattered wave is obtained as -

$$f(\theta) = \frac{1}{2ik}\sum_{n=0}^{\infty}(2n+1)\left(e^{2i\delta_n}-1\right)P_n(\cos\theta) \qquad (18).$$

Then the intensity scattered through an angle θ is given by the square of the modulus of this function. But since $f(\theta)$ is complex, the square of the modulus is equal to the sum of the squares of its real and imaginary parts, so that

$$I(\theta) = \frac{1}{4k^2}\left[\sum_{n=0}^{\infty}(2n+1)(\cos 2\delta_n - 1)\,P_n(\cos\theta)\right]^2$$

$$+\frac{1}{4k^2}\left[\sum_{n=0}^{\infty}(2n+1)\sin 2\delta_n\cdot P_n(\cos\theta)\right]^2 \qquad (19)$$

Both these formulae (18) and (19) are exact, but to solve them requires a knowledge of the δ_n , exact values for which it is in general very difficult to obtain.

Since we now have the intensity scattered elastically through an angle θ into unit solid angle from a beam of unit current intensity, it is possible to obtain the total elastic cross section Q by integration of this scattered intensity through all values of θ from 0 to π and all azimuths. Doing this we obtain -

$$Q = 2\pi\int_0^{\pi}\left|f(\theta)\right|^2 \sin\theta\,d\theta \qquad (20)$$

Knowing that $\int_0^{\pi} P_n^2(\cos\theta)\sin\theta\,d\theta = -\frac{2}{2n+1}$

we can at once reduce this to

$$Q = \frac{4\pi}{k^2}\sum_{n=0}^{\infty}(2n+1)\sin^2\delta_n \qquad (21)$$

The method of this development is due to Faxen and Holtsmark (45).

For the case of a Coulomb field, that is where the potential V is proportional to r^{-1}, $f(\theta)$ can be determined exactly and it is found that it leads to a value of $I(\theta)$ -

$$I(\Theta) = \left[\frac{ZZ'e^2}{2mv^2}\right]^2 \operatorname{cosec}^4\frac{\theta}{2} \qquad (22)$$

which is the Rutherford scattering formula for particles by nuclei. For electrons and atoms this formula does not agree with experiment except at high velocities, the explanation being that the field in an atom falls off much more rapidly than 1/r.

The scattered intensity can be calculated somewhat more easily from an approximate formula due to Born (46), outlined as follows -

Starting with the same asymptotic form of the solution -

$$\psi \sim e^{ikz} + r^{-1}e^{ikr}f(\theta). \qquad (23)$$

he applies the well known theorem that the most general solution of $(\nabla^2+k^2)\psi = F(xyz)$ (24)

is $$\psi = \psi_0 - \frac{1}{4\pi}\iiint\frac{\exp(ik|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|}F(x'y'z')\,dx'dy'dz' \qquad (25)$$

where ψ_0 is the general solution of

$$(\nabla^2+k^2)\psi = 0 \qquad (26).$$

Thus writing the wave equation as

$$(\nabla^2+k^2)\psi = \frac{8\pi^2 m}{h^2}V.\psi. \qquad (27)$$

and making the solution of this equation have the asymptotic form of the equation (23), we see that the scattered wave is represented by

$$\psi_1 = -\frac{1}{4\pi}\iiint \frac{\exp(ik|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|}\cdot\frac{8\pi^2 m}{h^2}\cdot V(r')\,\psi(r')\,dx'dy'dz'$$

$$= -\frac{2\pi m}{h^2}\iiint \frac{\exp(ik|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|} V.\psi.dx'dy'dz'.$$

(28).

From this latter equation it can be seen that the amplitude of the wave at a distance R scattered by the volume element dx dy dz is $-\frac{I}{R}\frac{2\pi m}{h^2}$ V dx dy dz, multiplied by the amplitude of the original wave, that is, it is proportional to the potential field V.

Born's approximation is obtained from the equation (28) by making the assumption that the original wave is not much diffracted by the scattering centre, that is, he replaced ψ in the above equation (28) by the original wave, $e^{ikz'}$.

Then for large r the following expression can be obtained for $f(\theta)$, -

$$f(\theta) = -\frac{2\pi m}{h^2}\iiint \exp(ik|z-r|)\,V(r)\,dx\,dy\,dz.$$

(29).

By transforming to polar coordinates and integrating the θ and ϕ variables, we obtain -

$$f(\theta) = -\frac{8\pi^2 m}{h^2}\int_0^\infty \frac{\sin \mu r}{\mu r}\cdot V(r)\cdot r^2 dr$$

(30)

where $\mu = \frac{4\pi \sin \theta/2}{\lambda}$, which is Born's approximation.

Using the atomic fields worked out by methods due to Thomas (47), Fermi (48), and Hartree (49) it is possible to obtain theoretical scattering curves from the above equation which can be compared with the experimental curves. These fields are only approximate and are very laborious to calculate; the fields for hydrogen and helium being the most easily and accurately calculated. Most of the work therefore on the comparison of theory and experiment has been done on the latter atoms.

Born's formula gives a scattering curve which falls off montonically with increasing angle for all velocities. The agreement between theory and experiment is quite good for velocities above about 400 volts. The formula is found to be accurate over a larger angular range for light atoms such as neon, than for heavier atoms such as krypton or xenon. The angular range of agreement decreases as the energy is decreased. In no case does the Born formula predict the diffraction effects which have been experimentally observed by many workers. When the exact formula of Faxén and Holtsmark is used the diffraction effects appear in the theoretical curves and the agreement with experiment is good down to much lower velocities. At still lower velocities where the agreement is not so good, more accurate results can be obtained by using a more accurate potential field, in which allowances are made for the polarisation of the atomic field by the electron waves, and for electron exchange. For heavy atoms, it has been shown by Allis and Morse (50) that exchange effects are not important so that better agreement would be expected there, which is what is found. The same authors find that exchange effects are not important for electron energies greater than about 30 volts for elastic scattering, and that even below this value exchange does not effect much the total cross section curves but only the angular scattering curves.

In deriving the expression

$$Q = 2\pi \int_0^\pi \left| f(\theta) \right|^2 \sin\theta \, d\theta \qquad (31)$$

for the cross section, we chose $f(\theta)$ so that it was finite at $\theta = 0$. Theoretically it should be impossible to extend the integration right to $\theta = 0$, since then the original unscattered beam would be included. But since $f(\theta)$ is finite at $\theta = 0$, Q will vary little with θ as θ is decreased from a finite small value to 0. It is in this definition of $f(\theta)$ as finite at $\theta = 0$ that the main difference lies between the classical theory and the wave mechanics theory. Under the classical theory, $f(\theta)$ becomes infinite at $\theta = 0$, so that the differential cross section $I(\theta)$ will be infinite at $\theta = 0$, while under the wave mechanics theory it remains finite, as seen above. The differential cross section per unit angle is $2\pi I(\theta)\sin\theta$ which is infinite from the classical theory and zero from the wave mechanics theory at $\theta = 0$. Here experiments decide between the theories. The experimental scattering curves per unit angle at small angles are found to bend over so as to pass through the origin.

Again the classical theory leads to a value of the total cross section which is infinite, since under this theory no matter how far from an atom an electron passes, it is affected by the atom and should therefore be included in the cross section. The finite cross sections actually observed would then be due solely to an insufficiency of resolving power in the apparatus. Under the wave mechanics, the cross section is finite provided the field of the atom falls off sufficiently rapidly with distance, which is the case for all atoms. The finite observed values are then in agreement with theory. This difference really depends on the fact that $\sum_{r=1}^{\infty} 1/r^n$ is infinite for $n \leqslant 1$ (classical theory) and finite for $n > 1$ (wave mechanics), since the field is of the general form $\frac{1}{r^n}$.

THEORETICAL EXPLANATION OF THE RAMSAUER EFFECT.

On the classical theory the Ramsauer effect of a decrease in the cross section at low energies, for certain rare gases, is quite unexplainable. Wave mechanics, however, affords a simple explanation. For the rare gases, the outer shell has its full number of electrons so that it is reasonable to suppose that field will be symmetrical and will fall off more rapidly with the distance from the atom than for an atom with uncompleted external shell. Thus the rare gas atom will appear to have a smaller size than the other atoms. Low velocity electrons, that is electrons of long wave length, will then pass over the atom unaffected as in the analogous case of a very small obstacle in the path of light of long wave length. Alternatively, it may be said that the electron wave at the atom meets a region where the potential field increases rapidly, so that the refractive index changes rapidly, consequently the wave length decreases rapidly. Thus it may be that a whole number of waves can be fitted into the region occupied by the scattering field. The electron wave is thus unaffected by the field and the small cross section results.

A mathematical explanation which depends on the same assumptions can be obtained as follows -

It has been seen that the cross section Q can be written as

$$Q = \frac{4\pi}{k^2}\sum_{n=0}^{\infty}(2n+1)\sin^2\delta_n \tag{32}$$

This may be put as

$$Q = \sum_{n=0}^{\infty} Q_n \tag{33}$$

where $$Q_n = \frac{4\pi}{k^2}(2n+1)\sin^2\delta_n \tag{34}$$

Q_n is then called the partial cross section of order n. It can be shown that, for low velocity electrons, and light atoms, the most important partial cross section is the one of zero order. Q is then determined for the most part by Q_o. Thus to explain the Ramsauer effect, the conditions must be found for which Q_o becomes small as the wave length increases to infinity. This is done by expanding the original wave e^{ikz} in a series of spherical harmonics, as has already been shown, in equation (12) of this section. When the wave length tends to infinity, k tends to zero. Thus the first term only of this expansion need be taken. This term is (sinkr)/kr. Since the scattered wave is spherically symmetrical and small outside the atom it may be taken as $c_o r^{-1} e^{ikr}$ at a distance r. Thus outside the atom but for small r, the complete wave function for incident and scattered waves is -

$$\psi \sim \frac{\sin kr}{kr} + c_o r^{-1} e^{ikr}$$

Inside the atom the wave function is taken as $F_0(r)$, where F_0 is the solution, finite at the origin of the differential equation -

$$\frac{d^2}{dr^2}\left(rF_n\right) + \left[k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{n(n+1)}{r^2}\right] rF_n = 0 \qquad (36).$$

The quantity F_0'/F_0 can thus be determined where the dash denotes differentiation with respect to r. The method then is to fit F_0'/F_0 to the same quantity derived from equation (35) above, at a point where r = R consid:ering R as the value of r at the outer boundary of the atom at which point F_0' is zero. k, which is inversely proportional to the wave length, is then allowed to tend to zero. The deduction, which is on the lines of one given by Mott and Massey (51) with however a slight variation, proceeds as follows -

From equation (35) ψ' has the form -

$$\psi' \sim \frac{rk\cos kr + c_0 r k^2 i e^{ikr} - \sin kr - c_0 k e^{ikr}}{kr^2} \qquad (37).$$

Therefore

$$\frac{\psi'}{\psi} = \frac{\cos kr + c_0 k i e^{ikr} - \frac{\sin kr}{kr} - \frac{c_0}{r} e^{ikr}}{r.\frac{\sin kr}{kr} + c_0 e^{ikr}}$$

$$= \left[\frac{F_0'}{F_0}\right]_{r=R}. \qquad (38).$$

If we now let k tend to zero and put r = R this becomes -

$$\lim_{k\to 0} \frac{\psi'}{\psi} = \frac{-\frac{c_0}{R}}{R+c_0} = \frac{F_0'}{F_0} \qquad (39).$$

Solving for c_0, we obtain -

$$\lim_{k\to 0} c_0 = \frac{-R^2F_0'}{F_0+RF_0'} \qquad (40).$$

Thus we see that if F_0' becomes zero at r = R, then c_0 is also zero; that is the scattered wave vanishes and so the cross section vanishes. Thus the decrease of cross section with velocity is explained, i.e. the Ramsauer effect.

The theory can also be used to explain the variations in the cross section with velocity and also the similarity in cross section for atoms belonging to the same column in the periodic table.

From the formula for the partial cross sections, we obtain that the maximum value of Q_n is -

$$Q_n = (4\pi/k)(2n+1) \qquad (41).$$

for values of $\delta_n = (2s+1)\pi/2$.

Now it is known that the phases δ_n decrease monotonically as n is increased. The value of Q depends therefore on the rate of convergence of the series of partial cross sections. For low velocities the convergence is known to be quite rapid, so that the partial cross sections for which δ_n is nearest to $(2s + 1)\pi/2$ will determine the total cross section Q. From the above maximum value of Q_n it is seen, since k is proportional to the velocity, that Q_n will be larger the larger n becomes and the smaller the velocity becomes. But the rate of convergence of the series of partial cross sections which determines the number of terms of the series which it is necessary to take to get a reasonably correct result, depends on the extent of spread of the atomic field. Now the fields for the alkali metals are known to extend the farthest so that we would expect these atoms to have the largest cross sections, and such is actually observed. Slater (52) has developed some empirical rules for the effective nuclear charges of atoms. From these we can find the distance r_o from the centre of the atom at which the radial charge density due to the outer shell electrons is a maximum. This has been defined as the diameter of the atom for the purposes of this discussion, and has been used as a measure of the distance to which the field of the atom extends. We see that for potassium this distance is $r_o = 6{\cdot}1$ atomic units, while for the rare gases it is of the order of one atomic unit; these latter being the least values recorded; so that the rare gases would be expected to have the smallest cross section values. This also verifies the explanation of the Ramsauer effect.

The explanation of the similarity of the cross section curves for atoms in the same columns of the periodic table is not so simple. For similar elements, such as sodium and potassium, the number of the valency electrons is one, so that it would be reasonable to expect that the fields of these atoms would be similar and so their cross sections would be similar. Allis and Morse (53) demonstrated that the periodicity of the cross sections followed that of the periodic table, by using a simplified atomic field. They assumed that the field was given by the following -

$$\left.\begin{aligned} V &= 2Z(1/r - 1/r_o) & r &\leqslant r_o \\ &= 0 & r &\geqslant r_o \end{aligned}\right\} \qquad (42)$$

where r_o is defined as above, and Z is a constant depending on the atom used. Z can be calculated from Slater's rules. In using this assumption they defined two further quantities β and x, such that -

$$\beta^2 = (Zr_o)/2 \quad \text{and} \quad x = kr_o \qquad (43).$$

r_o is a function of the field of the atom, and k is proportional to the velocity. The method of demonstrating the periodicity of the cross sections was to plot the partial cross sections for all elements as functions of β, for a number of different values of x. The functions were found to have an approximate period of unity in β for all x. By suitably adjusting the constant Z, this period of one in β can be found to correspond to a whole period in the periodic table; that is by increasing β by unity, we pass from one element in the periodic table to the next in the same column, i.e. sodium to potassium.

With the above potential field, and values of β and r_0 determined by Slater's rules, theoretical cross section curves have been calculated by Allis and Morse for quite a number of atoms. The agreement is in general very good. The main differences between theory and experiment lie at low voltages, and are explained by the neglect in Allis and Morse's method of the field of the atom beyond r_0. A more accurate result is obtained by using some such potential field as that calculated by Hartree's or Fermi's methods, and then evaluating, by numerical integration, the phases δ_n, which appear in the exact formula given previously. This method gives very good agreement for the total cross section in those cases for which the potential field is known. For most atoms comparison has usually been confined to comparison of the differential cross sections or angular scattering curves, since these are much more sensitive to the accuracy of the method of calculation. For mercury Henneberg (54) and Massey and Mohr (55) have carried out calculations of the phases δ_n using a Thomas-Fermi field.

The agreement with Arnot's experimental curves (56) is very good. In general the agreement is better for heavy atoms, such as mercury. For light atoms, such as helium and hydrogen, the method breaks down. It is then necessary to include the effects of electron exchange. In certain cases it is also necessary to include the effects of the polarisation of the elastically scattered wave by the inelastically scattered wave. Allowances for each of these latter effects tends towards a greater agreement between theory and experiment, but as they are relatively unimportant for heavy atoms such as mercury, they will not be discussed here.

THEORY OF INELASTIC SCATTERING.

A theoretical discussion of the inelastic scattering of electrons by atoms is much more difficult than for elastic scattering, since, in the elastic case, the interaction between the electron and the atom is negligible except at particular velocities and in particular cases. For inelastic scattering, however, the interaction cannot be neglected. Thus in most cases only approximate solutions of the problem are possible. Using the Born Approximation, which is valid only for high velocities, quite good agreement can be found with experiment in the region of validity.

In considering an atom which has been excited from a state m to a state n, we use a scattered intensity $I_{m,n}(\theta)$. Usually we change the variable from θ to a quantity K such that $K^2 = k_{m,n}^2 + k^2 - 2kk_{m,n}\cos\theta$ where $k = (2\pi mv)/h$ and $k_{m,n} = (2\pi mv_{m,n})/h$, v and v_{mn} being the initial and final velocities of the colliding electron. Instead of using limits of integration 0 and π for θ, we use $K_{min} = k - k_{mn}$ and $K_{max} = k + k_{mn}$ for K. The effective cross section for excitation of the atom from state m to state n is then given by -

$$Q_{mn} = \int_{K_{min}}^{K_{max}} I_{mn}(K)\,dK. \qquad (44).$$

In using $I_{mn}(K)$ the greatest difficulty is in determining the wave functions of the atom in the two excited states. The most usual method of solving the problem is to use a matrix development first proposed by Dirac.

The method can be applied to the calculation of the probabilities of excitation of discrete levels and also to the probability of ionisation. The differential cross section for all inelastic collisions can then be found by summation. Thus if the initial state in each case is the ground state, the differential cross section is $\sum_{n=1}^{n} I_{on}(K)$. This formula is only applicable to the case of hydrogen. For a complex atom, such as mercury, the inelastic differential cross section is given by a complicated double summation of the type

$$\sum_{nl} \sum_{n'l'} I_{nl,n'l'}(K). \tag{45}$$

where nl and n'l' refer to the different shells of the atom.

A considerable amount of work has been done on helium for which the wave functions can be determined with a fair degree of accuracy. The agreement with experiment is usually quite good for high velocity electrons. Much of the experimental work done on the probabilities of excitation of discrete levels has been confined to the study of electrons which have been deflected through small or zero angles. A rigid comparison between such results and cross section curves in which all angles are included is thus not possible.

In the case of ionisation, after the collision, two electrons are present, the impacting electron and the ejected electron. The remaining energy of the impinging electron after ionising the atom, is available to these two electrons in any proportions. It is obvious that these two electrons are quite indistinguishable. However it is a common practice to label the slower electron, the ejected electron, and the faster, the impacting electron. From theoretical considerations Massey and Mohr (57) have shown that the velocity distribution curves of the ejected electrons show a maximum at a low velocity; that is, it is highly probable that the available energy is divided between the two electrons after ionisation so that one electron gets most of the energy and the other very little. This work has been confirmed experimentally by Tate and Palmer (58) working on mercury vapour.

When we come to consider the case of slow electrons for which Born's approximation is not valid, we find that there are many more effects which must be considered.

Born's theory fails to show the diffraction maxima and minima in the inelastic angular scattering curves at low velocities which have been observed by Mohr and Nicoll (59) and others. Born's theory also predicts too high a value of the inelastic scattering at small angles and also of the inelastic cross section generally. These discrepancies show that the distortion of the incident and scattered waves by the fields of the atom in its normal and excited states must be allowed for, These latter are the effects which Born's approximation neglects, as negligible at high velocities.

In a previous section it has been seen that the experimentally determined probabilities for excitation of singlet and triplet levels are quite different. The singlet levels give curves which rise to a broad maximum some 20 volts above the excitation potential and then fall slowly, while the triplet levels give curves which rise to a sharp maximum close to the excitation potential and then fall rapidly. Intercombination lines give similar curves to triplets in general, if the higher state is triplet. Born's approximation demonstrates that the probability of such an intercombination transition is very small at high velocities, since the wave functions for the two states are antisymmetrical. Thus in integrating their product, along with other symmetrical functions, to obtain the probability , the integral vanishes. This only holds for high velocities: for low velocities the effect of electron exchange has to be taken into account, and so the probability of such a transition can become quite large.

To explain the difference between the singlet and triplet curves, the quantum theory must be used. For a singlet state of the atom, the spin quantum number is zero, while for triplets it is equal to unity. For the valency electrons in an atom the spin vectors are always equal to $\frac{1}{2}$. If they are opposed in direction, as they are for singlets, their resultant is zero. But if, as for triplets, their directions are the same, then their resultant is unity. Thus to pass from a singlet state to a triplet or vice versa, requires that the spin vectors shall be changed relative to each other. In cases where the coupling between the spin and orbital motions of the electrons in the atom is small, which is the case for light atoms such as helium, this transition cannot occur spontaneously. The only method by which it can occur, is when electron exchange takes place; the impinging electron goes into the triplet level and the valency electron in the singlet level flies out of the atom taking the excess energy of the impacting electron with it. Now it has been stated previously that the probability of electron exchange decreases very rapidly with increase in the velocity, so that the probability of such a transition will also fall off rapidly with increasing velocity. But for excitation of a singlet from a singlet, or a triplet from a triplet initial level, electron exchange is not necessary; so that we would expect the probabilities of such transitions to fall off more slowly with increasing velocity, as is actually observed experimentally.

In the case of heavy atoms however, such as mercury, the coupling between the spin and orbital motions becomes appreciable, so that spontaneous transitions between singlet and triplet levels can take place, and also these transitions can be excited by electron impact without electron exchange. Thus we would expect the probabilities of such transitions to persist to higher velocities in such cases. Penney (60) has derived theoretical curves for the excitation of the P states in mercury by using wave functions in which this interaction was allowed for. He finds that the probability of excitation of the 2^3P_1 state (4·86 volts) from the ground state has a small but finite value at large velocities, since his wave functions are now not antisymmetrical. The 2^1P_1 transition from the ground state is found to be by far the most probable at high voltages, and even down almost to its excitation

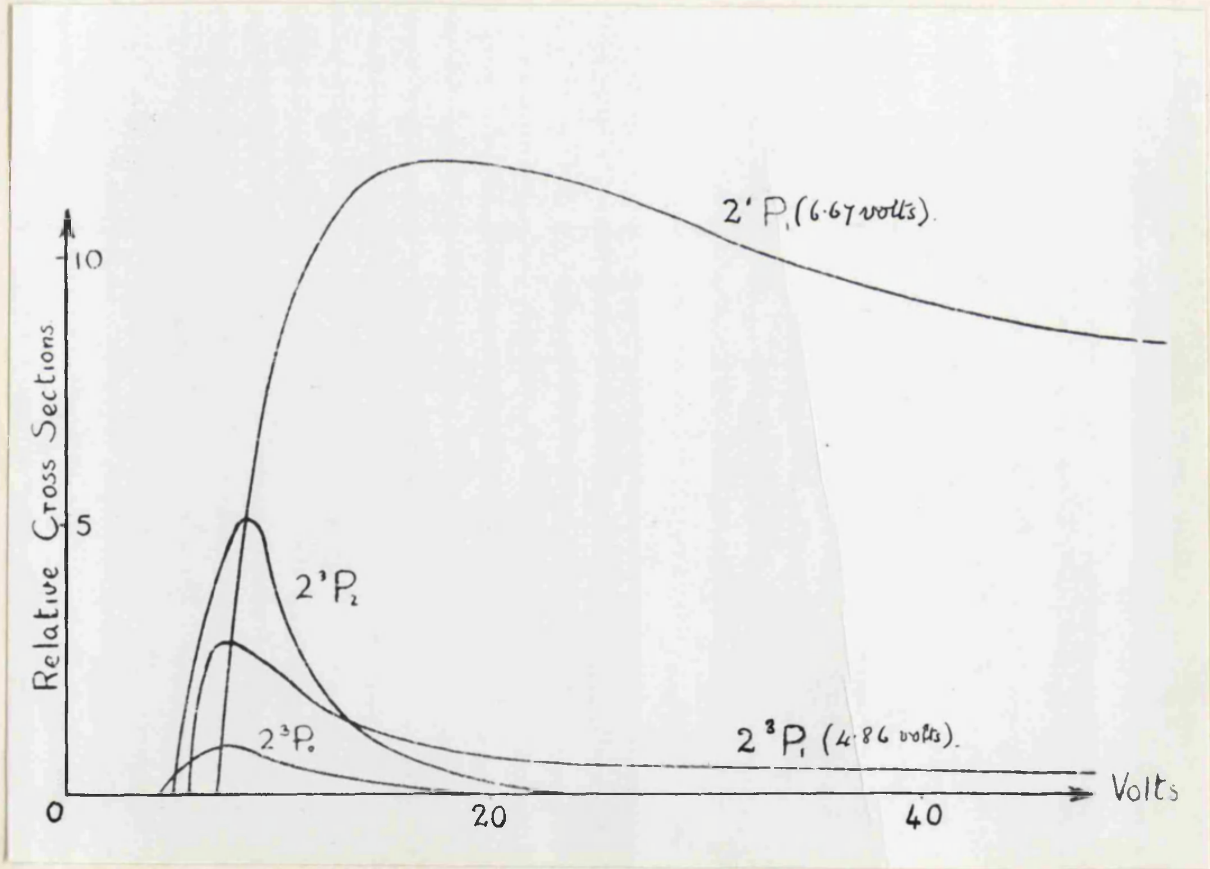

Relative Cross Sections
10
5
0
20
40
Volts
2' P₁ (6·67 volts).
2'P₂
2³P₀
2³P₁ (4·86 volts).

Fig. 6.

potential. Penney's curves are shown in Fig. (6). The experimental results for the excitation functions for the 4·86 and 6·67 volt states will be compared with these curves, in the experimental section.

In the cases of certain simple atomic fields, such as that of hydrogen or helium, theoretical excitation cross section curves can be obtained which are in very good agreement with experiment especially for triplet S levels. Massey and Mohr (57) have obtained such curves for helium, in which the variations of the differential cross section with velocity and angle is shown for different levels in the atom. An interesting feature is that, at zero angle, the differential cross section increases with the velocity, for nearly all transitions. This result has been confirmed experimentally by Whiddington and Taylor (33), and also by Van Atta (61). The theoretical method is to obtain two functions f and g; f is virtually the result obtained by the Born approximation, and g is the correction due to electron exchange. A combination of these two functions gives the cross section in the form of two terms, one being the directly scattered wave and the other the electron exchange wave. Each is in the form of the integral of the interaction energy over the initial and final wave functions of the atom. From the resulting equations it can easily be shown that the probability of excitation of triplet levels decreases as v^{-4} for S states, as v^{-6} for P.states and as v^{-8} for D states; while the probabilities for singlet S, P, and D states decrease as v^{-2}, $v^{-2}\log\alpha v$ and v^{-2} respectively; v being the velocity of the incident electrons and α a constant.

For the inelastic angular scattering in mercury vapour of electrons which have excited the most probable transition, the 2^1P_1 level, Mohr and Nicoll have discovered a number of maxima and minima. The positions of these maxima and minima agree for moderate and large velocities with similar ones obtained for elastically scattered electrons. A theoretical explanation of this has been derived by Mott and Massey (62). Neglecting exchange, they derive an expression for the differential cross section for excitation to the $n^{th.}$ state, $I_n(\theta)$, in the form -

$$I_n(\Theta) = \frac{k_n}{k}\cdot\frac{4\pi^2 m^2}{h^4}\left|\int V_{on}\exp\left\{i\left(kr'\cos\Theta' - k_n r'\cos\Theta\right)\right\}d\tau' + \sum_{S=0}^{\infty} P_S(\cos\theta)\int V_{on}\, H_S(r'\theta'\phi')\,d\tau'\right|^2 \qquad (46)$$

where $(k_n h)/(2\pi m)$ is the electron velocity after exciting the $n^{th.}$ state, and $(kh)/(2\pi m)$ is its original velocity. V_{on} is an element of a matrix and represents the potential field of the atom in its $n^{th.}$ excited state. H_S is a complicated function of the polar coordinates, r', θ', ϕ'. . $d\tau'$ is the element of volume. In the above expression the first term under the modulus is the Born expression, which is approximately zero for all angles greater than about 30°. Thus for larger angles the scattering depends almost entirely on the series part which will exhibit maxima and minima on account of the Legendre coefficients P_s. For large velocities, k_n and k will be approximately equal, and the fields V_{oo} and V_{on} of the normal and excited atom can be taken as approximately equal so that the elastic scattering and the inelastic scattering due to the 2^1P_1 transition will also agree. As mentioned above, this is the experimental result. For low velocities, however, the two sets of results diverge, owing to the non equality of k and k_n, and V_{oo} and V_{on}.

Following on the results of the above theory, Massey and Mohr (57) and Nicoll and Mohr (63) have developed a suggestion to explain qualitatively the fact that the elastic scattering predicted by the Born theory falls off less rapidly at small angles than does the experimental, and also to explain the similarity between elastic and and inelastic curves at moderate and high velocities. Their assumption is that an electron can make a double collision with the same atom. They suggest that this can occur in different ways. Firstly the electron may excite the atom without much change in direction; it then passes on through the field of the atom and is possibly slightly deflected by the field in so doing; finally, while it is still in the field, the atom returns to its normal state giving the energy of excitation back to the electron, again possibly with little deviation. The result is that the electron leaves with practically its original velocity but with a distribution in direction corresponding to inelastic scattering; the total deflection of the electron being quite small. Thus it will be seen that the number of electrons observed to be scattered elastically at small angles will be greater than that predicted by Born's theory, which is the experimental result obtained by Hughes and McMillen (64). When such a superelastic collision occurs with frequency, the elastic scattering will increase and the inelastic scattering will decrease. Actually for ionisation and elastic impacts in helium Massey and Mohr have found that too large and too small values respectively are predicted by Born's theory. Also it should be noticed that the total cross section for all types of collisions will be unaltered, since in obtaining such a cross section, both elastically and inelastically scattered electrons are added together and no account is taken of the angle through which they are scattered or of the number in each group.

Secondly the electron may be first diffracted elastically by the atom and then, later, excite or ionise it, possibly without further deflection. Or conversely, the inelastic impact without deflection may come before the elastic impact with deflection. Thus the inelastic scattering so obtained will resemble the elastic scattering of electrons of the original energy, provided that the original energy of the electrons is large in comparison with the energy lost in the inelastic impact.

For lower energies, comparable with the energies lost in the inelastic impacts, it is probable that such double collisions are not so likely, so that agreement between elastic and inelastic curves cannot be expected.

Also it has been shown from theory that the differences in the fields of the atom in its normal and excited states have more effect at these velocities. It has also been shown that exchange effects become prominent at low velocities for light atoms, so that they must also be considered.

SECTION 4.

APPROXIMATE METHODS OF CALCULATING PHASES AND THEORETICAL SCATTERING CURVES.

The results given in this section have already been published in a joint paper by the author and Dr. F.L. Arnot in the Proceedings of the Royal Society of London (65).

In a previous section an expression for the intensity of electrons elastically scattered through an angle θ, by a spherically symmetrical field was derived to be -

$$I(\theta) = \frac{1}{4k^2}\left[\sum_{n=0}^{\infty}(2n+1)(\cos 2\delta_n - 1)P_n\right]^2 + \frac{1}{4k^2}\left[\sum_{n=0}^{\infty}(2n+1)\sin 2\delta_n \cdot P_n\right]^2 \tag{1}$$

In this expression P_n is the n^th.^ Legendre coefficient and k is given by $k = 2\pi/\lambda = 2\pi mv/h = (2\pi/h)(eVm/150)^{\frac{1}{2}}$, where V is the velocity of the electrons in volts. The following differential equation derived from the general wave equation -

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right) + \left[k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{n(n+1)}{r^2}\right]L = 0 \tag{2}$$

was found to have a solution zero at the origin of the form

$$L_n \sim \frac{1}{r}\sin\left(kr - \tfrac{1}{2}n\pi + \delta_n\right) \tag{3}$$

where as before V(r) is the potential field of the atom, and the δ_n are phase constants, previously defined.

If we substitute $L_n(r) = \frac{1}{r}\psi(r)$ in the above equation (2), we obtain -

$$\frac{d^2\psi}{dr^2} + \left[k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{n(n+1)}{r^2}\right]\psi = 0 \tag{4}$$

or

$$\frac{d^2\psi}{dr^2} + a\psi = 0 \tag{5}$$

where $a = k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{n(n+1)}{r^2}$ (6).

This equation can then be shown to have the asymptotic solution $\psi \sim \frac{\psi}{\cancel{k}} \sin\left(kr - \frac{1}{2}n\pi + \delta_n\right)$ (7)

if for large r, V(r) tends to zero faster than 1/r, that is faster than the Coulomb field. This will be the case for most atoms so that the asymptotic form will then hold.

If V(r) becomes zero in equation (4), the solution of (4) which is zero at the origin has the form

$$\psi \sim J_{n+1/2}(kr)$$

where $J_{n+\frac{1}{2}}$ is the Bessel function of order n. It is then known from the theory of Bessel functions that the asymptotic form of this is -

$$\psi \sim \sin\left(kr - \frac{1}{2}n\pi\right) \tag{8}$$

Comparing equations (7) and (8) we see that the phases

δ_n are the difference in phase between the asymptotic solutions of equation (4) when V(r) is zero and when V(r) has its value corresponding to the position of the electron in the atomic field. Also if V(r) is zero δ_n will also be zero.

To solve equation (4) exactly is almost impossible except for a few particular and simple potential fields. The only method of solution is in general one of numerical integration. An approximate solution has however been developed by Jeffreys (66), for cases in which a in equation (5) does not vary rapidly with r.

For a constant 'a', the solutions of (5) are given by -

$$\psi = A \exp\left(\pm i a^{1/2} r\right) \tag{9}$$

A being a constant. Jeffreys assumes that A and a are functions of r and writes his solution as -

$$\psi = A(r) \exp\left(\pm i \int a^{1/2} dr\right) \tag{10}$$

Substituting back in equation (5), we obtain -

$$\frac{d^2A}{dr^2} + 2 i a^{1/2} \frac{dA}{dr} + i A \frac{d(a^{1/2})}{dr} = 0 \tag{11}$$

Both A and a are assumed to vary very slowly with r so that $\frac{d^2A}{dr^2}$ can be neglected in comparison with the first differentials.

Thus we have $2a^{1/2}\frac{dA}{dr} + A\frac{d(a^{1/2})}{dr} = 0$ (12)

Integrating this we get $A = Ba^{-1/4}$

where B is an arbitrary constant.

Thus the approximate solutions of equation (5) are -

$$\psi = Ba^{-\frac{1}{4}}\exp\left[\pm i\int a^{1/2}dr\right] \tag{13}$$

We now have to determine the limits of the integral in this expression.

If in a, r is zero, a will be infinite and negative, provided $n > 0$ and $V(r)$ is positive, or if negative, it falls off as r^{-s} where $s < 2$. If r is infinite, a will be positive, being equal to k^2. So bhat 'a' will have a positive zero r_0, such that a is negative for $0 \leqslant r < r_0$ and positive for $r > r_0$. Thus the expression for ψ will be exponential in the range $0 \leqslant r < r_0$, and oscillatory in the range $r > r_0$. Jeffreys has shown that the solution which is zero at the origin has the asymptotic form

$$\psi \sim \sin\left[\frac{\pi}{4} + \int_{r_0}^{\infty} a^{1/2}dr\right] \tag{14}$$

Similarly if V(r) is zero we get -

$$\psi \sim \sin\left[\frac{\pi}{4} + \int_{r_0'}^{\infty} b^{1/2}dr\right] \tag{15}$$

where $b = k^2 - \frac{n(n+1)}{r^2}$ (16)

the zero of this latter being r_0'.

Since, by previous deductions, we found that δ_n is the phase difference between (14) and (15), we thus have -

$$\delta_n = \int_{r_0}^{\infty} a^{1/2}\,dr - \int_{r_0'}^{\infty} b^{1/2}\,dr. \qquad (17)$$

r_0 and r_0' are here the zeros of the respective integrands.

In deriving this expression, we have found that it is necessary that a and b should have positive zeros. This will be the case under certain conditions as given above. These conditions hold generally with the exception of the stipulation $n > 0$. It is possible for n to be equal to zero. In the case of $n = 0$ the following method must be used.

For 'a' in the case of an attractive field for which $V(r)$ will be negative, there is no zero and a will remain positive. b also will have no zero for $n = 0$. This will be the case for electrons and atoms. To determine the lower limits for a and b in such a case we must then choose from equation (13) the solution which is zero at the origin. This will be

$$\psi = B a^{-1/4} \sin\left[\int_0^r a^{1/2}\,dr\right]$$

which has the asymptotic form

$$\psi \sim \sin\left[\int_0^{\infty} a^{1/2}\,dr\right] \qquad (18).$$

Similarly for V(r) zero we get the form

$$\psi \sim \sin\left[\int_0^\infty b^{1/2}\,dr\right] \tag{19}$$

Thus we obtain for δ_0 the expression -

$$\delta_0 = \int_0^\infty a^{1/2}\,dr - \int_0^\infty b^{1/2}\,dr \tag{20}$$

which is the same as the expression for δ_n with the lower limits of the integration replaced by zeros.

A difference exists however in the case of a repulsive field; here V(r) is positive and thus 'a' has a zero. b is of course unaffected by the type of field, since in any case the field is zero, for b. To obtain δ_0 for such a field we must combine equations (14) and (19). The result is that -

$$\delta_0 = \frac{1}{4}\pi + \int_{r_0}^\infty a^{1/2}\,dr - \int_0^\infty b^{1/2}\,dr \tag{21}$$

for a repulsive field.

When V(r) is zero, the error between the asymptotic form of the solution of equation (5) and Jeffreys' approximation can be found as follows - The two expressions for ψ are -

$$\psi \sim \sin\left(kr - \tfrac{1}{2}n\pi\right) \tag{22}$$

and $$\psi \sim \sin\left(\tfrac{1}{4}\pi + \int_{r_0'}^\infty \left(k^2 - \frac{n(n+1)}{r^2}\right)^{1/2} dr\right) \tag{23}$$

The integral can be evaluated thus -

Consider the expression -

$$F = \int_{r_0'}^{R} \left[\left(1 - \frac{s^2}{r^2}\right)^{1/2} - 1 \right] dr - s \tag{24}$$

where $s^2 = \frac{n(n+1)}{k^2}$ and r_0' is the zero of $1 - s^2/r^2$, i.e. $r_0' = s$, and R is a quantity which will be eventually allowed to tend to infinity.

The integral can be evaluated simply by putting $r = s\sec\theta$; we then get -

$$F = \int_{r=s}^{r=R} s \tan^2\theta \, d\theta - \Big[r \Big]_s^R - s$$

$$= s \Big[\tan\theta - \theta \Big]_{r=s}^{r=R} - \Big[r \Big]_s^R - s$$

$$= s \left[\frac{\sqrt{R^2 - s^2}}{s} - \sec^{-1}\frac{R}{s} + \sec^{-1} 1 - \frac{R}{s} \right]$$

$$= s \left[\frac{R}{s} \left\{ 1 - \frac{s^2}{2R^2} + O\left(\frac{1}{R^4}\right) \right\} - \sec^{-1}\frac{R}{s} - \frac{R}{s} \right]$$

$$= s \left[O\left(\frac{1}{R}\right) - \sec^{-1}\frac{R}{s} \right]$$

$$\therefore \lim_{R \to \infty} F \to -s \sec^{-1}\infty \to -s\frac{\pi}{2}$$

Multiplying (24) by k and putting $s^2 = \frac{n(n+1)}{k^2}$ or $s = r_0'$, we obtain -

$$\int_{r_0'}^{\infty} \left[\left\{ k^2 - \frac{n(n+1)}{r^2} \right\}^{1/2} - k \right] dr - k r_0' = -\sqrt{n(n+1)} \cdot \frac{\pi}{2}$$

Integrating the k under the bracket from r_0' to r which is assumed large, and letting R tend to infinity, we obtain the result -

$$\int_{r_0'}^{\infty}\left(k^2-\frac{n(n+1)}{r^2}\right)^{1/2}dr = kr-\sqrt{n(n+1)}\,\frac{\pi}{2} \qquad (25).$$

If this value of the integral is substituted in equation (23) the result is -

$$\psi \sim \sin\left[kr-\left(\sqrt{n(n+1)}-\frac{1}{2}\right)\frac{\pi}{2}\right] \qquad (26).$$

A comparison of this result with the exact asymptotic form of equation (22) shows that Jeffrey's result is greater by the amount -

$$\left[n+\frac{1}{2}-\sqrt{n(n+1)}\right]\frac{\pi}{2} \qquad (27).$$

The values of this for n = 1 and n = 2 are 0•13 and 0•08 respectively. For larger n it becomes very small, so that the error is seen not to be large for $n > 0$.

For n = 0 the error appears to be $\pi/4$, but it has been shown above that in this case instead of equation (23) we must use equation (19) for which the phase is seen to be less than that of equation (23) by $\pi/4$. Hence the error is zero for n = 0 and V = 0, and Jeffreys' value of ψ is then exact, as would be expected since b is then a constant.

This discussion only determines the error in the second part of the expression (17) for the phases, not the complete error in the phases. The complete error depends also on the error in the part $\int a^{1/2}dr$ which may be much more in error than the second part, since here we have the field V(r) and for a small error its rate of variation with r must be small.

Starting from the same equation (4), and taking a solution in the form of the sum of the bounded solution of $\frac{d^2\psi}{dr^2} + b\psi = 0$ and a further function Φ whose product with V could be neglected, and also neglecting terms involving the squares of the phases, Mott (67) deduced an expression for the phases which is valid for small values of the phases δ_n.

His expression is -

$$\delta_n = \frac{\pi}{2} \cdot \frac{8\pi^2 m}{h^2} \int_0^\infty V \cdot \left[J_{n+\frac{1}{2}}(kr) \right]^2 r\,dr \qquad (28).$$

The J's, as before, are the Bessel functions. This expression is called the Born Approximation, since it involves Born's assumption that the effect of the atomic field on the wave function is small and can be neglected.

We thus have two expressions for the phases, Jeffreys' and Born's, which are -

$$\left.\begin{array}{ll} \text{Jeffreys' formula} & \delta_n = \int_{r_0}^\infty a^{1/2}dr - \int_{r_0'}^\infty b^{1/2}dr \\ \text{where} & a = k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{n(n+1)}{r^2} \\ \text{and} & b = k^2 - \frac{n(n+1)}{r^2} \end{array}\right\} \qquad (29)$$

and r_0 and r_0' are the greatest positive zeros of the respective integrands. For $n = 0$, both r_0 and r_0' are zero. This approximation should give reasonable results provided a does not vary rapidly with r; the error in b has already been shown to be small.

Born's formula is -

$$\delta_n = \frac{\pi}{2}\cdot\frac{8\pi^2 m}{h^2}\int_0^\infty V\left[J_{n+\frac{1}{2}}(kr)\right]^2 r\,dr \qquad (30).$$

Calculation of Phases.

Holtsmark (68) by a method of numerical integration has been able to calculate a number of exact phases for krypton. He used an atomic field calculated originally by Hartree, to which he applied a correction for the polarisation of the field by the incident and scattered waves. The effect of this polarisation correction is to make the field fall off more slowly with r. The field is thus effective up to much larger values of r. By means of his calculations he was able to get a theoretical cross section curve which agreed very well with Ramsauer and Kollath's experimental curve. Both the experimental and theoretical curves show the Ramsauer effect. This exact method of Holtsmark's is however very laborious. It was therefore decided to calculate the phases by applying Jeffreys' and

Born's approximate methods, and by a comparison with Holtsmark's exact values, find the range of validity and the extent of the errors in the approximate methods. The atomic field with the same polarisation correction as Holtsmark used, was employed; it is the field which he calls No. 2 in his paper.

In performing the calculations all the quantities in the formulae were converted to atomic units. The atomic unit of length is the radius a_0 of the first Bohr orbit of the hydrogen atom, which is given by $a_0 = 0\cdot53 \times 10^{-8}$ cms. The unit of energy is the ionisation potential of the hydrogen atom, which is 13•56 volts, i.e. $\frac{e^2}{2a_0}$ in atomic units. k is given by $k = \frac{2\pi m v}{h} = \frac{2\pi}{h}\sqrt{\frac{me}{150}}\sqrt{V}$ where V is in volts, k is measured in units of $1/a_0$, so that we have -

$$k = \frac{2\pi}{h} \cdot \sqrt{\frac{me}{150}}\, a_0 \sqrt{V}$$

$$= 0\cdot272\sqrt{V}$$

The atomic field is expressed in the form -

$$\frac{8\pi^2 m}{h^2} V(r) = -\frac{2Z_p}{r} \tag{31}$$

where Z_p is a function of r, values for which for various r have been given by Hartree. The negative sign is included since the field is attractive. Holtsmark's field with polarisation correction is in the form

$$\frac{8\pi^2 m}{h^2} V(r) = -2\left[\frac{Z_p}{r} + \frac{\Phi}{r^2}\right] \tag{32}$$

Φ is also a function of r, which for large r falls off asymptotically as r^{-4}.

The phases can now be written as -

Jeffreys' - $\delta_n = \int_{r_0}^{\infty}\left[k^2 + \frac{2(Z_p \cdot r + \Phi)}{r^2} - \frac{n(n+1)}{r^2}\right]^{1/2} dr - \int_{r_0'}^{\infty}\left[k^2 - \frac{n(n+1)}{r^2}\right]^{1/2} dr$ (33).

Born's - $\delta_n = \pi \int_0^{\infty}\left[Z_p + \frac{\Phi}{r}\right]\left[J_{n+\frac{1}{2}}(kr)\right]^2 dr$ (34).

The values of k run from 0 to 3 for energies from 0 to 121 volts.

To determine the values of the δ_n a method of numerical integration is used. Values of the integrands are calculated for the values of r for which the field is known. A graph is then drawn in which these values of the integrands are plotted against r. By means of a planimeter the area under the graph is determined and so the value of δ_n is determined. In special cases, certain modifications were employed. For the case of δ_0 Jeffreys' formula reduces to -

$$\delta_0 = \int_0^{\infty}\left\{\left[k^2 + \frac{2(Z_p r + \Phi)}{r^2}\right]^{1/2} - k\right\} dr \tag{35}$$

When r is small, that is $r < 0{\cdot}01$, the field is large so that k and k^2 can be neglected in comparison with it.

Thus in determining δ_0, the method is to divide the integral into two parts as follows -

$$\delta_0 = \int_0^{0\cdot01} + \int_{0\cdot01}^{\infty}$$

The second part can be evaluated graphically, while the first is given by, neglecting Φ which is zero for small r, -

$$\int_{0.}^{0\cdot01} \left[\frac{2\left(Z_p r + \Phi\right)}{r^2} \right]^{1/2} dr$$

$$= \int_0^{0\cdot01} \left[\frac{2 Z_p}{r} \right]^{1/2} dr$$

$$= 2 \left[2 Z_p \right]^{1/2} \left[0\cdot01 \right]^{1/2}$$

$$= \frac{2}{10} \left[2 Z_p \right]^{1/2}$$

which can then be determined directly from the value of the field at r = 0·01.

In the determination of δ_n for $n \neq 0$, by Jeffreys' method, the greatest positive roots of the two integrands have to be found. For the second integrand the root is given by $r_0' = +\sqrt{\frac{n(n+1)}{k^2}}$. By plotting a graph of the field against r the value of the field can then be found at this point. This value will be seen to be the value of 'a' at $r = r_0'$, the root of b, since at this point $k^2 - \frac{n(n+1)}{r^2}$, which is b, is zero. For the first integrand however, the root has to be determined graphically. If the first integrand is zero we may write it as

$$\frac{n(n+1)}{r^2} - \frac{2\left(Z_p \cdot r + \Phi\right)}{r^2} = k^2 \qquad (36).$$

By inspection of columns of values for $\frac{n(n+1)}{r^2}$ and $2\frac{(Z_p r + \phi)}{r^2}$ the region of the root can be found. By plotting the difference of these two columns against r, the root can be found exactly. It is always found that r_0 is less than r_0'. Thus in calculating the phases, the formula can be written as -

$$\delta_n = \int_{r_0}^{\infty} a^{1/2} dr - \int_{r_0'}^{\infty} b^{1/2} dr = \int_{r_0}^{r_0'} a^{1/2} dr + \int_{r_0'}^{\infty} a^{1/2} dr - \int_{r_0'}^{\infty} b^{1/2} dr$$

$$= \int_{r_0}^{r_0'} a^{1/2} dr + \int_{r_0'}^{\infty} \left[a^{1/2} - b^{1/2} \right] dr \qquad (37).$$

The integrands are then determined for different r, the graph plotted and the phase δ_n found as before, by numerical integration.

In calculating the phases by the Born method, tables of Bessel functions are used and graphs to interpolate intermediate values, for various kr. As before the integrands are plotted against r, and the areas determined. In this case the phase is given by π x area.

A number of phases have been calculated for k = 1 and for k = 2, by both Born's and Jeffreys' methods. They are given in table I, along with Holtsmark's exact phases for the same values of k. It should be noticed that δ_5 for k = 2 has been omitted. Holtsmark did not give a value for this phase. δ_0 for k = 0 is also given in the table.

Table I - Exact and Approximate Phases for Krypton.

k^2 volts	k atomic units	Phase	Exact phase	Jeffrey's approx.	Born's approx.	Exact phase minus Jeffreys' approx.	Exact phase minus Born's approx.
0	0	δ_0	12·568	15·310		-2·742	
13·54	1	δ_0	10·996	12·024		-1·028	
		δ_1	8·489	8·781		-0·292	
		δ_2	4·368	4·880		-0·512	
		δ_3	0·226	0·286	0·242	-0·040	-0·016
		δ_4	0·107	0.107	0.107	0·000	0·000
54·15	2	δ_0	9·696	10·612		-0·916	
		δ_1	7·452	7·710		-0·258	
		δ_2	4·469	4·748		-0·279	
		δ_3	1·238	1·410	0·779	-0·172	0.459
		δ_4	0·445	0·557	0·414	-0·112	0·031
		δ_6	0·143	0·190	0·144	-0·047	-0·001

An examination of the results shown in the table indicates that the difference between the exact phases and Jeffreys' approximate phases is small except in the case of zero order phases. The values by the approximate method are always the higher.

In the case of the phases calculated by the Born method the error is small in all cases where the phase is reasonably small, i.e. less than 0·5. The sign of the error varies, and in the case of phases less than 0·5, the error is less than by Jeffreys' method.

It should be noticed that it is the actual error which is important, and not the percentage error, since the addition of multiples of π to the phase does not affect the scattered intensity as given by formula (1).

The abnormally large error that appears in δ_2 for $k = 1$ is probably due to a mistake in Holtsmark's calculation since the approximate value was carefully checked.

An important conclusion which can be found from a study of table I is that the error between Jeffreys' phase and the exact phase decreases as the order of the phase increases. Previous workers have always assumed that Jeffreys' method is only valid for phases of low order having a value greater than unity. Massey and Mohr (69) have found that for a repulsive field, as in the case of a collision between two helium atoms, the values of the phases less than unity are far too low. Table I, however, shows that for a heavy atom such as krypton, in the case of an attractive field, the method is applicable down to very low values of the phases. For the lowest values actually determined, $\delta_4 = 0.107$, $k = 1$, the error was zero by both Jeffreys' and Born's methods.

The largest errors found were in the case of the zero order phases and for zero velocity, i.e. $k = 0$. The magnitude of these errors was rather surprising, so that δ_0 phases were calculated for $k = 0$, for the four rare gases, krypton, argon, neon and helium, for which the Hartree fields are known. The field for argon is given by Holtsmark (70), for neon by Brown (71), and for Helium by McDougall (72).

The results are given in Table II, in which the elements are arranged in order of decreasing atomic numbers. It is known that the exact phase in each case is an exact multiple of π.

Table II - δ_0 Phases for $k = 0$ for the Rare Gases.

Atom.	Exact Phase.	Jeffreys' Approx. Phase.
Kr.	4π	$4\pi + 2{\cdot}742$
Ar.	3π	$3\pi + 1{\cdot}040$
Ne.	2π	$2\pi + 0{\cdot}852$
He.	π	$\pi + 0{\cdot}180$

The table shows that Jeffreys' approximation gives too high a value in each case and that the error decreases with the atomic number of the element.

A further calculation was carried out to study the variation of the error in δ_0 with k, for krypton, by Jeffreys' method, for all the values of k for which

Holtsmark gives exact phases. The results are given in Table III and fig. (7).

Table III - Exact and Approximate Values of δ_0 in Krypton.

k in atomic units.	Exact value.	Jeffreys' Approx.	Difference.
0	12·568	15·310	2·742
0·1	12·709	14·418	1·709
0·2	12·579	13·956	1·359
0·5	11·975	13·050	1·075
0·7	11·536	12·620	1·084
1·0	10·996	12·024	1·028
2·0	9·696	10·612	0·916

The range of k is seen to be 0 to 2. In fig. (7) are the exact and approximate phases against k, and also the difference between them plotted against k. The latter graph shows that the error in Jeffreys' phase at first decreases rapidly as k increases from zero, and then becomes almost constant above a value of k = 0·5. It thus seems fairly reasonable to extrapolate the graph to higher k to obtain the correction in δ_0.

An explanation of the large error in δ_0 can be obtained if we consider our original assumption in deriving Jeffreys' approximation, which was that

$$a = k^2 - \frac{8\pi^2 m}{h^2} V(r) - \frac{n(n+1)}{r^2} \qquad (38)$$

should vary slowly with r. The potential energy V(r) varies as some inverse power of the distance r, so that the rate of variation of a with r depends on the second two terms of the above expression. The rate of variation of V(r) varies with r, becoming less as r increases. In determining δ_n, we integrate $a^{\frac{1}{2}}$ from its greatest positive zero r_o to infinity. Now r_o increases with n. Thus, as n increases, the integration of 'a' extends over a region in which it varies more and more slowly with r, that is, over a region in which our original assumption holds more and more closely. We would thus expect the higher order phases to be more accurate than the lower, which is what is seen to be the case from Table I.

For the special case of the zero order phase, the integration has to extend right to r = 0, that is into a region in which the field varies very rapidly with r. Thus our original assumption is not fulfilled and a large error may be expected.

For atoms of low atomic number the field is not so powerful and its rate of variation with r is less than for atoms of higher atomic number. Our original assumption is thus more nearly fulfilled and we would therefore expect a better approximation. Both these latter effects are verified by an examination of Table II.

In the special case of a repulsive field, V(r) is positive so that the second and third terms in equation (38) have the same sign. In this case the third term will increase the rate of variation of a with r as n increases, instead of diminishing it as in the case of an attractive field. Thus we may expect the error in such a case to increase with n, as was found by Massey and Mohr. Again for V(r) positive, and n = 0, a has a positive zero, so that for the case of δ_0 the integration would not then extend to $r = 0$. The error in this case would then probably be less than for an attractive field.

From equation (1) we find that by treating $I(\theta)$ as a function of $(\cos 2\delta_n - 1)^2 + \sin^2 2\delta_n$, $I(\theta)$ has its maximum value for $\delta_n = (2s+1)\pi/2$; that is the phases which are nearest $(2s+1)\pi/2$, will have the most effect on the scattered intensity. The error in δ_0 should then not be serious provided δ_0 is not of the order of $(2s+1)\pi/2$. For krypton δ_0 is seen to be 4π for $k = 0$, which is as far from the given values $(2s+1)\pi/2$ as possible. The effect of a large error in δ_0 will thus not be serious in this case, since there will be phases of higher orders which will be close to $3\pi/2$ and $\pi/2$. The effect of these on $I(\theta)$ will be so large, that the error in δ_0 will not be important. The same argument applies to any case in which δ_0 is large, say greater than 2π, which is the case for small values of k, as seen from Table III. For

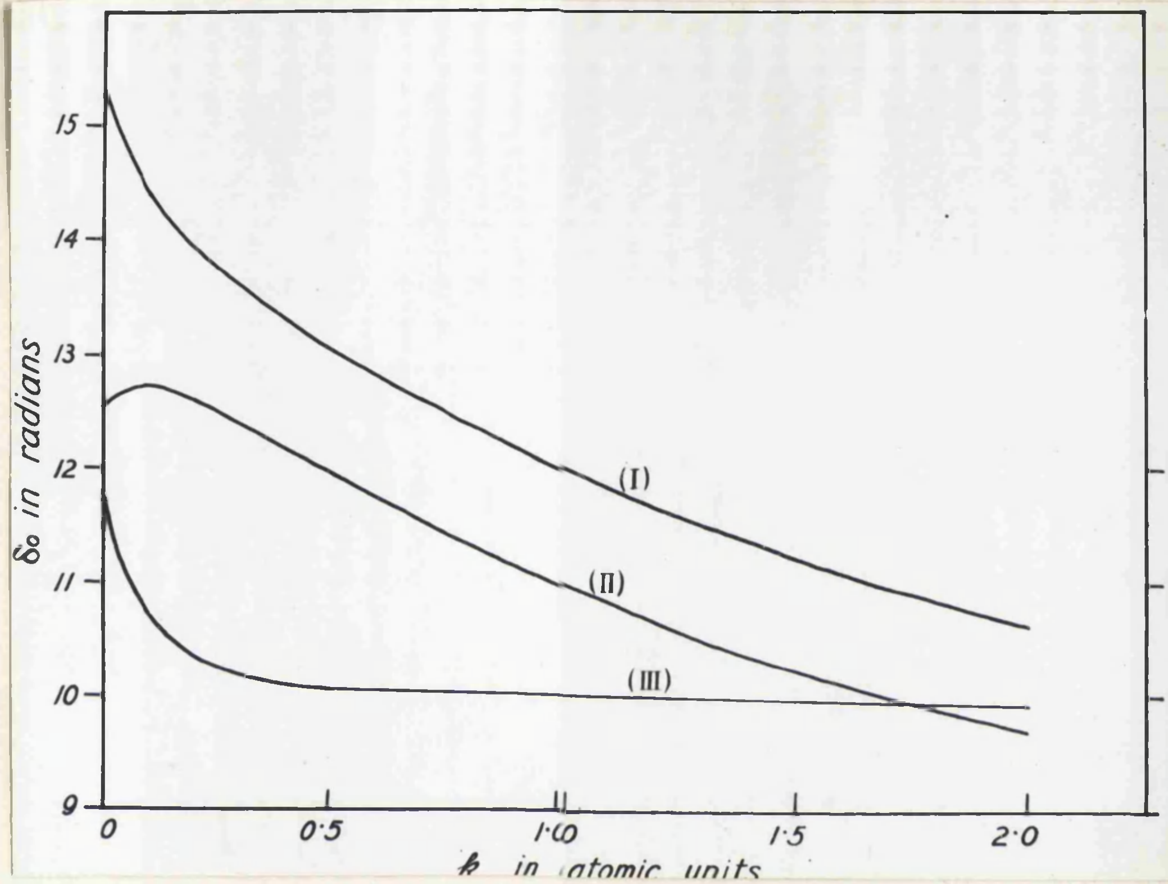


Fig. 7. (I). Jeffrey's values, (II) Exact values, (III) Difference.

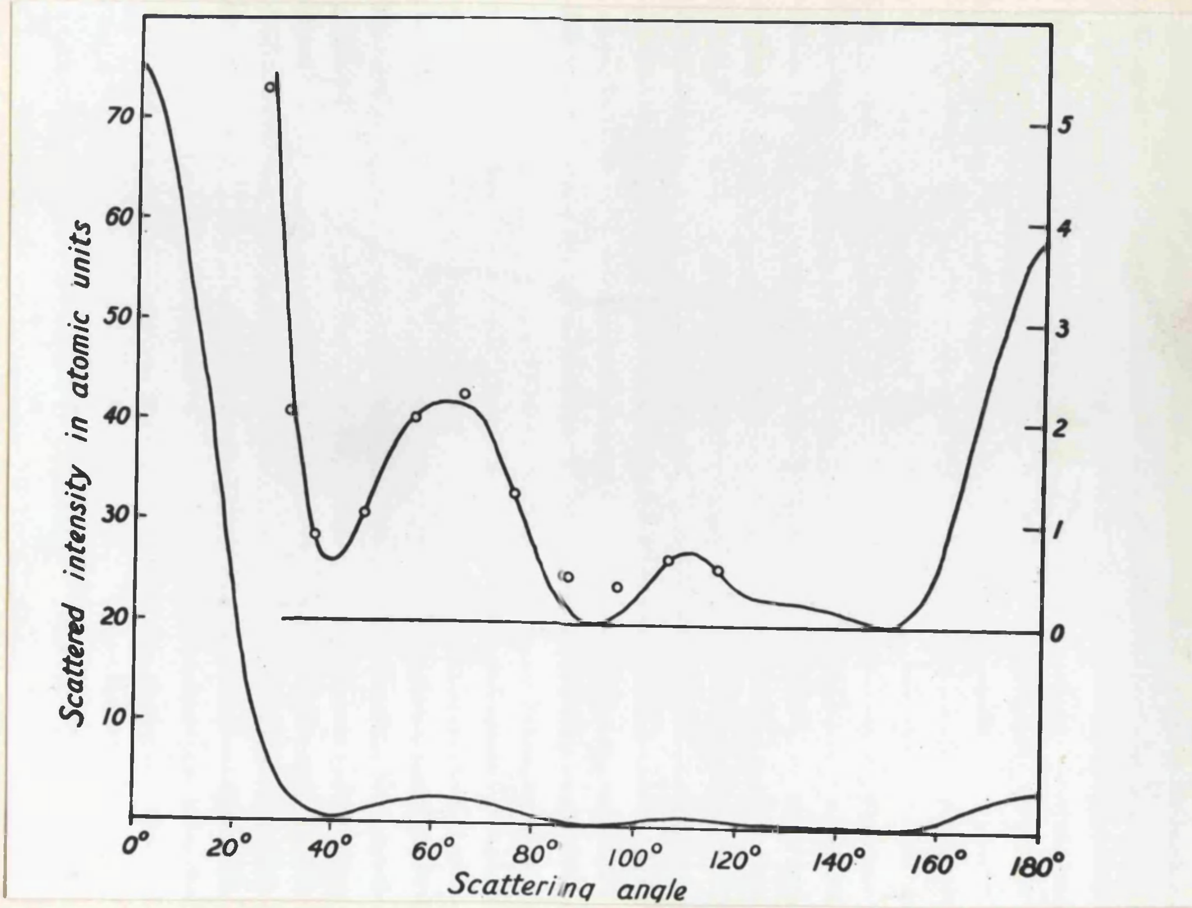


Fig. 8. Circles are Arnot's Experimental Points.

large values of k and a heavy atom, δ_0 might be the most important phase; the error in it would then be important and might even alter the shape of the scattering curve completely. A more accurate method of calculation would then be necessary.

For phases of small value, i.e. less then 0·5, either Jeffreys' or Born's method gives results which are almost exact.

Previous workers on the calculation of phases by approximate methods have used Jeffreys' method for phases greater than unity and Born's for phases less than 0·5, since these were the supposed regions of validity. Intermediate phases were obtained by drawing phase-order diagrams and interpolating on them for those phases not otherwise calculated.

This method was probably very inaccurate since the slope of such a diagram varies very rapidly in just the region of interpolation. The above work has shown that this is not necessary, at least in the case of krypton, for which Jeffrey's method gives results which increase in accuracy with the order of the phase, and with decrease in value of the phase. From general considerations of the field and the assumptions involved in the method, it seems reasonable to expect that this conclusion will hold for other similar atoms in the case of collisions with electrons.

THEORETICAL ANGULAR SCATTERING CURVE FOR 122 VOLT ELECTRONS IN KRYPTON.

In order to test the general accuracy of the phases by the approximate methods, it was decided to calculate the angular scattering curve for a certain velocity and compare the result with an experimental curve. The velocity shosen was that for which $k = 3$, which corres::ponds to a beam velocity of 121·6 volts. The phases were calculated using the same field as in the previous part of this section. For the phases δ_0 to δ_4 Jeffreys' method was used, and for δ_5 and δ_6 Born's method. The scattered intensity $I(\theta)$, as defined in a previous section, was calculated from equation (1). It will be in atomic units, since k and the phases are in these units. The phases are given in Table IV, and the scattered intensity, for each angle, in Table V.

Table IV. - Phases for $k = 3$ for Krypton.

δ_0	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
9·824	7·003	4·411	1·830	0·980	0·460	0·302

Table V - Scattered Intensity I(θ) in Atomic Units for 122-volt Electrons in Krypton.

θ°	0	10	20	30	40	50	60
I(θ)	75·21	55·76	22·18	3·35	0·608	1·57	2·13
θ°	70	80	90	100	110	120	
I(θ)	2·00	0·749	0·007	0·293	0·721	0·335	
θ°	130	140	150	160	170	180	
I(θ)	0·218	0·122	0·009	0·676	2·56	3·83	

In fig. (8) the theoretical curve is plotted as a continuous line. The region from 20° to 180° is also plotted to a larger ordinate scale. The circles on the latter curve are Arnot's experimental points (73), for scattering of 121 volt electrons in krypton. The experimental curve is fitted to the theoretical curve at one point, since the ordinates of the experimental curve are in arbitrary units. The agreement is seen to be very good. Both theoretical and experimental curves exhibit maxima and minima at practically identical angles. The theoretical curve also shows a pronounced intensity of backward scattering between angles of 160° and 180°. This effect has actually been found experimentally in another gas, mercury vapour, by Arnot (74) where the angular range of investigation was extended almost to 180°.

The general conclusions arrived at from the results of this section are that Jeffreys' approximation gives values of the phases which are sufficiently accurate for all values of n greater than zero; the accuracy increasing with n. The error in the zero order phase decreases with the atomic number of the element, and is shown to be relatively unimportant if δ_0 is large and not equal to $(2s + 1)\pi/2$. Born's approximation is valid for phases whose value is less then 0·5. Phases calculated by these methods are shown to give an angular distribution curve which is in very good agreement with the experimental curve for the same velocity. The number of phases required to determine the curve for 121·6 volt electrons is seven.

PART II. EXPERIMENTAL.

SECTION 5.

DESCRIPTION OF THE APPARATUS.

The apparatus used in the experimental part of this thesis is essentially of the modified Lenard type; that is the beam passes in a straight line through the defining holes, into the scattering region and then into the collecting chamber. In the original Lenard apparatus and in the Ramsauer apparatus, as used by Brode, the only measurements taken are those of the currents in the beam at the beginning and end of its path. No actual measurements are taken of the current scattered from a certain length of the beam. In the modified form of the Lenard apparatus as used by Jones and others, this current is measured. Observations on this scattered current, in cases where measurements of the cross section have been made, have been confined to studying the total current scattered by all possible types of collisions, elastic and inelastic. The cross section obtained in this way is the total effective cross section, or the probability of a collision of any type, no particular type being specified or excluded. In cases, however, where the differential cross section has been measured, that is the intensity scattered through a certain angle, methods have been employed to analyse the scattered electrons, into groups with different velocity distributions, thus separating groups such as the elastically or inelastically scattered electrons. There are three main methods of analysis which have all been used by different workers.

Firstly, there is the method of using retarding potentials to separate out electrons which have lost certain amounts of energy. This method has been used by Arnot, in his work on elastic angular scattering in many gases; and by Tate and Palmer and others.

Secondly, there is the method used by Nicoll and Mohr, and by Hughes and McMillen and others, of resolution by applying an electrostatic field between two curved plates. The electrons passing between the plates are then separated out into groups with the same velocity any desired group can then be made to pass through the slits at the end of the analyser and into the collecting chamber.

Finally there is the magnetic resolution method, as used frequently for the separation of positive ions of various velocities by Smyth and others, and by Whiddington and his co-workers in separating electrons of different velocities. In this method a magnetic field is applied in a direction perpendicular to the direction of the beam, which is then bent into the arc of a circle of radius depending on the velocity and the magnetic field strength, exactly as in the Ramsauer apparatus, except that in Whiddington's apparatus the electrons are recorded photographically.

In most of these methods, measurements are confined to electrons scattered through a certain angle; the total cross section is then obtained from a number of angular scattering by numerical integration. As mentioned previously the results of this method may thus be far from accurate. Little work seems to have been done on the direct determination of the cross sections for particular types of collisions by a method of resolution of all the scattered electrons at once into velocity groups.

Such a method has been devised in the apparatus to be used here. The method of resolution is one employing the first method of above, namely a method of resolution by grids and retarding potentials.

A scale drawing of the apparatus is given in fig. (9), while a photograph of it mounted on its supporting glass tube is given in Plate I. All the metal parts of the apparatus, which was constructed entirely in the laboratory workshops, were made of copper with the exception of the grids, which were of nickel gauze,

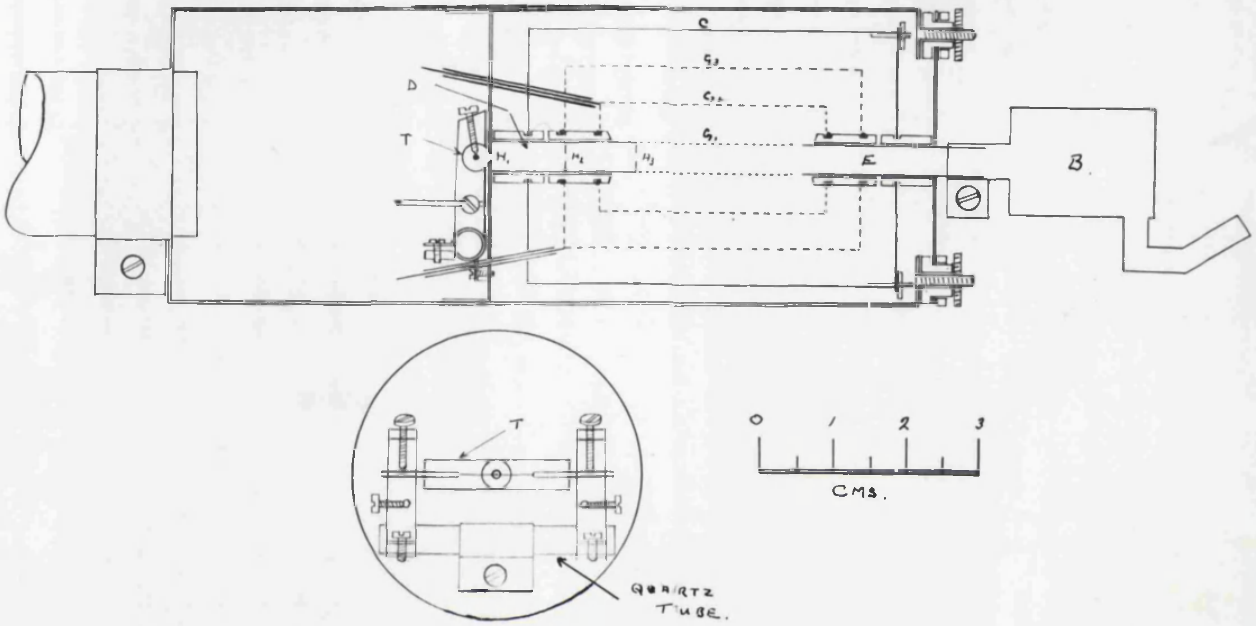


Fig. 9.

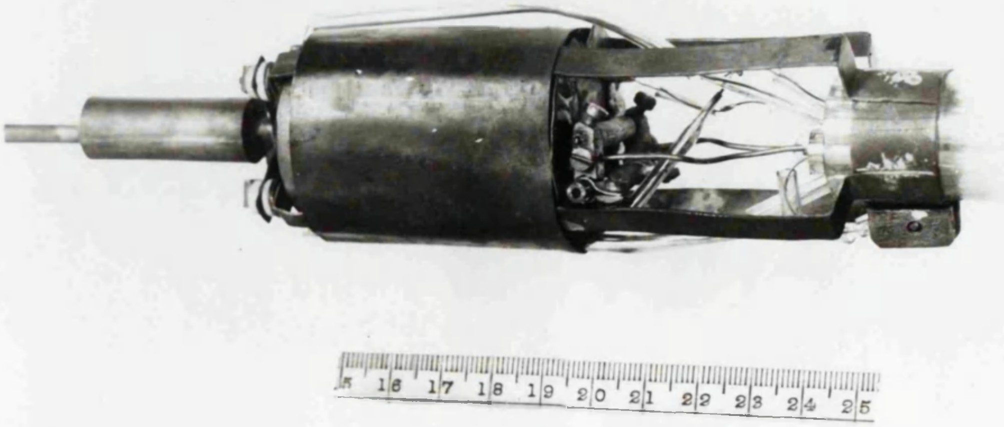


Plate I. Scale in cms.

and the filament which was of tungsten. All joints on the copper parts of the apparatus were silver soldered; many of them being rivetted as well. The joints on the grids were spot-welded where possible. All the wire leads to the apparatus were of nickel, except the filament leads which were of copper, on account of its greater conductivity and the large currents these leads would have occasionally to carry. The leads to the two outer grids were of copper for the first few inches, and then of nickel. This was done since nickel leads were found to be not sufficiently flexible and also too brittle to use in places where it was necessary to bend them frequently. Nickel leads were originally used but they were found to break easily; considerable dismantling of the apparatus was then necessary to effect repairs.

Some considerable time was spent in experimenting with various types of electron gun. In the first one constructed, the filament was arranged so as to be across a diameter of a cylindrical box, with the first defining hole of the beam at the centre of one of the plane end plates. The filament itself was carried on two thick copper wires, which were always as close together as possible. In this way it was hoped to minimise any effects due to the magnetic field of the filament heating current, which might be quite large as, at times, filament currents up to five amperes were used. With this type of gun however it was found impossible to obtain an electron beam for any energy below 40 volts. This must have been partly due to the difficulty of getting the filament exactly over the gun hole; but there must have been other causes since experiments with focussing cylinders round the filament, and variations of the position of the filament in its containing cylinder failed to effect any improvement. This same effect has also been noticed by other workers with this type of gun.

As it was desired to obtain beams of much lower energy than 40 volts, another gun was constructed on the same lines as that used by Arnot (74). The diagram of the apparatus is given in fig. (9). In this type the filament is placed along the axis of a cylinder T; the first beam defining hole being then at the middle of the length of the curved surface. The potential necessary to accelerate the electrons to the desired speed is applied between the filament and the box surrounding it. It should be noticed that this type of gun is probably much more efficient than the one described previously, since there is much less chance of electrons escaping from the ends of the tube T, while also, since the ends are quite open, gas will escape easily from the cylinder, and so the life of the filament will be longer, and there will be less chance of low voltage arcs between the filament and the case.

The dimensions of the filament containing box T are, diameter 4 mm, and length 2 cms., while in the first gun the dimensions were, diameter 2 cms., and length 1 cm. The filament in this new gun was of tungsten, 0·2 mm. in diameter, and about 10 mm. long. The tungsten was carefully cleaned with fine emery paper before use. Each end of the filament was spot-welded to a short length of thick nickel wire. These nickel ends are clamped by set screws, in copper posts at each end of the filament box, so that the filament lies exactly along the axis of the box and also exactly in the centre of the length of the box. With this arrangement, the centre of the filament which is the hottest part and will thus emit electrons most freely, will be exactly over the first gun hole. In each of the copper posts there is a further hole in which the wires leading to the external batteries can be clamped by set screws. Each post is itself clamped to a short piece of quartz tubing which is independently clamped to the main frame of the apparatus. Again, behind each post, mica plates are fixed to the frame of the apparatus to act as insulation should they move so as to touch the frame.

The filament is thus well insulated from the rest of the apparatus.

Three holes H_1, H_2, and H_3, each of one mm. diameter, and with bevelled edges, are present in the tube D, which is silver soldered to the tube T and at right angles to it. These holes define the beam. The tube D is 2 cms. in length so that the holes are 1 cm. apart. The diameter of this tube is also 4 mm. To the end of this tube is soldered the first grid G_1. The space inside this grid forms the field free scattering region. After passing through this space the beam enters the tube E and the collecting chamber B. The tube E is again 4 mm. in diameter. The electron trap B is about 3 cms. long and one cm. in diameter. The outlet from it is quite wide but the outlet tube is bent twice, and placed at the opposite end of the cylinder to that at which the electrons enter, so as to insure that B is as good a collector of electrons as possible, but also gives free passage in and out to the gas in the apparatus. The grid G_1 stops about 1 mm. short of the tube E, so that they are electrically insulated from each other. The distance between the end of tube D and the beginning of tube E is equal to 2·2 cms., which is then the length x of the beam for scattering.

In section (1), the mean free path for electrons in mercury vapour at a pressure of 10^{-3} mm. was calculated to be about 20 cms. A comparison of this value with the above value of x, namely 2·2 cms. and the dimensions of the apparatus shows that the probability of an electron, which has made a collision, making another collision before it reaches a collector is very small. We can thus assume that all the results shown in the experimental section (7) are due to single collisions.

Coaxial with the grid G_1 and the electron beam, are the two grids G_2 and G_3 and the collecting cylinder C. In the original apparatus the three grids were all made of fine copper gauze, the wire of which was about 0·1 mm. thick, while the open spaces of the gauze were also about 0·1 mm. square. Besides being very difficult to construct with such fine gauze, the grids were found on testing not to pass a current of sufficient intensity to be measured. Calculations from the dimensions of the meshes of the gauze showed that the open area was only 25% of the total area so that the actual intensity collected by C was only 1/64 of the intensity scattered from the beam, which was much too small to permit of accurate measurement. Three new grids were therefore constructed of nickel gauze woven from 36 s.w.g. wire, with a mesh of 20 per inch. The apertures of the gauzes were found to be 1·08 x 1·08 mm., so that the transmission or "sifting" area is 71%. The grids G_2 and G_3 which are complete cylinders, are fastened, by copper rings, into slots cut in insulating sleeves of sindanyo. These sleeves slide over the tubes D and E. The thickness of these sleeves is about 1·5 mm., and the distance between successive grids and between the grid G_3 and the collector C, is 5 mm. The leads to the grids G_2 and G_3 are insulated by thin quartz tubes which can be easily slipped over the wires, as shown in the figure. The collecting cylinder C was also originally insulated. on sindanyo sleeves but the insulation of this was found to be insufficient when dealing with small currents and high sensitivity galvanometers. These sindanyo sleeves were therefore replaced by quartz insulators which fitted tightly over the tubes D and E. The right end plate of the box C was removable, being secured by two small screws and nuts, in order that the two outer grids could be slipped inside. The tube E and the collecting box B were supported by the main frame of the apparatus but were insulated from it by bushes of sindanyo. A further case was constructed to fit completely round the frame of the apparatus so as to shield the cylinder C externally from any stray electrons from the gun casing.

The apparatus was supported on a Pyrex glass tube with a large ground glass joint at the end, by means of which the whole apparatus could be fitted into a large pyrex tube; the diameter of the tube and ground joint being 5 cms. All the leads to the apparatus, of which there were seven, entered through tungsten-pyrex seals, with the exception of the copper filament leads which were waxed in. The nickel leads were spot-welded to the tungsten at each end. All the leads were insulated from each other by long sleeves of pyrex tubing, while close to the apparatus the leads were frequently insulated by quartz tubing. By means of the ground glass joint the whole apparatus could easily be removed from the tube for adjustments and repairs to the filament. The ground joint was kept well greased with a hard vacuum grease of very low vapour pressure.

The earth's magnetic field was balanced out by means of two pairs of large Helmholtz coils, 48 cms. in diameter. One pair was adjusted to equalise the horizontal component of the field and the other the vertical component. The number of turns of wire on the coils necessary to do this with a current of 0·2 amperes in the coils was first calculated; the nearest exact number of turns to the result was then put on each coil. By calculating back and testing with a small magnetometer, the exact current was found for each pair of coils. The centre of the four coils was arranged to be exactly at the position of the scattering region where there should then be no field due to the earth's field, over quite an appreciable region.

The general arrangement of the apparatus, coils and circuit can be seen in Plates (II) and (III).

By means of a side limb in the main glass chamber a connection was made through a liquid air trap to a sensitive McLeod gauge for which the calibration had been accurately determined. A further side limb, which was never used during the course of the experiments on mercury vapour, was provided through which a supply of another gas might be allowed to enter the collision chamber. This tube can be seen in the Plate (III) with an arrangement for letting in a small quantity of a gas, connected to it. This the author has been constructing for work on neon and helium.

Through a small 2 cm. ground glass joint at the opposite end of the main glass tube to the large joint a connection was made to the evacuating system through a liquid air trap again. The pumping system consisted of an electrically heated, steel Kaye mercury diffusion pump, backed by an ordinary Hyvac. A trap bottle with phosphorus pentoxide as a drying agent, was included between the two pumps. Taps were also included between the pumps and on each side of the trap bottle. A further tap beside the Hyvac served to emit air when it was

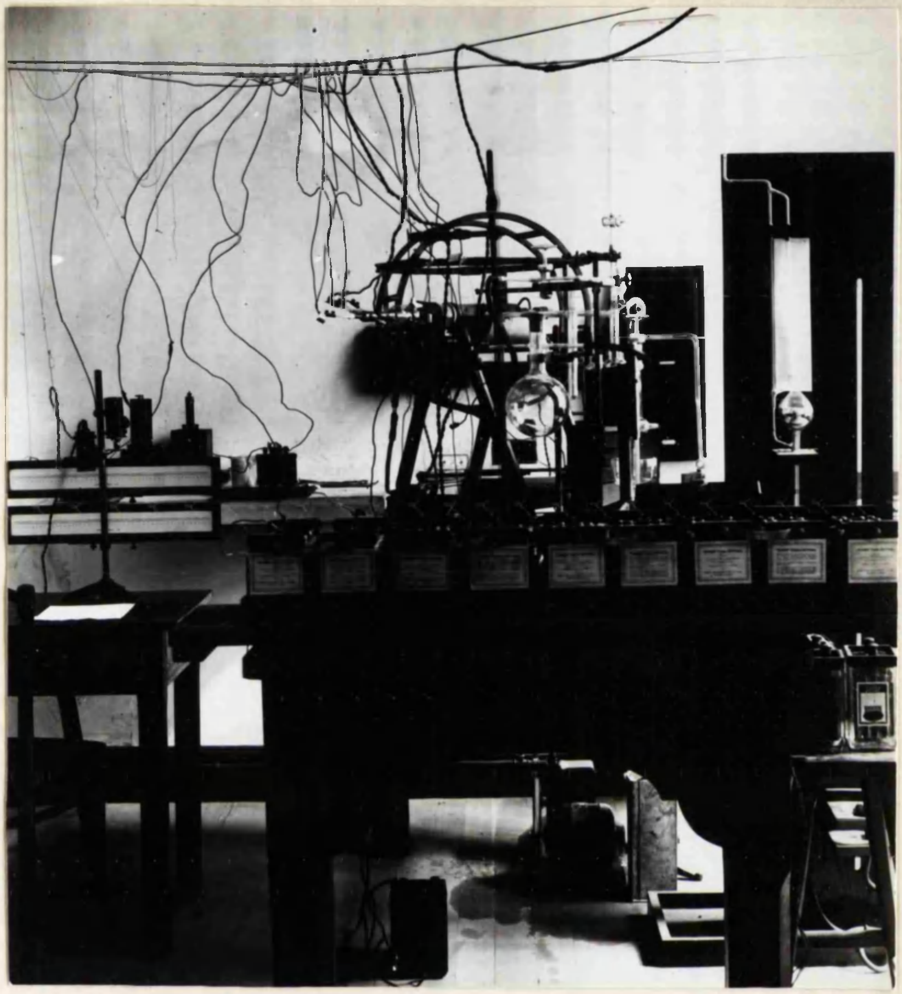


Plate II.

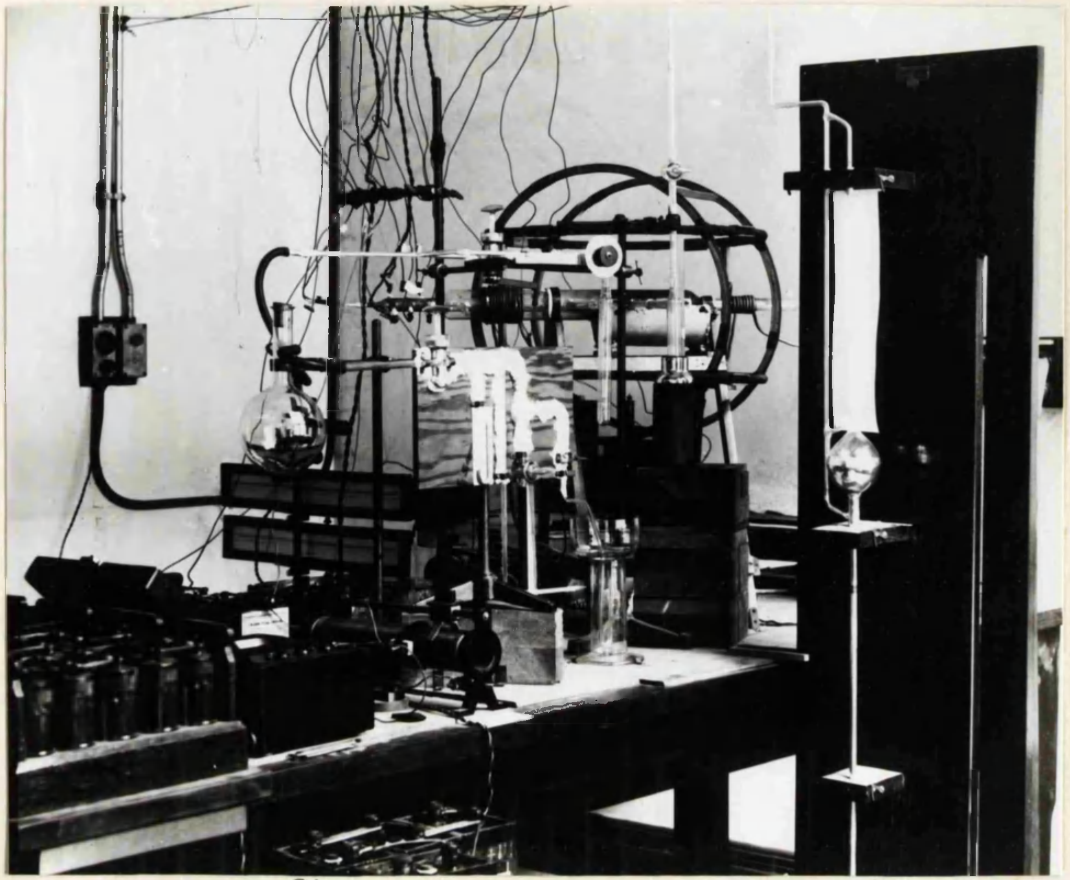


Plate III.

desired to let down the apparatus. When this had to be done the air was always let in through a drying tube so that only dry air got in. Thus on pumping down again little trouble was experienced due to the presence of much water vapour. The McLeod could also be cut off by means of a tap, which was always closed when air was let in to the apparatus so that the mercury in the gauge had as little chance as possible of becoming contaminated.

A small electrical furnace was constructed to fit round the pyrex chamber at the position of the apparatus, so that gas could be removed from the metal of the apparatus and the glass walls by baking out at a high temperature. This was done originally at 450°C but later at about 350°C. since at the higher temperature a metallic vapour, probably zinc was found to come off the silver solder and settle on the insulation, thus rendering it conducting. Coils of composition piping were fitted round the outsides of the two ground joints so that, by passing water through the pipes, the joints could be kept cool during baking out and so prevented from cracking or sticking.

The apparatus was baked out until the pressure became less than 10^{-3} mm. of mercury with the furnace still on; the filament was then switched on with the highest possible accelerating potential applied to it, and the furnace was kept on till the pressure again fell to the above value. By this means all gas was effectively removed from the filament box C. If this was not done it was found that the heat of the filament brought off a lot of gas from the box C during a run, and quite an appreciable pressure would build up in the apparatus. After baking out, a pressure in the apparatus, when cold, of the order of 10^{-6} mm. of mercury or less, could be obtained with the filament off, i.e. a sticking vacuum. During a run the pressure was of the order of 10^{-4} mm. of mercury, due to the foreign gas, which was negligible compared to the pressure of the mercury vapour.

When a new filament was put in, it was first of all run for some two minutes at about 2 to 3 milliamps emission with the full potential on; and then for a short time at a large emission, of the order of 100 ma. This was done in order to remove gas from the filament.

In the case of the experiments on mercury vapour, described later in this thesis, no liquid air was used on the traps. A plentiful supply of mercury vapour was obtained from the McLeod gauge and the diffusion pump. The pressure of the mercury vapour was obtained from a knowledge of the temperature of the scattering chamber as determined by a sensitive thermometer placed as close as possible to it. The vapour pressure was obtained from the International Critical Tables Vol. III, page 206. The range of pressures was approximately from $1{\cdot}0 \times 10^{-3}$ to $1{\cdot}5 \times 10^{-3}$ mm. of mercury.

A diagram of the electrical circuit used is given in fig. (10). The potentials used were read on a Weston standard voltmeter. The total emission from the filament was obtained from a milliammeter (ma.) provided with a built-in shunt. This instrument was protected by a fuse from an overload, due to an electrical short between the filament and its case C, or due to an arc between the filament and its case. The galvanometer G_1 which recorded the scattered current as received by the collector C was a Leeds and Northrup instrument having a sensitivity originally of 3×10^{-11} amps per millimetre at one metre; but a breakage of the suspension caused the sensitivity to decrease to $5{\cdot}87 \times 10^{-11}$ amps per mm. at which value most of the results later on were obtained. To measure the unscattered primary beam reaching the collector B, a Gambrell galvanometer G_2 was used whose sensitivity was $10{\cdot}4 \times 10^{-11}$ amperes per mm. at one metre. Both galvanometers were used in conjunction with universal shunts. Protecting fuses were also used. The average value of the current in the beam was of the order of 10^{-8} amperes, while the total emission from the filament was seldom greater than 1 ma. and usually of the order of

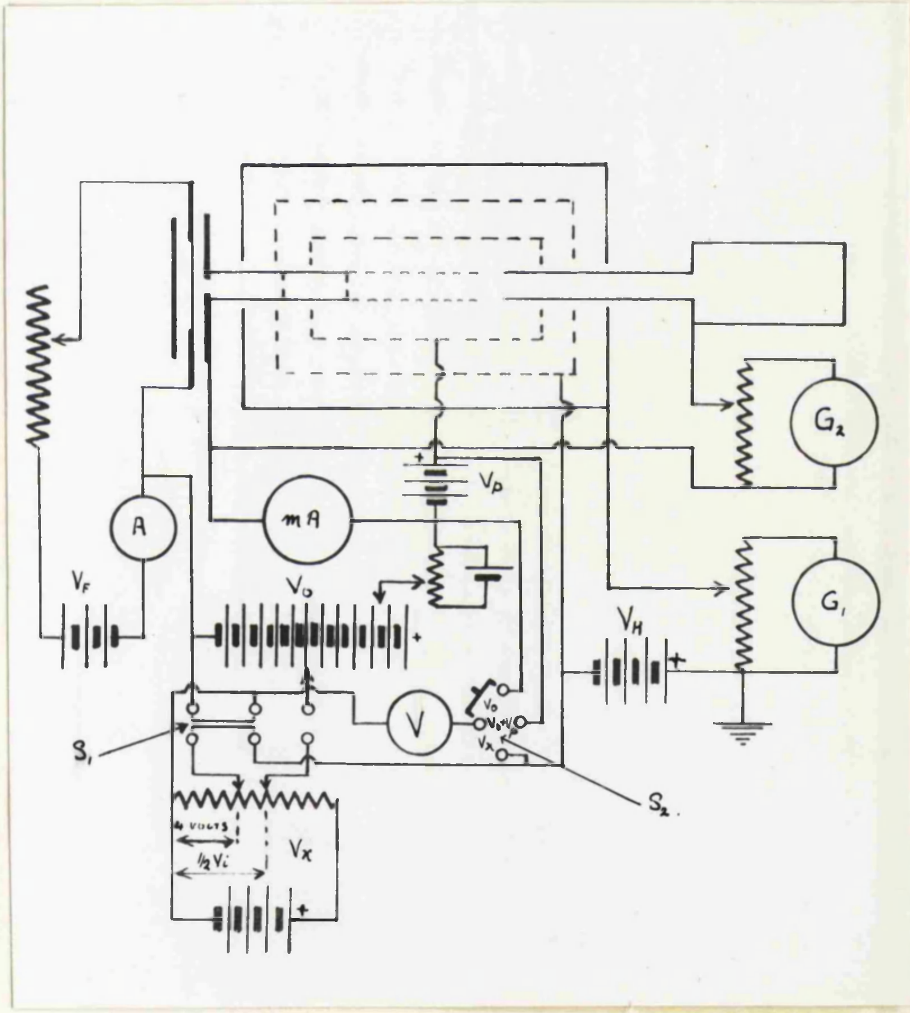


Fig. 10.

0·1 ma. By passing a known current through the galvanometers from a potential divider, graphs were obtained of the current against the deflection for each instrument. In both cases the relation was found to be accurately linear over the whole experimental range, i.e. 0 to 25 cms., on the galvanometer scales. The sensitivities of the instruments were obtained exactly from the slopes of these graphs. In the experimental work the galvanometer readings were corrected for the sensitivities by multiplying the readings of one instrument by the ratio of the sensitivities of both.

The current to the filament was controlled by two resistances, one of a large value and one of a small value, connected in parallel so as to give a fine control. These resistances were kept cool by being immersed in a bath of oil so as to prevent fluctuations in the filament current and so in the emission from the filament.

The arrangement of the various potentials applied between the grids etc. is as follows:-

The potential applied to the primary electrons as they leave the filament is denoted by V_o. It varied between 4 and 180 volts. It was derived from a block of accumulators of 4000-6000 ma. hour capacity. The filament is heated by a six volt block of large capacity accumulators, denoted in the diagram by V_f. A potential

V_p, obtained from two blocks of dry cells giving about 9 volts, is maintained between grids G_1 and G_2, G_2 being positive, so as to stop any positive ions from passing G_2 and reaching the collector C. It has been shown by Arnot (75) that the velocity of the positive ions diffusing from the path of an electron beam is never greater than about 3 volts. Between the grids G_2 and G_3, a retarding potential V_r for electrons is applied. By means of the mercury switch S_1, this retarding potential could be changed rapidly from one value to another. Finally between the grid G_3 and the collector C there was a potential V_H of 20 volts, with G_3 negative, in order to prevent the escape of secondary electrons from C. These secondary electrons might be brought off either by impact of the scattered electrons, or by impact of metastable atoms, or of photons arising from transitions due to excitation of the gas atoms by the electrons in the beam.

The values given to the retarding potential V_r varied with the object of the experiment. When it is desired to obtain measurements of the elastic and total scattering simultaneously, the two values of V_r obtainable by means of the switch S_1 are adjusted to be $(V_o + V_p - 4)$ volts and $\left[\frac{1}{2}(V_o - V_i) + V_p\right]$ volts respectively where V_i is the ionisation potential of the gas atoms. With the first of these values all electrons are stopped between G_2 and G_3 except those which have lost less than 4 volts energy. The electrons collected by C will then be all the elastically scattered electrons but none of those inelastically scattered, since the first excitation potential is at 4·86 volts, and any electrons which have excited this state will have lost this amount of energy and will therefore be stopped.

For a value of $V_r = \frac{1}{2}(V_o - V_i) + V_p$ volts it will be seen that both the elastically and inelastically scattered electrons are collected, as follows -

The energy of all electrons which have excited an atom in any way will be $(V_o + V_p - V_x)$ volts when they reach the grid G_2, where V_x is the excitation potential of the state which the electron has excited in the atom. Since V_x is always less than V_i all these electrons will be able to reach the collector C. When ionisation takes place, however, we have a different result. In such a case there are two electrons after the collision, the impacting electron and the ejected electron, where there was only one before the collision. Now we wish to collect only one of these electrons and since all the electrons are indistinguishable from each other it does not matter which one we collect. The total energy available to be divided between them immediately after the collision will be

$V_o - V_i$, where as before V_i is the ionisation potential, Now for every electron with energy greater than half this amount, there will be one with energy less than half; therefore if we make the grid G_3, $\frac{1}{2}(V_o-V_i)$ positive with respect to the filament, the probability is that we will collect half the electrons available after ionisation that is, we will collect the same number of electrons as those which have ionised atoms. Thus a value of $V_r = \left[\frac{1}{2}(V_o - V_i) + V_p\right]$ volts between grids G_2 and G_3 will insure that we will collect all the electrons which have been scattered, elastically and inelastically.

A second mercury switch S_2 is used to obtain the value of the potentials V_o, V_p or V_r rapidly. The amount which is to be subtracted off $V_o + V_p$ to get V_r is denoted in the wiring diagram by V_x, which should not be confused with an excitation potential.

The switch S_1 is necessary when it is desired to obtain results for the inelastic cross section by subtracting the elastic cross section from the total, since if the elastic and total curves were not taken simultaneously small variations of gas pressure, filament emission and position, and potentials of the batteries, might cause considerable errors in the difference curve, especially at low voltages where space charge effects might come in. Such errors had been found to occur when taking elastic and total curves consecutively before the switch was included in the circuit.

In passing through the various grids, some of the scattered electrons may bring off secondary electrons from the gauzes. These might cause considerable errors in the results if they were included in the scattered current. However it is known that most of these secondary electrons have very low energies. The ones brought off from the first and second grids will therefore be stopped by the retarding potential V_r. Secondaries brought off from the third grid would be able to reach the collector C. In the case of the elastic scattering, the energy of the scattered electrons when they reach G_3 is only 4 volts at the most so that they will not bring off many secondary electrons. The error in the result should then not be appreciable. When the inelastically scattered electrons are being collected, the retarding potential between G_2 and G_3 is much less than for elastic scattering, so that some electrons will reach G_3 with quite a large energy. In this case we might expect the secondary electron emission to be large. However it is shown in a later section that the error in the inelastic curves is never greater than 6% at low velocities and 10% at large velocities; most of this is probably caused by secondary electron emission from G_3 but even then the error is not serious.

Any secondary electrons liberated from C as mentioned before, will be prevented from leaving, by the potential V_H, since these electrons in general have low energies.

Since the apertures in the grids are approximately one millimetre square, and the distances between the grids are 5 mm., it is unlikely that there will be any errors in the results due to the interpenetration of the electrostatic fields between the grids.

A correction is however necessary for the stopping area of the grids. The transmission area has already been given as 71% of the total area, so that at each grid, the current will be reduced by the factor 71/100. Therefore after passing three grids, the current will only be $(71/100)^3$ of its original value. It is therefore necessary to multiply the current collected by C by this factor $(100/71)^3$, which works out to be 2·8, to get the original scattered current. This has been done in calculating the results for the total cross section; it will be seen later that this effect does not alter the elastic or inelastic cross sections. The correction factor is probably only approximate since electrons may be deflected past the meshes of the grids and so not be lost from the scattered current, or vice versa, they may be drawn on to the meshes by the lines of force. These effects will almost certainly vary with the velocity, so that they cannot be allowed for.

We can therefore only use the factor given above, which on the average, will probably be fairly correct.

Knowing the scattering distance x and the radius of the tubes D or E with the insulation on them, we can find the minimum angle through which an electron can be scattered and still be received by the collector C. Since the thickness of the sindanyo insulation is 1·5 mm., and the diameter of the tubes is 4 mm., this angle is $\tan^{-1}(0{\cdot}35/2{\cdot}2)$, which is equal to $9^\circ 2'$. The largest angle is then $180^\circ - 9^\circ\,2' = 170^\circ\,58'$. It should be noticed that these angles are for scattering just at the beginning and end of the length x, respectively. Also at these minimum and maximum angles, the maximum and minimum angles respectively are 90°. By the integration method of averaging, the average angular scattering range over the whole distance x, is found to be 25° to 155°. This however assumes that the scattering is uniform along the distance x. In practice the scattered intensity decreases with increasing x, since the beam decreases exponentially with x. Again since more electrons will be scattered at the beginning of the path length x than at the end, and since the majority for most velocities are scattered in the forward direction, for which for small x the limiting angle is small, this effective angular scattering range is probably too small.

No correction has been employed for the fact that electrons scattered through certain angles will pass through the grids obliquely, so that even although their velocity might be sufficient to overcome the retarding field, their direction is such that the component of their velocity in the direction of the field is not. Thus such electrons which should get through and be collected, are stopped. The agreement between the results and the work of other investigators, which is shown later, indicates that any errors due to this cause must be quite small. For very few scattering angles will the angle between the electron's path and the direction of the field be sufficiently large as to cause a serious error, due to this cause.

SECTION 6.

EXPERIMENTAL PROCEDURE AND TESTS OF THE APPARATUS.

The theory of the passage of a beam through a gas has been given in a previous section (1) where the P20 following formula was obtained -

$$I = I_0 e^{-x\alpha p} \qquad (1)$$

I_0 being the intensity of the beam when it enters the distance x and I the intensity when it leaves it, and p the gas pressure. α was shown to be the cross section of all the molecules in unit volume at unit pressure and at 0°C. The unit of pressure is 1 mm. of mercury. is variously called the cross section, the absorption coefficient and the probability of collision.

From the above expression the cross section is obtained as $\alpha = 1/xp \cdot \log_e I_0/I.$ (2)
This expression gives the total cross section for all types of collisions denoted by α_t.

In order to determine any specialised type of cross section, this formula cannot be used. The reason for this is that neither I nor I_0 are affected in any way by the manner in which the electrons leave the beam, nor by any velocity analysis which may be applied to the scattered electrons. In practice I_0 is determined by adding the beam current and the scattered current. This

This cannot give a correct result when the measurements of the elastic cross section or the discrete inelastic cross sections are being made, since it is equivalent to neglecting from the beam, I_o, all those electrons which have made collisions other than of the specified type. This is obviously wrong since we require to know the fraction of the total number of electrons, which had started on the path, which was scattered in a certain manner, and not the fraction of the number given by the sum of the unscattered electrons and the number scattered in the given manner.

The correct formula which must be used to obtain the elastic cross section α_e is -

$$\alpha_e = \frac{N_e}{N_t} . \alpha_t \qquad (3)$$

where N_e is the number of electrons scattered elastically from the beam and N_t is the number scattered by all types of collisions, in the path length x. Multiplying each of these by the charge on the electron, we obtain the scattered intensities I_e and I_t. Thus

$$\alpha_e = (I_e/I_t)\alpha_t . \qquad (4).$$

This relation is exact. If I_e and I_t were small compared to I, equation (2) could be used to give α_e, since it can be shown that it reduces to the above expression. However for low velocities, I_e and I_t are not small compared to I, so that the exact relation must be used.

The exact relation is more simple to calculate than the approximate one, but it requires a knowledge of the total cross section α_t.

The inelastic cross section α_n, can then be found from the difference of the total and the elastic cross sections, as -

$$\alpha_n = \alpha_t - \alpha_e \qquad (5).$$

If I_x is the intensity scattered due to electrons which have excited the atom to any particular energy level, then the cross section α_x for excitation of this level is -

$$\alpha_x = \frac{I_x}{I_e}\alpha_e$$

$$\text{or} \qquad = \frac{I_x}{I_t}\alpha_t \qquad (6).$$

Similarly if I_i and α_i are the scattered intensity and cross section respectively for ionisation to be a certainty, we get -

$$\alpha_i = \frac{I_i}{I_e} . \alpha_e$$

$$\text{or} \qquad = \frac{I_i}{I_t}\alpha t \qquad (7).$$

The values of V_r used in the determinations of the elastic and total cross sections have already been given. The experimental method is, at each velocity V_o to take consecutive readings of the two galvanometers, with the two different values of V_r as obtained by the switch S_1. Let the readings of the scattered current be S_e and S_t, with the switch in the elastic and total positions respectively. If the two readings are done rapidly the beam current should not vary appreciably; however it was found that the beam current did vary, so that we read also the two values B_e and B_t of the primary unscattered beam current. The scattered currents are obtained from galvanometer G_1 and the beam currents from G_2. This procedure is repeated at each value of V_o.

Suppose that the currents S_e, S_t, B_e, and B_t are all in the same units, that is they have been corrected for the galvanometer sensitivities.

To obtain the total cross section, we see that I is given by B_t, and I_o by $B_t + 2{\cdot}8\ S_t$, where the factor 2·8 is the correction factor for the stopping power of the grids as previously explained.

Thus -
$$\alpha_t = 1/xp \cdot \log_e \frac{B_t + 2{\cdot}8\ S_t}{B_t} \qquad (8).$$

From this equation the value of α_t can be calculated for various values of V_o, and so the required cross section curves can be obtained.

The elastic cross section was determined from the equation (4). It can easily be seen to be given by -

$$\alpha_e = \frac{S_e}{B_e} \cdot \frac{B_t}{S_t} \cdot \alpha_t \qquad (9).$$

The presence of the B's in this equation will be discussed later.

The inelastic cross section is then obtained as in equation (5).

The method of determining the discrete inelastic cross sections was as follows. The switch S_1 was used to obtain two values V_{r1} and V_{r2} of the retarding potential between the grids G_2 and G_3. The two values used to obtain an excitation function were $V_{r1} = V_o + V_p - \delta_1$, and $V_{r2} = V_o + V_p - \delta_2$. In these expressions, δ_1 is chosen to be just below the critical potential of the level being studied and δ_2 is chosen to be just above the critical potential. The difference between the two scattered currents S_{x1} and S_{x2}, received by the collector C with the two values of V_r should then be due to electrons which had excited the given state and lost energy equal to the energy of excitation of the given level. For these values of V_r we have the values B_{x1} and B_{x2} of the primary beam current. The values of δ_1 and δ_2 used in studying the excitation function of the 4·86 volt state in mercury, were 4 volts and 5·7 or 6·3 volts respectively. Both values of δ_2 gave practically identical results within the limits of experimental error. For the 6·67 volt state δ_1 and δ_2 were 6 volts and 7·4 volts respectively.

In studying the cross section for ionisation, V_{r1} was made equal to $(V_o + V_p - 9{\cdot}5)$ volts, while for V_{r2} was used the value for the total cross section, i.e.

$\frac{1}{2}(V_o - V_i) + V_p$. The difference between the scattered currents in these cases should be due to electrons which have ionised atoms, generally in the simplest possible manner, with loss of 10·38 volts energy.

The excitation cross sections can then be calculated from expression (6) in either form. They reduce respectively to -

$$\alpha_x = \left[\frac{S_{x2}}{B_{x2}} - \frac{S_{x1}}{B_{x1}}\right] \times \frac{B_e}{S_e} . \alpha_e$$

$$\text{or} \qquad = \left[\frac{S_{x2}}{B_{x2}} - \frac{S_{x1}}{B_{x1}}\right] \times \frac{B_t}{S_t} . \alpha_t \qquad (10)$$

Similarly the ionisation cross section is given by -

$$\alpha_i = \left[\frac{S_{i2}}{B_{i2}} - \frac{S_{i1}}{B_{i1}}\right] \times \frac{B_t}{S_t} . \alpha_t \qquad (11).$$

Since S_{i2} and B_{i2} are the values with V_{r2} the same as for the total cross section, this expression reduces further to -

$$\alpha_i = \left[1 - \frac{S_{i1}}{B_{i1}} . \frac{B_t}{S_t}\right] . \alpha_t \qquad (12).$$

From these equations all the required cross sections can be calculated.

All the results which were averages of a varying number of readings, were reduced to their values at a pressure of one mm. of mercury and a temperature of 0°C. The correction factor for temperature and pressure whenever it was used, was $\frac{I}{p}\frac{273}{(273+T)}$ where p is the vapour pressure in mm. of mercury corresponding to a temperature of $T^{o}C$. In cases where the galvanometer readings had to be corrected directly as in equation (10) it should be noticed that S/B must be multiplied by the factor, not S and B separately. In all the above equations for excitation and ionisation cross sections, α_e or α_t must also be corrected for temperature and pressure independently of the factor $I_{x,i}/I_{e,t}$ by which it is multiplied. In cases such as equation (12) where the expression is symmetrical and all the readings have been taken together at the same temperature, the first factor is independent of temperature and pressure.

Finally it should be noticed that α_t as obtained from equation (2) must be corrected for the base of the logarithms by multiplying by 2·303.

In section (7), the left hand ordinate scale gives the cross section of all the atoms in one cubic centimetre in units of cm^2/cm^3.; while the right hand scale gives the cross section of a single atom in atomic units, πa_0^2.

TESTS ON THE WORKING OF THE APPARATUS.

During the early part of the work before the apparatus in its final form was evolved, the most usual method of testing was to connect the second and third grids to the collector C, thus eliminating all the fields V_p, V_r, and V_H. The apparatus could then be used as a simple Lenard apparatus and measurements could be taken of the total cross section directly. By comparing the results with Brode's for the same effect in mercury vapour (76), an idea could be formed of the faults in the working of the apparatus. By this means the faults in the original gun were detected. Attempts to obtain total cross section curves by using the grids and the appropriate value of the retarding potential, showed that the original grids were of too fine a mesh to pass a current of sufficient intensity to be measured. For this reason the new grids of nickel gauze were constructed. Variations of the value of V_o without the filament on, showed that there were considerable zero shifts in the galvanometers due to leaks, across the insulation of the apparatus, and to earth across the cases of the galvanometers. Great care had to be taken with the insulation of the galvanom: :eters. They were finally placed on small ebonite discs which had a ring of sulphur let into them. The V_o

accumulators and the filament batteries were insulated in the same way. This has been found to be one of the most effective methods of insulation. Much of the pyrex and sindanyo insulation of the apparatus had to be replaced by quartz, since the insulating properties of both the former were found to deteriorate considerably with rise in temperature and also with time, the latter being probably due to the deposition of a film of mercury vapour on them. These effects do not appear to be present to the same extent with quartz, which can also be cleaned easily by burning off the impurities, with a blow-pipe flame.

An interesting fact which was noticed was that even when the insulation of the whole apparatus and circuit was as good as possible, there were slight zero shifts with V_o on the galvanometers. The extent of this zero shift was found to vary with the state of the atmosphere. On dry days it was negligible, while on wet days it was quite appreciable. The effect was worse in the summer than in the winter. It was concluded that it was due to leaks over the galvanometer casings to earth through the atmosphere. This was verified by the fact a connection to earth on the circuit side of the high sensitivity galvanometer completely cured the effect in that instrument. The variation with summer and winter must have been due to the greater amount of ionisation, present in the atmosphere in the summer, due to the heat of the sun.

With the actual apparatus as used to obtain measurements of the cross sections, a number of tests of the working were applied.

Velocity distribution curves of the electrons in the main beam were obtained by applying a retarding potential between the tube E and the grid G_1. The readings obtained were corrected for variations in the initial beam current by employing a mercury switch similar to S_1, by means of which the retarding potential could be rapidly switched in and out. The results for beams of 12 and 100 volts energies are given in fig. (11), together with curves obtained by differentiating the velocity distribution curves. From these curves it is seen that the beams are very homogeneous. For the 12 volt beam, the curves show that 90% of the electrons have energies within a 2 volt range; while for the 100 volt beam 96% have energies within a range of $1\frac{1}{3}$ volts. The results of this test were thus very satisfactory. It was not possible to obtain velocity distribution curves for the scattered current, showing the various critical potentials, on account of the background of fast and slow electrons, which had not been scattered by gas atoms.

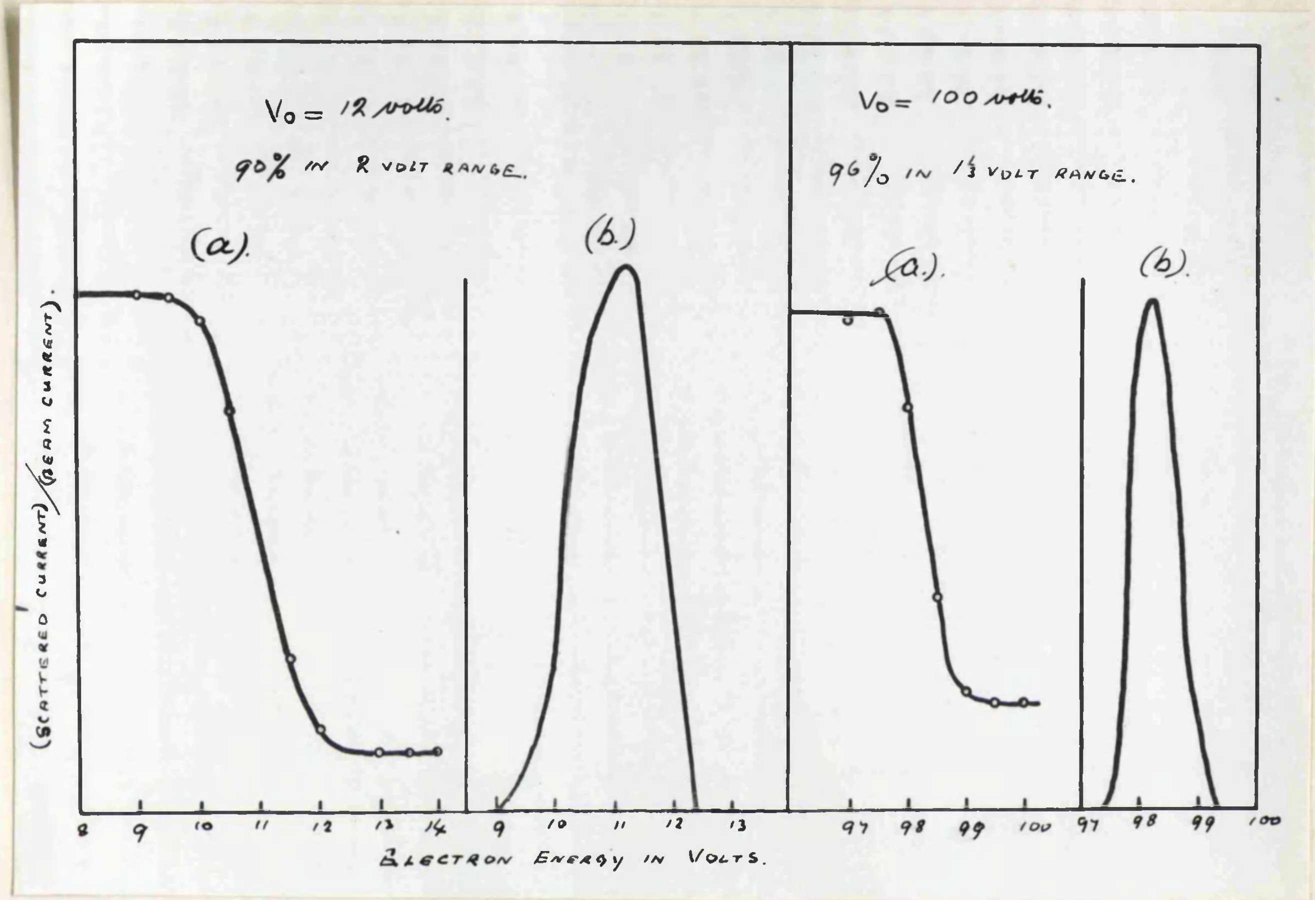


Fig. 11, (a) Retarding Potential Curves. (b) Differentiated Curves.

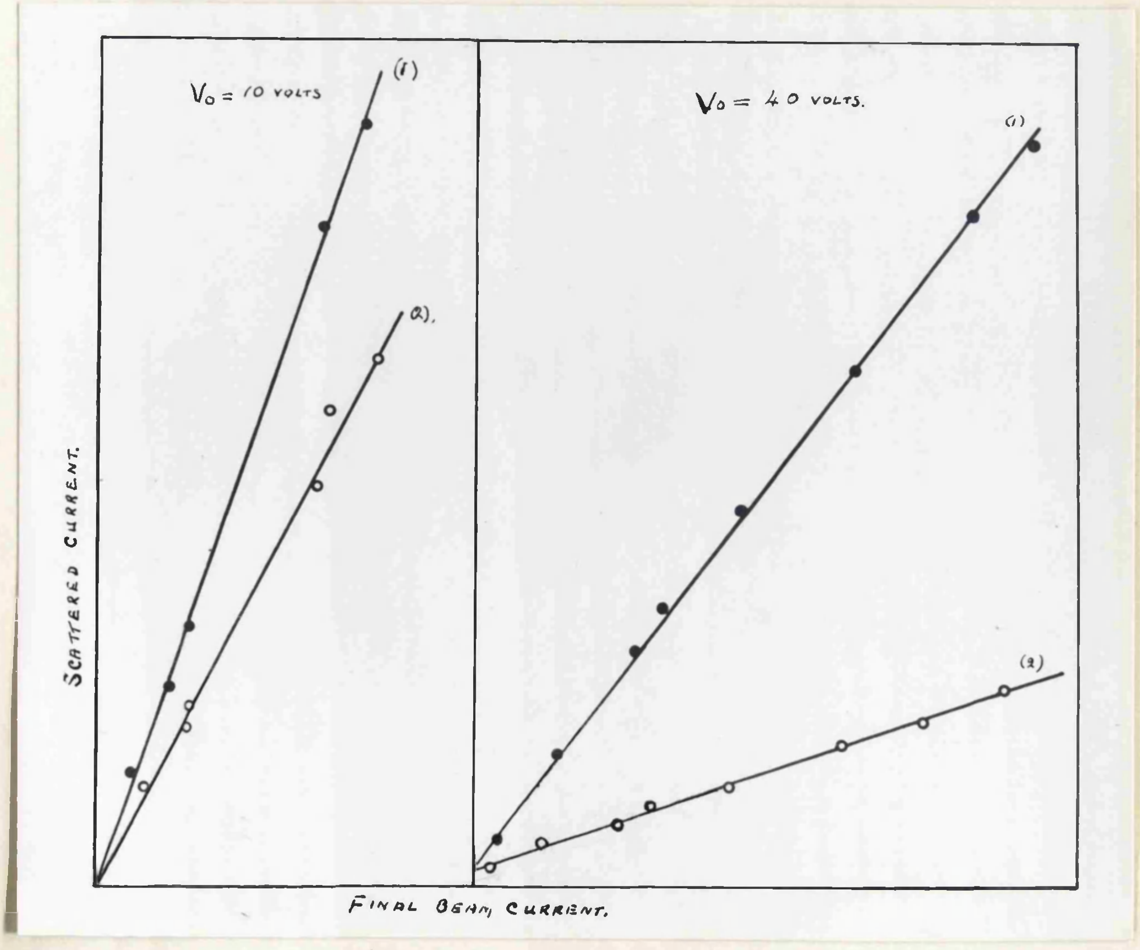


Fig. 12.

This background effect will be discussed later.

A further test applied was based on the following argument. The intensity of the beam entering the length x is proportional to $B + S$, while the scattered intensity is proportional to S. Now for a given velocity V_0, the scattered intensity should obviously be proportional to the intensity in the beam at $x = 0$. Thus $S \propto B+S$, which can be written as $\frac{B+S}{S} \doteqdot k'$ where k' is constant for given V_0. Thus $B/S = k' - 1$ or $S/B = 1/(k' - 1)$ k where k is also a constant. This relation should hold for all types of scattered currents S, elastic, inelastic and so on. Thus for a given value of V_0, S should vary linearly with B. By varying the filament heating current and so the emission from the filament, curves can be obtained for the variations of S with B. Such curves for a 10 volt beam and a 40 volt beam are given in fig. (12). The graphs marked (1) are for the total scattering, and those marked (2) for the elastic scattering. The curves are seen to be quite good straight lines, in agreement with the discussion given above. The region of linearity of the curves is the region in which measurements were made in determining the experimental cross sections.

A further test which was applied was to connect the third grid G_3 to the collector C, and then apply potentials between grids G_1 and G_2 and the collector C in the manner of

Davis and Goucher's method for determining critical potentials (77). By this means curves similar to the results of these two workers were obtained. Knowing the ionisation potential of mercury to be 10·38 volts, the correction to the experimental voltage scale necessary to bring the observed ionisation potential to the correct value, was found. This correction was caused by the potential drop along the filament and also by stray contact potentials in the apparatus. The correction was found experimentally by this method, to be only a few tenths of a volt, which value is within the limits of experimental error, so that no value of the correction is apparent from this method. A correction of about one volt is applied to the excitation and ionisation curves, having been indicated by the retarding potential curves, and being necessary to make them extrapolate to their appropriate critical potentials.

Test runs made with liquid oxygen on the traps, showed that there was a background scattered current of quite large magnitude at moderate and low velocities. This background, the effects of which on the experimental results will be discussed fully in a later section, is apparently due to slow secondary electrons brought off from various parts of the apparatus by the primary electrons in the beam and scattered current, and also to electrons which reach the collector C due to the spreading of the beam. A number of tests were carried out to try and reduce this effect due to the spreading of the beam. The final hole of the gun was carefully bevelled and smoothed to remove roughness; the filament was tried at various positions in its box, in attempts to obtain a focussing effect; and finally the final gun hole and the first grid were coated with soot as this had been found by many workers to reduce secondary emission. None of the modifications produced any improvement however. The sooting was especially troublesome since it was difficult to keep it from the insulation of the grids and collectors on which it formed conducting layers, which were exceedingly difficult to remove.

SECTION 7.

EXPERIMENTAL RESULTS FOR THE CROSS SECTIONS OF THE MERCURY ATOM.

For the total cross section of the mercury atom some thirty results extending over a number of months were reduced to unit pressure at $0^{\circ}C$. and then averaged. The range of energies was 4 to 180 volts. The results are shown in fig. (13) along with Brode's curve also for the total cross section. It will be seen that the experimental curve agrees in absolute magnitude with Brode's curve at 60 volts, but that above this value it falls off more rapidly, and below this value it rises more steeply. The value of the total cross section at 180 volts is approximately half that obtained by Brode, while at 4 volts the value is some eight times Brode's value.

This large difference is almost certainly due to the beam spreading at low energies and not entering the tube E. This would have the effect of increasing I_o/I in equation (2), Section 6, by substracting an equal amount from both numerator and denominator of this fraction since $I_o > I$.In addition the beam may become so diffuse that some of it may pass through the grids and reach the collector C, thus further increasing I_o and so

α_t, since I_0 is experimentally determined by being given by $I_s + I$, where I_s is the scattered intensity. This explanation was further substantiated by the tests made with liquid oxygen on the traps. When this was done, theoretically a negligible scattered current should be obtained, actually in practice, zero current is obtained down to about 50 - 60 volts, below this a scattered intensity increasing with decrease in V_0 is obtained. It had been hoped to be able to apply a correction to the total cross section curves by substracting the cross section obtained with liquid oxygen from the experimental total cross section. This however was found not to be possible since with liquid oxygen, the beam spreads at low voltages even more than with gas in the apparatus. As has been explained in a previous section, most workers overcame this difficulty bybusing an equation for the intensity I of the beam in the form $I = kI_0 e^{-x\alpha p}$, k being a factor depending on the velocity. By using two or more different values of p, k can be eliminated and the correct total cross section determined. This method was not possible in the case of these experiments on mercury, since to vary the pressure of mercury requires a change in temperature. A rise in temperature, however, as explained previously, causes the insulation of the grids and collectors to deteriorate, and thus cannot be used.

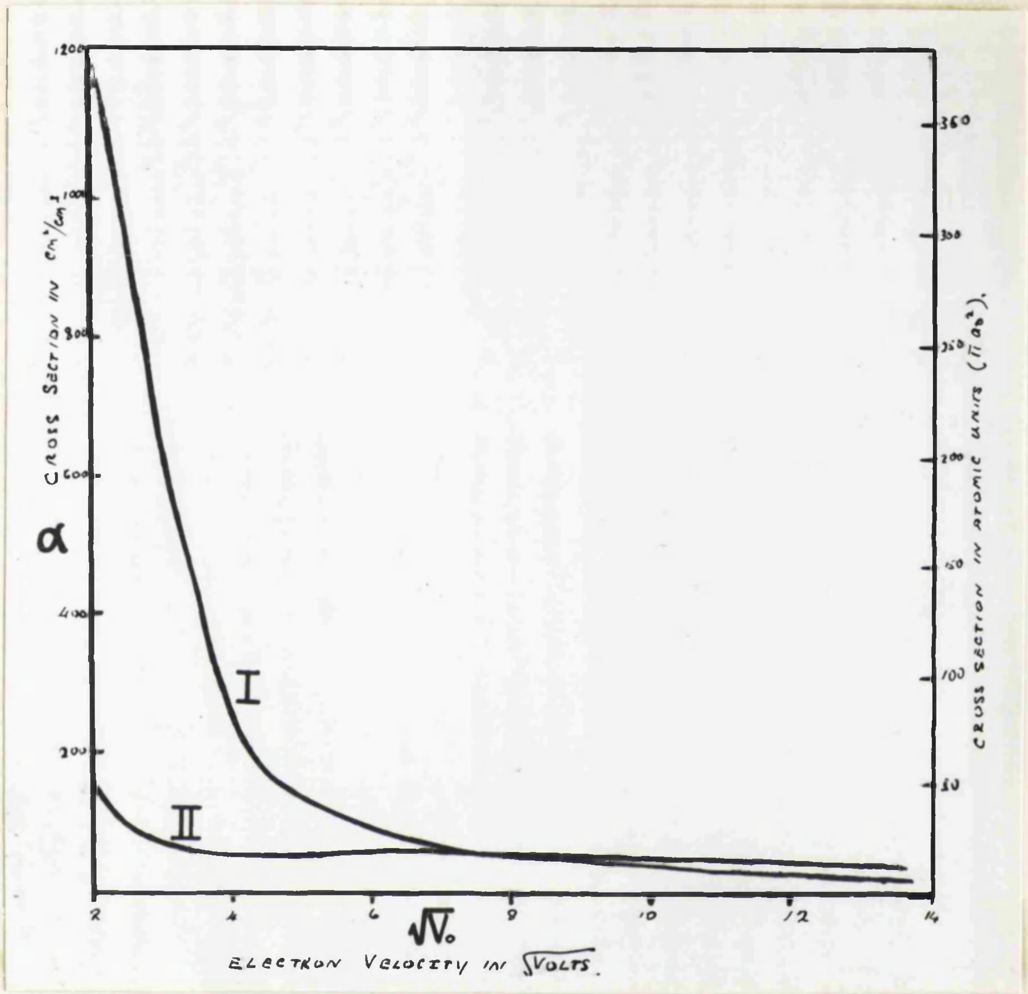


Fig. 13. (I) Experimental Curve. (II) Brode's Curve.

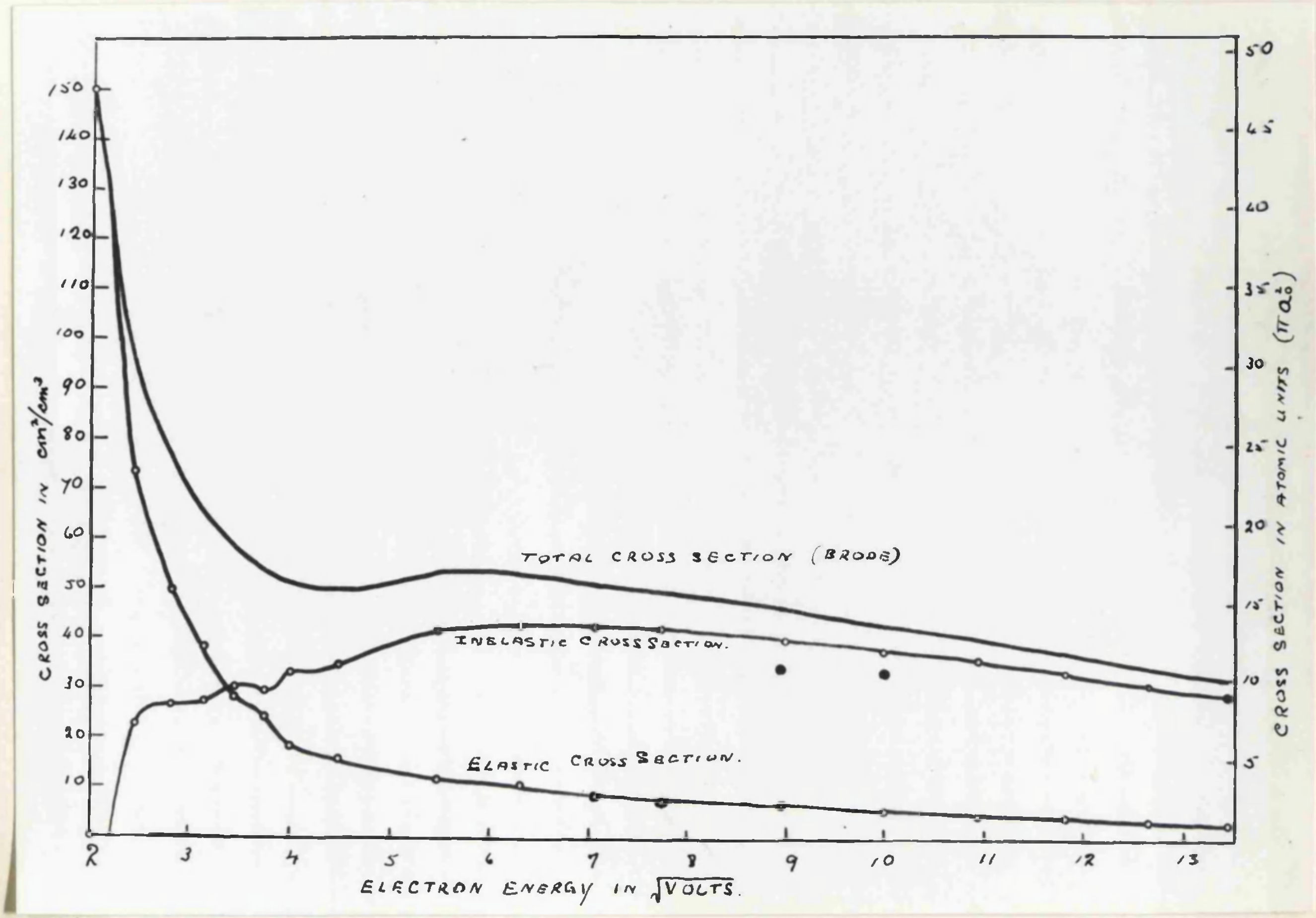


Fig. 14.

The more rapid fall of the cross section at higher energies than 60 volts was probably due to the loss of a number of electrons scattered forward through small angles, since angular distribution experiments have shown that at energies of 100 volts and over, the scattering per unit angle shows a large maximum at small angles, less than about 30°. The angle decreases with increasing velocity, so that we would expect the agreement to become steadily less as the energy is increased.

On account of the wide deviations of the experimental values of the total cross section from Brode's result, which has been found to be in good agreement both in shape and absolute magnitude with the results of annumber of other workers, it was decided to use Brode's values for the total cross section as a basis in calculating the elastic and inelastic cross sections.

In the calculation of the elastic cross section from equation (4), section (6), Brode's values for α_t have been used, and also the average of eighteen sets of values for the elastically and totally scattered intensities I_e and I_t, at each voltage. Since the values of I_e and I_t i.e. S_e/B_e and S_t/B_t, are always taken at the same temperature and pressure for each set, no correction is necessary in I_e/I_t for these latter. An error might be introduced into α_e due to the spreading of the beam but this is discussed later and it is shown there that the error is probably quite small.

The elastic cross section curve obtained by this method is shown in fig. (14), along with Brode's total cross section curve and the inelastic cross section curve obtained from their difference. The interesting features of the elastic cross section curve are, that it shows a monotonic decrease of cross section with increasing velocity, and that the small maximum which is present in the total cross section curve at 35 volts does not appear in it. Brode has postulated that this maximum is due to a rapid increase of the probability of ionisation at this energy; the above results further strengthen this view. A very slight change of slope at 14 volts energy in the elastic curve is probably due to experimental error.

The inelastic cross section rises from zero at about the first excitation potential, to a broad maximum at about 40 volts and then falls steadily as the energy of the electrons is further increased. The small maximum and minimum at low voltages may be due to experimental error, or they may be due to the sudden onset or rapid increase of the excitation of discrete levels in the atom at these particular energies. It is interesting to note that if, at each of these points at low energies, where an upward change of slope occurs as the energy is increased, the direction of the curve be extrapolated to zero cross section, the value of the energy obtained lies at one of the main critical potentials of the mercury atom. This, however, may only be an interesting coincidence. Too much attention should not, therefore, be paid to it.

The only other experimental results for the inelastic cross section which can be obtained, are to be had from Tate and Palmer's work (78). They have integrated their angular distribution curves for excitation and ionisation and so obtained curves for the excitation cross section and the ionisation cross section. By adding these curves, we obtain the inelastic cross section. Their energy range is 80 to 700 volts, so that not much comparison is possible. The solid points appearing in fig. (14) are Tate and Palmer's values for the inelastic cross section at 80, 100 and 180 volts. The agreement is seen to be quite good, especially in the case of the 180 volt point which lies exactly on the author's curve.

IONISATION AND EXCITATION CROSS SECTIONS.

In figure (15) is given the curve for the probability of ionisation obtained from equation (12), section (6), using Brode's values for the total cross section. The curve for the efficiency of ionisation as determined by Bleakney (79) is also given. A number of workers have obtained curves for the efficiency of ionisation with quite good agreement between their results; Bleakney's being a typical curve. The method used by him, is one in which the positive ions are recorded. It has been fully discussed in a previous section, and the differences between the method and the one used here have been fully dealt with. The conclusion arrived at was that since the author's method involved measurements of the number of electrons which ionised the atom, by ejecting the most loosely bound electron, while Bleakney's method included ionisation by ejection of any electron, or more than one electron, the results might differ considerably.

The agreement between the curves in fig. (15) is then possibly as good as can be expected from two such totally different methods. It should be noticed that the method used in this work would include electrons which had lost about 10 volts energy by exciting an atom twice

This however would probably require two separate collisions which has been made very unlikely by suitable choice of the gas pressure. Again, it should be noticed that the method might include at high velocities some of the electrons which had ionised an atom by ejecting an electron other than the most loosely bound one, or by ejecting more than one electron in one collision. The next ionisation potential for single ionisation is of the order of 30 volts, and since it has been shown by Tate and Palmer and others that, when ionisation takes place, it is most probable that the available energy will be divided between the impacting electron and the ejected electron so that one of them takes the most of it, we would expect to collect some of the electrons which had ionised the atom in this way when, -, $\frac{1}{2}(V_o - 10{\cdot}4) \leq V_o - 30$ i.e. when $V_o > 50$ volts. Since the probability of ionisation in this way is quite small at moderate velocities and since owing to the division of the available energy between two electrons we are not collecting them all with a retarding potential of $\left[\frac{1}{2}(V_o - 10) + V_p\right]$ volts, the effect of ionisation in this manner can be neglected in the experimental results obtained by the method used here, at least in the energy range up to 180 volts. To cause double or treble ionisation of an atom will require even more energy than for the above method of single ion:

:isation and so any error due to this effect is also quite negligible in the given velocity range. It is thus seen that we are here most probably measuring the probability of single ionisation by ejection of the most loosely bound electron, which process requires an amount of energy equal to 10·38 volts.

From a comparison of the experimental curve with Bleakney's curve, it may be concluded that the apparatus is working very satisfactorily, especially in the method of analysing the scattered electrons into energy groups by means of the system of grids, and also in the method of collecting the electrons, both scattered and unscattered

The experimental ionisation curve shows a steady rise from the ionisation potential to a broad maximum at about 65 volts of about 33 cm^2/cm^3 value. Beyond the maximum the curve falls again fairly steadily. The small maximum at about 15 volts energy will be discussed later, where it will be shown that it is not due to ionisation. Bleakney's curve exhibits a broad maximum of about 25 cm^2/cm^3 at 80 volts energy. The difference between the curves at low energies is very small, and also at high energies, between 150 and 180 volts the difference is seen to be decreasing. Both these facts will be seen to be important when the error in the experimental curve is discussed later.

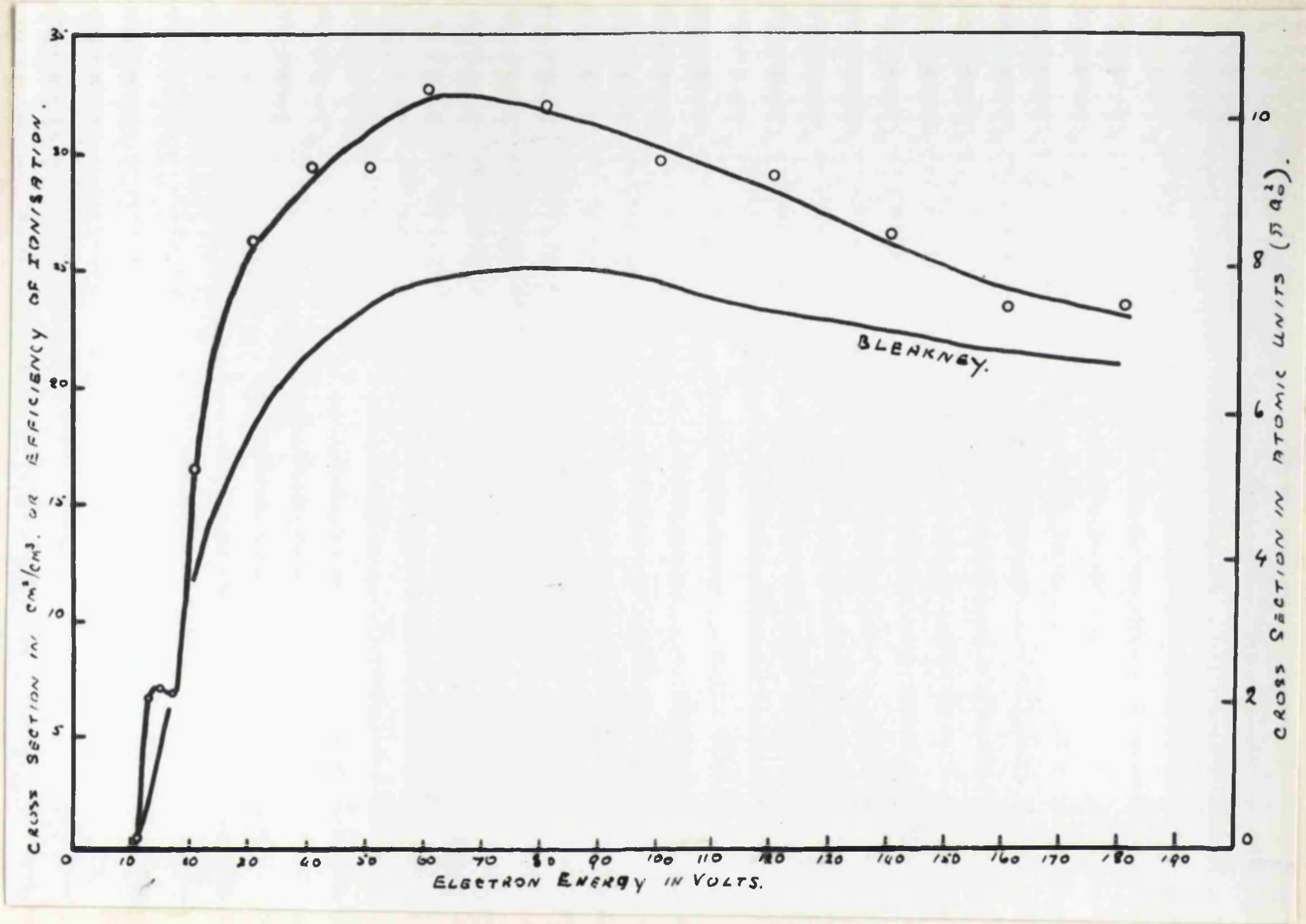

CROSS SECTION IN CM²/CM³. OR EFFICIENCY OF IONISATION.
5
10
15
20
25
30
CROSS SECTION IN ATOMIC UNITS (πa₀²).
0
2
4
6
8
10
BLENKNEY.
0
10
20
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ELECTRON ENERGY IN VOLTS.

Fig. 15.

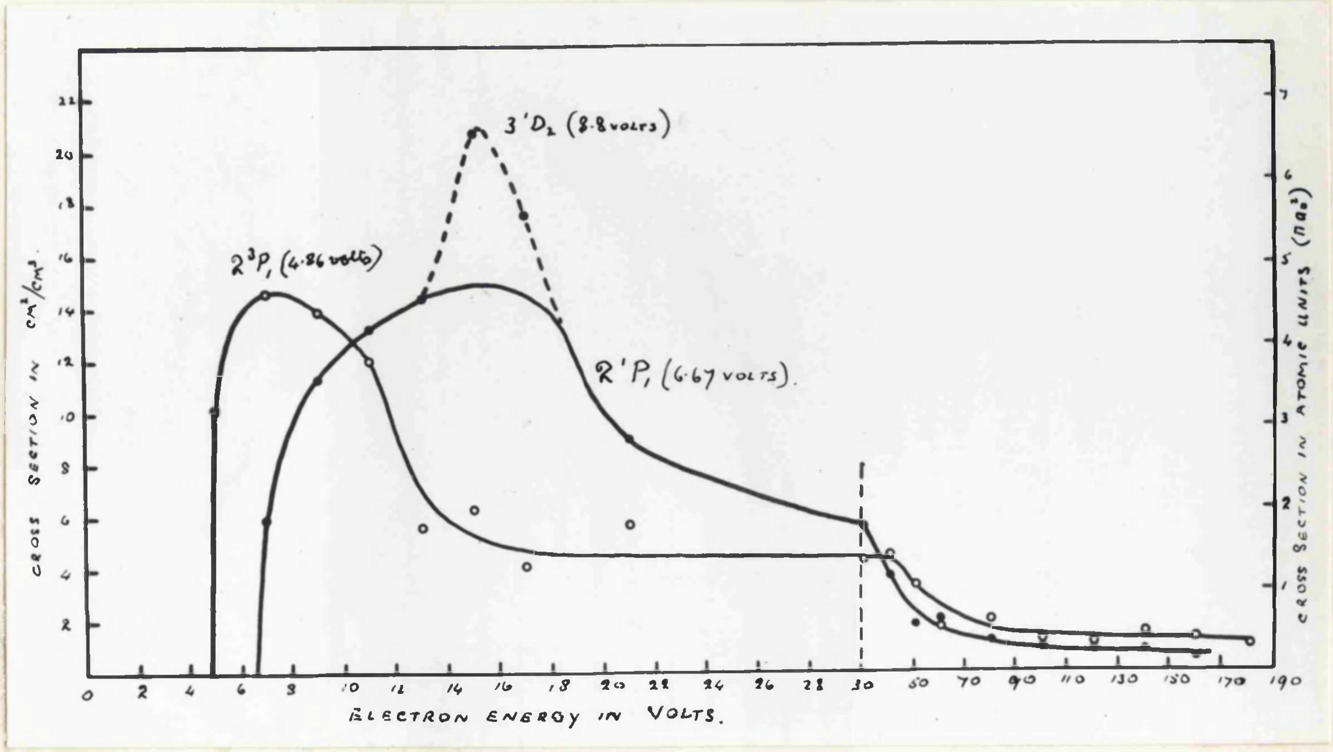

3'D₂ (8.8 volts)
2³P₁ (4.86 volts)
2'P₁ (6.67 volts).
CROSS SECTION IN CM²/CM³.
2
4
6
8
10
12
14
16
18
20
22
CROSS SECTION IN ATOMIC UNITS (πa₀²)
1
2
3
4
5
6
7
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
50
70
90
110
130
150
170
190
ELECTRON ENERGY IN VOLTS.

Fig. 16.

The experimental results for the cross sections for excitation of the 2^3P_1 (4·86 volt) state, and the 2^1P_1 (6·67 volts) state from the normal state are shown in fig. (16). They have been calculated from equation (10), section (6). It should be noticed that the scale of electron energies has been changed at 30 volts. In both these curves and in the ionisation cross section curve a correction of one volt has been applied to the voltage scale; one volt being added to the experimental energy values. This correction was obtained from the velocity distribution curves shown in fig. (11), it being found that in general the voltage spread of the main beam was approximately 2 volts, the upper limit of the energy being the point corresponding to the actual potential applied to the beam as measured by the voltmeter, so that the average energy of the beam was one volt less than this recorded value. With this correction the excitation and ionisation curves were all found to extrapolate to the correct critical potential. No correction has been applied for the velocity distribution of the electrons in the beam, since the results of the retarding potential curves as given in fig. (11) show that the beam is sufficiently homogeneous to make this correction unnecessary. If a correction were applied for this effect it would have the effect of making the maxima

maxima in the curves slightly more sharp, and possibly of making them move in to slightly smaller energies.

For the triplet state, the 4·86 volt level, the cross section curve rises fairly quickly to a maximum at 7 volts of about 15 cm^2/cm^3 and then falls sharply to a value of about 4 cm^2/cm^3, remaining fairly constant at this value as the electron energy increases up to about 40 volts. Beyond this point it steadily decreases with increasing energy. Comparing this curve with the theoretical curve for the same state given by Penney (80) and shown in fig. (6) in a previous section, we see that the agreement is remarkably good. Penney's curve shows the finite and appreciable probability of excitation of this level at relatively large velocities, which is actually shown in the experimental curve. Excitation of intercombination transitions such as the 2^3P_1 state from the 1^1S_0 ground state has been discussed in a previous section, where it was shown that they could only take place by electron exchange, if the interaction between the orbital and spin motions was small as in the case of light atoms, and since the effects of electron exchange are only appreciable at low energies, the excitation probability falls rapidly to zero for such levels in light atoms. In the case of the mercury atom, the interaction between the spin and orbital motions is strong, so that excitation of the triplet state from the singlet ground state has a finite probability at relatively large energies, since electron exchange is not necessary. This effect is shown in the experimental curve.

Larché (81) by an optical method has obtained the excitation function for the corresponding triplet state 2^3P_1 in cadmium, which is a similar atom to mercury. His curve agrees well with the curve shown in fig. (16) except that his maximum is more sharp. In a previous section the probable cause of difference between the results by the optical and electrical methods were discussed and it was concluded that the two methods would not necessarily give the same result. The agreement between these curves is then very interesting.

Most of the work done on the excitation function of this state in mercury has been done by the optical method. The results of other workers by this method are reviewed by Ostensen (82) who concludes that the agreement is quite good as to the shape of the curve; some variation in the absolute magnitude is however found. The general result is that a tall sharp maximum is found between 6 and 7 volts energy. Whitney (83) by an electrical method found the maximum to occur at about 7 volts. The experimental value of 7 volts found by the author, is in good agreement with most of the previous work. As mentioned above this value would be slightly less for a perfectly homogeneous beam.

The excitation function for the 2^1P_1 state, 6·67 volts energy, is also given in fig. (16). An interesting feature of this curve is a marked change in slope at about 13 volts. A study of Whitney's experimental curve for this state and also Larche's curve for the same state in cadmium, shows the same inflexion at about the same position. Comparing the experimental curve with the theoretical curve obtained by Penney, we see that Penney's curve shows a broad flat maximum at about 15 to 20 volts, while the experimental curve shows a sharp maximum. If, however, the experimental curve is treated as having a broad flat maximum with a sharp maximum imposed on it, as shown by the dotted line in the figure, the agreement between theory and experiment is much better. Doing this removes the inflexion at 13 volts. Both the sharp maximum and the broad maximum occur at 15 volts. Returning now to the ionisation curve, we see that a small maximum and minimum were obtained there also at approximately 15 volts. The height of the maximum above the main curve is seen to be approximately 7 cm^2/cm^3, from both the excitation and the ionisation curves. This it seems likely that in both these curves we have a sharp maximum imposed on the main curve at about 15 volts energy.

A further argument in favour of this can be obtained from a study of the experimental procedure. The energy losses corresponding to the two curves considered in the last paragraph are 6·67 and 10·38. If this subsidiary sharp maximum is to occur in both curves, it must be due to a transition having energy lying somewhere between these two values. For a strictly homogeneous beam only those electrons which had lost 6·67 and 10·38 volts energy would be collected, in determining the respective curves. But in making the experimental readings, all electrons with energies between 6 and 7·4 volts are collected for the singlet excitation function, and all those which have lost more than 9·5 volts energy for the ionisation function. The energy spread of the beam has already been shown to be about 2 volts, which would thus bridge the gap between the two values 7.4 and 9·5 volts, so that some electrons which had excited a transition midway between these values would be collected in both curves. This seems to explain the irregularity in both curves at about 15 volts. An examination of the lower stationary states in the mercury atom shows that there is an important state at 8·8 volts energy, the 3^1D_2 level. It therefore seems likely that the subsidiary sharp maximum at 15 volts energy is due to excitation of this level. At 8·8 volts there is also present the triplet state, $3^3D_{3,2,1}$, but it is unlikely that the peak is due to excitation of this level, since it has already been shown that triplet states have a maximum probability of excitation very close to the excitation potential.

The sharpness of the peak is probably due to the fact that singlet D states in general show a sharper maximum than do singlet P states, in results obtained by optical methods.

If we adopt the assumption that this maximum is due to this singlet D state, we can derive the general trend of the excitation function for this level. It must rise fairly sharply to a maximum at about 15 volts energy and then fall again fairly sharply beyond this point. The height of the maximum is also seen to be about 7 cm^2/cm^3.

The shape of the 6·67 volt state is then seen by the dotted curve. It has a broad flat maximum at about 15 volts, and falls off slowly beyond the maximum. The height of the maximum is about 15 cm^2/cm^3.

Again, a comparison of the experimental curve and Penney's theoretical curve, shows quite a good agreement at least up to the maximum, which is at approximately the same position in both curves. Beyond the maximum the theoretical curve falls off more slowly than the experimental. As has been mentioned before this can be explained by the fact that at higher velocities the majority of electrons are scattered forward through small angles after exciting the given state. Many of these electrons will not be collected on account of the lower limit of the angular collecting range being too large.

The relative magnitudes of the maxima for the 2^3P_1 and the 2^1P_1 states are by no means in agreement with the values obtained by Penney. In the experimental work they are almost the same, while in the theoretical paper the singlet transition has a maximum about four times the value of the triplet maximum.

Finally a comparison may be made of the absolute magnitudes of the cross sections at the maxima of the various experimental curves, with the values obtained by other workers.

For the 2^3P_1 state the result obtained by Hanle (84) and also by Sponer as calculated by Hertz (85) from her results, is 1·1 cm^2/cm^3. Whitney however finds a value of 34 cm^2/cm^3. The author's result is 14·6 cm^2/cm^3, which being midway between the two previous sets of results does not decide in favour of either.

In the case of the singlet state 2^1P_1, Whitney gives a value of 7 cm^2/cm^3, while Brattain (86) does not give an exact value but estimates it at between 4·3 and 13 cm^2/cm^3. The result obtained in this work is 15 cm^2/cm^3., which is in fair agreement with both the above.

Whitney's value for the 3^1D_2 state is 3·4 cm^2/cm^3., while the experimental value is of the order of 7 cm^2/cm^3.

A FURTHER TEST ON THE WORKING OF THE APPARATUS AND A DISCUSSION OF THE POSSIBLE ERRORS.

Using the various experimental results given above for the ionisation and excitation cross sections, we can obtain a very interesting and conclusive test of the satisfactory working of the apparatus. We have excitation functions for the 2^1P_1, 2^3P_1 and 3^1D_2 states which we know from Penney's theoretical work, and the experimental results of many other investigators, such as Schaffernicht and others, who have studied the excitation functions for a great number of transitions in the mercury atom, that these transitions along with the ionisation transitions are by far the most probable in the energy range used in this work. If therefore the cross sections for excitation of these states, and the ionisation cross section be added together, we should obtain a curve for the inelastic cross section. This curve can then be compared with the inelastic cross section curve as obtained previously by substracting the elastic cross section from the total cross section. It should be noticed that all the component excitation and ionisation cross sections for the former inelastic cross section curve are obtained independently; so that if they add up to give a result in agreement with the inelastic cross section obtained by the other, entirely different method, the result should be very conclusive of the accuracy and reliability of the method.

The results for the inelastic cross section as obtained by the two methods are given in fig. (17); the upper curve being the inelastic cross section determined by the difference of the total and elastic cross sections, and the lower curve, the summation of the excitation and ionisation curves. It should be noticed that the excitation function for the 3^1D_2 state must only be included once, although it is present in both the singlet excitation function curve and also in the ionisation curve. The figure shows that the curves are in excellent agreement, the only differences being a small vertical displacement throughout the entire energy range, and a small horizontal shift of less than half a root volt.

It can be shown as follows, that this vertical displacement is in all probability due to the ejection of slow secondary electrons from the grids and final hole of the gun.

The formula used to obtain the elastic cross section was -

$$\alpha_e = I_e/I_t \cdot \alpha_t \qquad (1).$$

Now consider the case of what happens to any slow electrons moving towards the collector C from the scattering region inside the grid G_1 or from the grids G_1 or G_2.

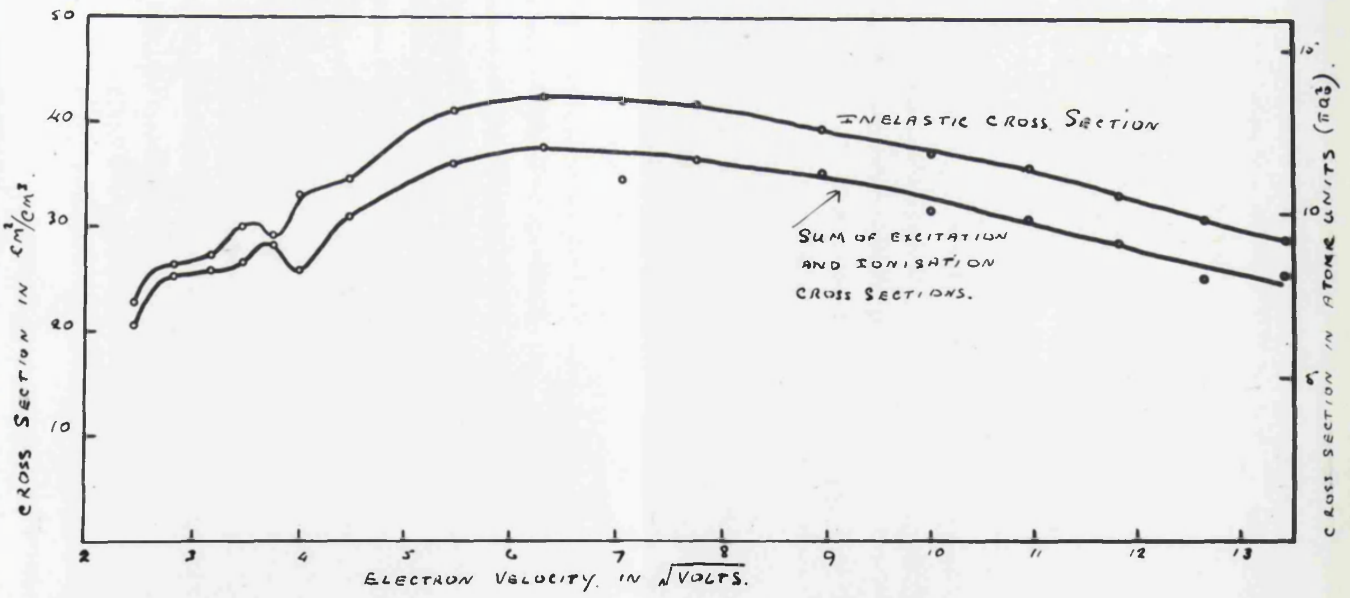

50
40
30
20
10
CROSS SECTION IN cm^2/cm^3.
2
3
4
5
6
7
8
9
10
11
12
13
ELECTRON VELOCITY IN $\sqrt{\text{VOLTS}}$.
15
10
5
CROSS SECTION IN ATOMIC UNITS (πa_0^2).
INELASTIC CROSS SECTION
SUM OF EXCITATION AND IONISATION CROSS SECTIONS.

Fig. 17.

By slow electrons we mean electrons which are considerably slower than the electrons in the beam; and when we speak of fast electrons during this discussion we mean electrons which have practically the same energy as the electrons in the beam.

The slow electrons may arise from secondary emission from the grids or the final gun hole, or they may be due to the beam spreading so much as to strike the grid G_1 directly, in which case a number of electrons both primary and secondary would be scattered with low energies towards grid G_2. When these slow electrons passed into the field between the second and third grids they would be stopped if the retarding field was large enough. This would be the case if the elastic cross section was being measured. However when the field has its value for the total cross section measurements, some of these slow electrons would have sufficient energy to overcome the field and reach the collector C. Thus I_t would be increased by these electrons and would be larger than it ought to be. Therefore α_e as given by the above equation would be too small, and the inelastic cross section $\alpha_n = \alpha_t - \alpha_e$, would be too large. Throughout this discussion $_t$ is Brode's value which is of course assumed unaffected by any of these experimental discrepancies.

Again consider the effect of these slow electrons on the excitation and ionisation cross sections. These latter cross sections can be both represented by the single equation $\alpha_{x,i} = I_{x,i}/I_t \cdot \alpha_t$. (2). Since in determining I_x, the field between G_1 and G_2 is only varied by a small amount from its value for the elastic measurements, and since I_x is the difference between two scattered currents for which the retarding potentials are practically identical, I_x will be practically unaffected by the presence of slow electrons. They will be included in I_t however as before so that the experimental values of α_x will be smaller than they ought to be.

The effect of these slow electrons on the ionisation cross section is not so simple. The ionisation cross section can be written as

$$\alpha_i = (1 - I_{9.5}/I_t)\, \alpha_t \qquad (3)$$

where $I_{9.5}$ is the current to the collector C when a retarding potential of $(V_o + V_p - 9.5)$ volts was applied between grids G_2 and G_3. Now if I_t is increased by the presence of slow electrons, then the part in brackets will be increased so that the value of α_i will be too large. The retarding potential used is however considerably smaller than for elastic scattering so that we would expect some secondary electrons to be included in

$I_{9\cdot5}$. As the number of secondaries in $I_{9\cdot5}$ is increased, it is easily seen that the error in α_1 will first of all decrease to zero and then increase on the other side. Now from an examination of the results given in fig. (15) for the ionisation cross section along with Bleakney's value, it is seen that the difference between the curves is small at low velocities and also at high velocities; the large difference at intermediate velocities seems unexplainable, but it appears reasonable to expect that it is not due to slow secondary electrons, but rather to some difference inherent in the methods of measurement, involving possibly the types of ionisation included by each method. Thus we conclude that the effects of slow secondaries are small in the case of the ionisation cross section.

Now consider the case of secondaries brought off from the third grid. All these electrons will reach the collector C since there is the field V_H drawing them to C. It is well known that the number of secondaries increases with the velocity of the primaries up to a velocity of a few hundred volts, and also that the energy of the secondaries is always small. In the cases when I_e or I_x are being measured, the velocity of the primaries on reaching the third grid is small, i.e. always less than 7·4 volts so that they will not bring off many secondaries. In the case of I_t, the velocity of the primaries is appreciable; they may therefore bring off a considerable number of secondaries. The net effect of this, is that the elastic and excitation cross sections will be further decreased by the secondary electron emission. The same argument will apply to the ionisation cross section except that $I_{9.5}$ will again include some secondaries, since the velocities of the primaries on reaching G_3 will be larger than for the elastic and excitation cases. Thus the ionisation cross section may be further increased or decreased according as the number of secondaries included in $I_{9.5}$ varies.

If we now study the curves given in fig. (17), we will see the extent of the errors due to secondaries. At low energies, say less than 15 volts, most of the inelastic curve is due to excitation cross sections, since the ionisation cross section is small and decreasing there. We find that the inelastic curve, obtained by adding the discrete cross sections is smaller than the curve obtained from the difference of the elastic and total cross sections by about 11%. Above we have shown that excitation cross sections are too small, and the inelastic cross section by the difference method, too large due to slow secondaries. The true inelastic curve might therefore be expected to lie between the two curves in fig. (17). The error due to secondary electron emission at low energies is thus not greater than 6%, which is quite a reasonable value.

At high energies, the inelastic cross section is mostly due to the ionisation transition. At these high energies, the retarding potential between the second and third grids will be sufficiently large even when I_t is being measured to stop all secondary electrons, which required to pass through it to get to the collector C. The only secondaries which could reach C in this case would be those brought off from G_3. The energy of the electrons reaching G_3 in the case of measuring I_t will be much greater than in the case of measuring $I_{9\cdot5}$, so that the secondary emission from G3 will be much greater for I_t, and so as shown above the ionisation cross section will be increased due to secondary emission. From fig. (15), we see that at high energies the difference between the experimental ionisation cross section and Bleakney's curve is only about 10%. We therefore conclude that at high energies the error due to secondary electron emission is not greater than 10%. Thus over the whole energy range the error due to secondary electrons increased from about 6% at the lowest energies to about 10% at the highest energies of the experimental range. Neither of these values amounts to a serious error.

The difference between Brode's total cross section and the experimental cross section has already been discussed. The conclusion was that the difference at low energies was probably due to the spreading of the beam, which prevented some electrons from reaching the collector B, and also brought more into the collector C. Most of these extra electrons which leave the beam, not due to a collision but simply due to diffusion, owing to the mutual repulsion of electrons for each other, will be fast electrons, so that if they pass through the grids without hitting anything, they will reach the collector C and be included in the scattered current no matter how it was being measured.

In the case of I_e/I_t since I_e is always less than I_t, the effect of the addition of a constant quantity to both the numerator and the denominator will be to increase the fraction. Thus α_e will be increased due to the presence of these fast electrons. Previously it was shown that the presence of slow electrons decreased α_e. It can now be shown that the combined effect of these slow and fast electrons together will probably be quite small, for determinations of α_e.

Measurements taken with liquid oxygen on the traps have shown that there is a certain "background" scattering when both elastic and total cross section measurements are being taken; this background is of course due to the fast and slow electrons mentioned above. Now if the scattered intensities actually measured with gas in the apparatus for the elastic and total cross sections are I_a^e and I_a^t respectively, while those measured with liquid oxygen on the traps are I_1^e and I_1^t, and if the true scattered intensities due to gas only are I_r^e and I_r^t, then we have that -

$$I_a^e = I_r^e + I_1^e \quad \text{and} \quad I_a^t = I_r^t + I_1^t \qquad (4).$$

Now suppose that for a given velocity, $I_1^e = k \cdot I_a^e$ and $I_1^t = k \cdot I_a^t$ (5) where k is a factor depending on the velocity. It really represents the fact that at a given velocity the background is proportional to the total intensity passed by the corresponding retarding potential. Substituting back we obtain -

$$I_a^e = I_r^e/(1-k) \text{ and } I_a^t = I_r^t/(1-k) \qquad (6).$$

Therefore $\quad I_a^e/I_a^t = I_r^e/I_r^t \qquad (7).$

That is the ratio I_a^e/I_a^t actually used in calculating the value of α_e is the same as the true ratio I_r^e/I_r^t, without background. By using the liquid oxygen curves and the experimental curves with gas, the relation (5) was tested and it was found to hold approximately. Thus the error in calculating α_e is probably not so serious as might at first appear.

For the cases of both excitation and ionisation cross section measurements, these fast electrons will increase denominator I_t in every case but will not effect the numerators at all since in each case the numerator is the difference of two currents, each of which will include the fast electrons, so that on substraction the effect of these electrons will disappear. The general effect of the fast electrons will be to reduce the value of the excitation and ionisation cross sections. From the comparison of the ionisation curve with Bleakney's we see that the experimental curve gives larger cross sections than Bleakney's. It is therefore concluded that the effect of these fast electrons is small. They probably leave the beam at such small angles that they are stopped by the sleeves on which the grids are supported and thus do not get into the scattered current.

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