IONISATION IN MERCURY VAPOUR AND HELIUM

Marjorie B. M'Ewen

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

1938

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http://hdl.handle.net/10023/11214

IONISATION IN MERCURY VAPOUR AND HELIUM

being a thesis presented by

Marjorie B. M'Ewen, B.Sc.

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 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 has been 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 Marjorie B. M'Ewen, B.Sc. has spent the equivalent of nine terms in Research Work under my direction, and that she has fulfilled the conditions of Ordinance No. 16 (St.Andrews) and is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

PERSONAL PREFACE.

I entered Bedford College, University of London, in October 1928, and obtained the B.Sc. (General) Degree in Mathematics and Physics in 1930, and the B.Sc. (Special) Degree in Physics in 1931, with Honours in both examinations.

After an interval of teaching at St.Leonards School, St.Andrews, I matriculated and was admitted as a research student in the University of St.Andrews in October 1936. I then commenced the work on the research which is now being submitted for the Ph.D. degree.

In January 1938 I was appointed Demonstrator in Physics in the University of St.Andrews.

INTRODUCTION.

The greater part of the experimental research, described in this thesis, has been devoted to an investigation, by direct electrical methods, of the formation of ionised molecules in mercury vapour and helium.

All chemical evidence, based on measurements of the vapour density and the ratio of the specific heats, indicates that under normal conditions mercury vapour and helium are strictly monatomic. This is contrary to the observations of the spectroscopists who have observed strong mercury and helium bands, both in emission and absorption. The mercury bands were examined by Wood (1) in 1907, while the helium bands were discovered simultaneously by Curtis (2) and Goldstein (3) in 1913. This latter result was surprising, since up to that time the existence of a molecule of one of the inert gases had not been considered possible. To account for the apparent discrepancy between the chemical and the spectroscopic results it has generally been assumed that an excited mercury or helium atom, in virtue of its changed electron affinity, can combine with a normal atom or another excited atom to form a molecule.

It is therefore of interest to investigate the details of the attachment process. A considerable amount of information can be obtained from band spectra measurements, but any other independent method of studying the same problem is of value when it leads to results which can be compared with the conclusions of the spectroscopists or the theoretical workers.

In 1936 Arnot and Milligan (4), by using a mass spectrograph apparatus, obtained the first direct evidence of the existence of molecules in mercury vapour when it was excited by electron impact. The original purpose of the research carried out by the author was to investigate still further the formation of mercury molecules by a balanced space-charge method. This has certain advantages over the spectrograph method, and the combination of the two methods provides a very strong means of attacking the problem.

At the conclusion of the work with mercury the space-charge method was extended to an investigation of the ions produced in argon, helium and neon by electron impact. Evidence for the existence of ionised molecules was obtained in helium but not in argon and neon, as was to be expected. Subsequently the results obtained for helium were checked and confirmed by the use of a mass-spectrograph. This part of the work has proved to be particularly interesting, for it is the first direct investigation of the formation of helium molecules that has been carried out. The results obtained give some unexpected information concerning the formation of helium molecules, and they also throw some light upon the results of the earlier workers who detected ionisation in helium below the atomic ionisation potential. This point attracted considerable attention at the time, but was never satisfactorily explained.

The thesis concludes with the account of an investigation of a process of ionisation by electron transfer which occurs in mercury vapour. Ionisation by the transfer of an electron from a normal atom to an ionised atom was first observed in 1927. Since that date several instances of this process have been observed, but the interchange of energy between the colliding particles has not been studied in any detail. The problem has attracted the attention of theoretical workers, who have been somewhat handicapped by a lack of experimental information for comparison with their results.

This thesis is divided into four parts. The first contains a brief outline of the quantuum theory of the atom and the molecule, a summary of our present knowledge of the interchange of energy in various collision processes, and a discussion of the theory of the thermionic emission from a heated filament and its applications. Particular reference is made to previous work which is of importance for the development of the experimental research described in Parts 2, 3 and 4.

To avoid interpolation of the thesis with definitions and simple calculations three appendices have been added. Where necessary, reference to the data given in the appendices is indicated by a superscript of the type "A "

The results of the experimental research have been published by Dr. F.L. Arnot and the author as follows:-

"The formation of mercury molecules. II"

Proc. Roy. Soc. A, 165, 133. (1938).

"The formation of helium molecules"

Proc. Roy. Soc. A, 166, 543. (1938).

and Proc. Roy. Soc. A, (1939) In the press.

"Electron transfer in mercury vapour"

Proc. Roy. Soc. A, (1939) In the press.

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PART I.

SECTION 1.

THE QUANTUM THEORY OF THE ATOM AND THE MOLECULE.

The classical view of the atom as a smooth, elastic sphere has now completely given way to the nuclear theory suggested by Rutherford in 1911 and extended by Bohr in 1913.

The atom is an openwork structure of electric charges. Its mass is concentrated in a small positively charged nucleus round which revolve a number of electrons. The number of the electrons is equal to the atomic number of the element, and the positive nuclear charge, measured in electronic units, is also equal to the atomic number. The resultant charge of a normal atom is consequently zero.

The electrons, each of which revolves in a separate orbit, are considered to be arranged round the nucleus in a series of shells. The normal helium atom has only two extra-nuclear electrons which form a complete and stable outer shell. The normal mercury atom has eighty electrons, seventy-eight of which are grouped in five inner stable shells, the remaining two electrons occupy orbits in a sixth outer shell. The outer structure of the two atoms is thus similar and they have, as a result, certain similar properties. The outermost or most loosely bound electrons are known as the valency electrons, and it is only with transitions of the valency electrons that we are concerned in this work.

Each electron possesses an angular momentum due to its orbital motion and an angular momentum due to a spin about its own axis. Both types of angular momentum, orbital and spin, are quantised, that is they are restricted to certain discrete amounts. The spin momentum of all electrons is the same. The quantisation of the angular momentum restricts the motion to certain clearly defined orbits, associated with each of which is a definite amount of energy. To account for the fact that the electronic motion does not degenerate into a spiral with a final collapse of the electron into the nucleus, it is assumed that an electron, if left undisturbed, can continue to revolve in one of its quantised orbits or stationary states without any radiation of energy. This is contrary to the laws of classical mechanics and is known as Bohr's first postulate. An atom can only absorb or radiate certain discrete amounts of energy equal to the difference in energy between two stationary states of an atomic electron. If an electron jumps from a higher level of energy E_2 to a lower level of energy E_1 the excess energy $(E_2 - E_1)$ is radiated as a photon with frequency ν given by the relation

$$h\nu = E_2 - E_1 \qquad (1)$$

where h is Planck's constant. This is known as Bohr's second postulate.

The wavelength (λ) of the photon is given by the relation

$$\lambda = \frac{hc}{E_2 - E_1} \qquad (2)$$

where c is the velocity of light. The quantum theory of the atom thus leads to a simple explanation of the existence of the line spectra associated with atoms.

By imparting sufficient energy to an atom one of the valency electrons may be raised to any of its higher levels, or it may even be completely removed from the atom. When this occurs the atom is said to be ionised. The different ways in which an atom can be excited will be discussed in the next section.

A diagrammatic representation of the energy levels of a mercury atom is given in figs. 1a and 1b. The symbols on the right hand side indicate the azimuthal, spin and inner quantum numbers of the atom associated with each level. The notation used is defined in Appendix 3 [A3]. The figures on the left give the energy of each level, measured from the ground state, in electron-volts [A2]. The numbers on the arrows give the wavelengths of the lines emitted by the atom in passing spontaneously from the higher state to the lower. A few of the energy levels of the helium atom are given in fig. 2.

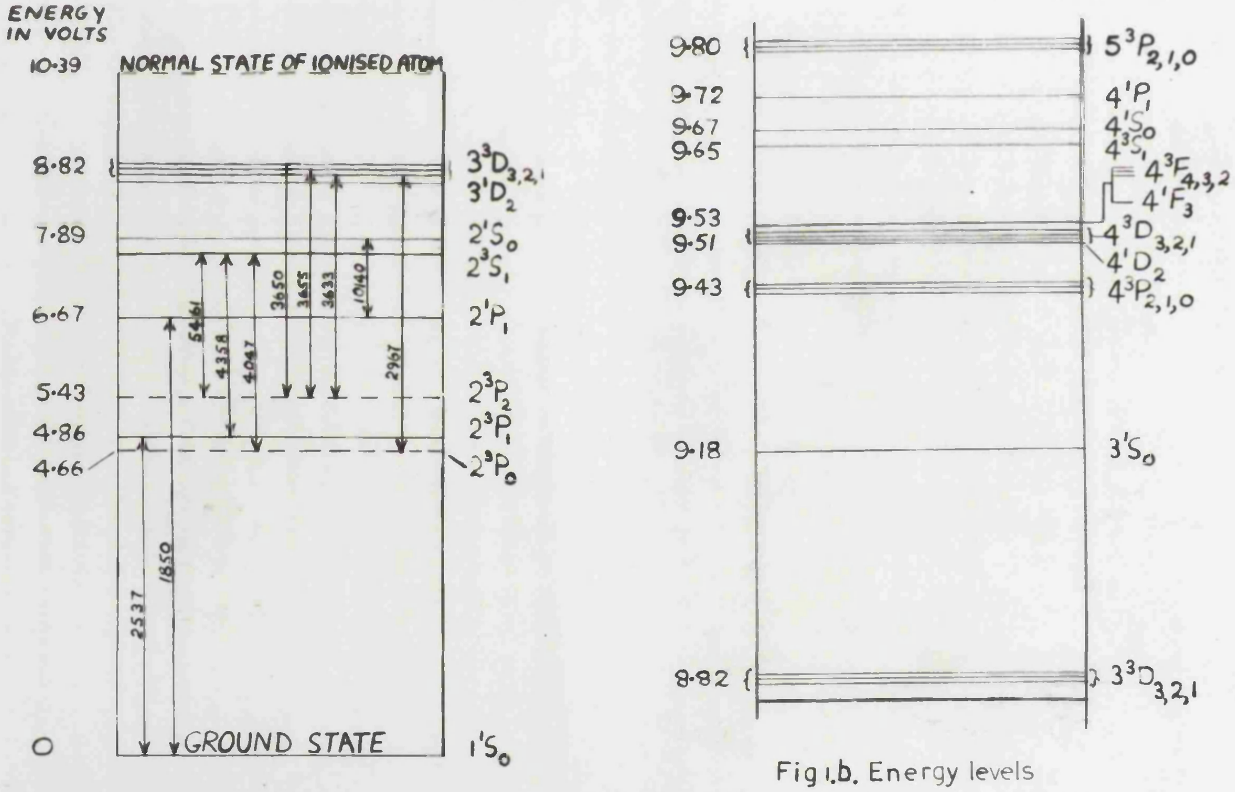


Fig 1.a. Energy levels of mercury atom.

Fig 1.b. Energy levels between 8·8V and 9·8V

FIG. 1.

The ground states of the helium and the mercury atoms are both singlet 1^1S_0 states. This means that the electron spins of the two valency electrons in the ground state are in opposite directions. The first excited state of the mercury atom is the triplet $2^3P_{2,1,0}$ state, while the first excited state of the helium atom is the triplet 2^3S state. In a triplet state the electron spins of the two valency electrons are in the same direction.

In light atoms, such as helium, the interaction between the spin and the orbital motions is negligible and consequently an electron excited to any of the triplet 2^3S levels cannot return spontaneously to the ground state with the emission of a photon, since such a transition requires a rearrangement of the electron spin. The three 2^3S levels are therefore called metastable since an atom excited to one of these states can remain in that state for as long as 10^{-2} seconds. It is then either raised to a higher state from which it can return to the ground state spontaneously, or it may be returned to the ground state by a collision of the second kind, which will be defined in the next section.

In heavier atoms such as mercury the interaction between the spin and orbital motions may be quite appreciable. A mercury atom excited to the 2^3P_1 level can

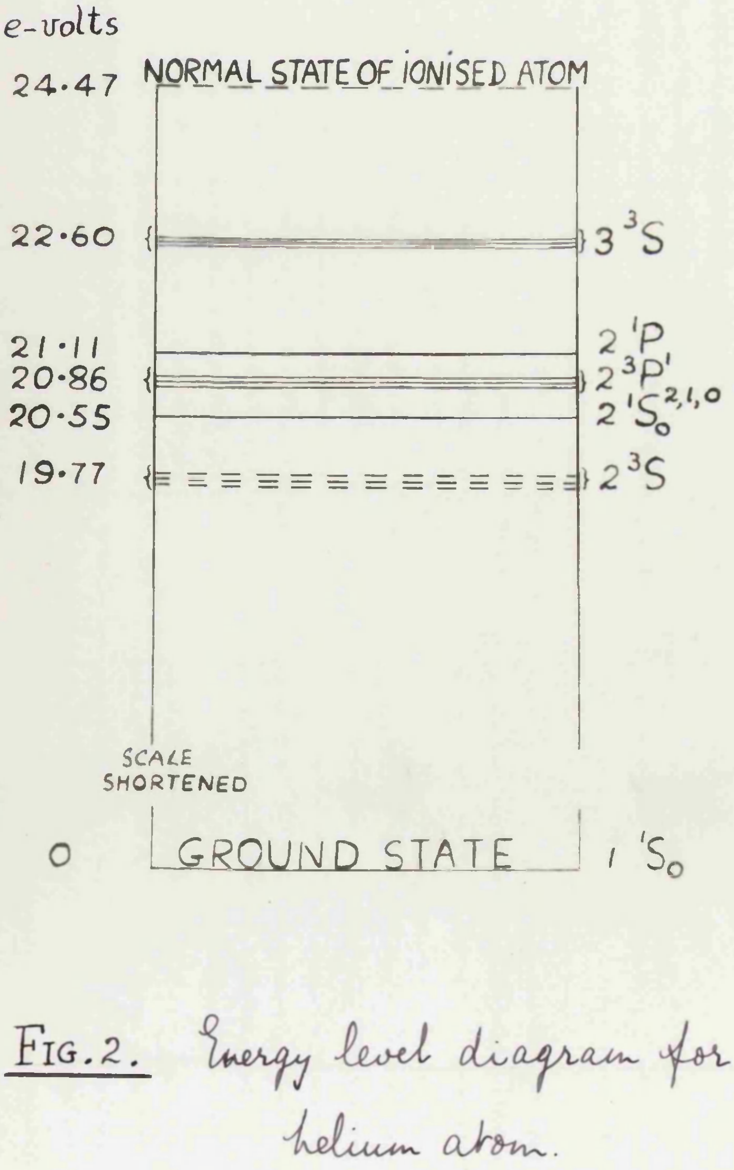


Fig. 2. Energy level diagram for helium atom.

consequently return to the ground state with the emission of the resonance radiation of wavelength 2537 A. Such lines emitted in transitions between triplet and singlet levels are called intercombination lines. The spectroscopic selection rule, however, forbids transitions between levels for which the inner quantum number, J, changes by any values except ± 1 or 0, the particular transition $J = 0 \rightarrow 0$ is also forbidden. The 2^3P_2 and 2^3P_0 levels of the mercury atom are therefore metastable. The life of a normal excited state is about 10^{-8} seconds.

The minimum energy required to ionise an atom may be determined from spectroscopic data. The absorption spectrum of a monatomic gas or vapour shows a number of lines which converge to a limit in the ultra-violet region of the spectrum. These lines arise from the excitation of normal atoms to the higher levels which lie closer together as the ionisation limit is approached. The ejected electron is no longer governed by quantum restrictions and consequently the series limit will be followed by a continuum. The wavelength of the series limit is related to the ionisation potential, V_i, by the equation

$$V_i = \frac{12336}{\lambda} \qquad (3)$$

The derivation of this equation is given in appendix 2.

For helium the series limit is in the far ultra-violet in the region of 500 A. Owing to the difficulties of experimental technique, an accurate spectroscopic determination of the ionisation potential for helium was not made until 1922, when it was successfully carried out by Lyman (5). In view of his work a correction has to be applied to the numerical values of the excitation and ionisation potentials used by workers before that date.

A molecule, in addition to its electronic energy, possesses vibrational energy due to a vibration of the nuclei along the internuclear axis and a rotational energy due to the rotation of the nuclei about the centre of mass of the molecule. The vibrational and rotational energies, like the electronic energy, are quantised, and the possible vibrational and rotational levels are specified by quantum numbers. The frequencies of the molecular bands obey the same relation as the atomic lines given in equation (1), i.e. $h(\nu) = E_2 - E_1$, where E_2 and E_1 are now the initial and final energies of the molecule. For a given change in the electronic energy, ν can now take a variety of values depending on the possible changes in the vibrational and rotational energies which can accompany the change in the electronic energy. All the bands, whose emission or absorption corresponds to all possible transitions between the vibrational and rotational levels for a given change in the electronic energy, form a band system. The small changes in the rotational energy, which accompany changes in the electronic and vibrational energies, give rise to the fine lines into which every band can be resolved under sufficiently high power.

Let us now consider what occurs as two atoms approach one another prior to the formation of a molecule. If the attractive force varies inversely as a lower power of the internuclear distance than the repulsive force, then as we decrease the internuclear distance the potential energy curve for the two atoms will take the form of the curve in fig. 3.

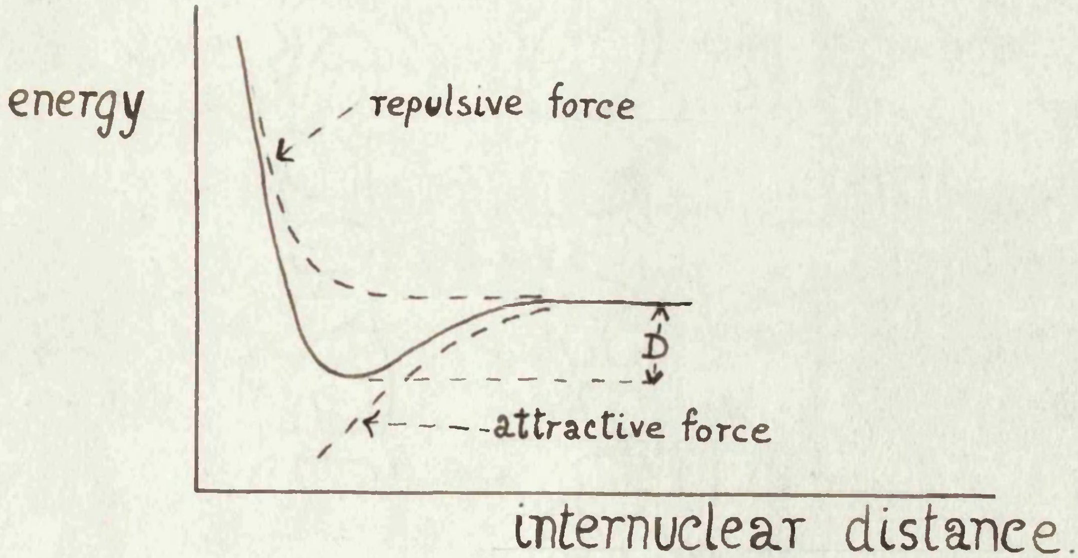


Fig. 3.

A stable molecule can then be formed provided an amount of energy represented by the distance D on the potential energy curve can be dissipated. Once the molecule has been got into that state represented by the minimum of the curve, the curve then represents accurately the dissociation of the molecule. It is doubtful if the converse process can always take place, that is if the products of dissociation can be brought together to form the molecule, since this requires the dissipation of an amount of energy equal to the energy of dissociation of the molecule.

The processes involved in the formation of ionised and excited molecules and the method of disposing of any excess energy will be fully discussed in the experimental section.

There are three possible types of binding for diatomic molecules, ionic binding as in NaCl, exchange forces as in H_2, and polarisation or van der Waals forces. For neutral mercury and helium atoms the binding cannot be ionic. Heitler and London (6) have shown that the exchange forces between normal helium and mercury atoms must be repulsive if Pauli's exclusion principle holds. Eisenschitz and London (7) have shown that the van der Waals forces at large internuclear distances may be greater than the exchange forces and can produce a definite equilibrium when the exchange forces are repulsive. The binding in normal mercury and helium molecules, if it occurs at all, must be of this type and the normal molecules will have very low energies of dissociation. The exchange forces between an excited atom and a normal atom may be attractive owing to the change in the electron affinity of the excited atom. A stable, excited molecule may then be formed when the nuclei approach to the distance at which the attractive exchange force is just equal to the repulsive force between the nuclei.

The existence of an absorption band spectrum does not necessarily indicate the presence of normal molecules. Atoms excited by the incident photons can combine with normal atoms to form stable excited molecules. These excited molecules may then be raised to higher states by other photons so that an absorption band spectrum will appear.

So far no bands have been observed in heluum which correspond to transitions between the ground state of the neutral molecule and the normal state of the ionised molecule. The ionisation potential of the molecule could be calculated from these bands in the same way as the ionisation potential of the atom is calculated from line spectra observations. The ground state of the helium molecule is generally supposed to be completely unstable, and the bands which Hopfield (8) reported in 1930, were subsequently stated by Mulliken (9) to be due to nitrogen. If no bands corresponding to the transition $He_2^+ \longrightarrow He_2$ exist then the ionisation potential of the molecule must be found by some other method. At the present time the energies associated with the excited states of the helium molecule are reckoned from the unknown ionisation potential of the molecule. A table of the excited states of the helium molecule is given by Jevons (10). These energy values are calculated from observations of the bands which originate from transitions between the different excited states and the normal state of the ionised molecule.

The knowledge of the excited states of the mercury molecule is even less complete than that of the helium molecule.

Several values for the energy of dissociation of the normal mercury molecule have been obtained. Koernicke (11) from measurements of the intensity of the 2540 A. band at different temperatures and pressures obtained a value of 0.06 electron-volts. Mrozowski (12) from similar measurements with other bands found the energy of dissociation to be 0.73 electron-volts. The latest determination is that of Winans (13), who obtained a value of 0.15 electron-volts. Winans based his calculation on observations of the correspondence between certain spectral lines and bands under different conditions. His method appears to be the most direct and reliable of the three.

The obtaining of molecular data from band spectra measurements is difficult and often uncertain. Direct electrical investigations are necessarily restricted to the formation of ionised molecules, but any values obtained by these methods are of value for comparison with the spectroscopic results.

A useful relation between the ionisation potential of a diatomic molecule and the ionisation potential of one of its atoms can be obtained. Let us suppose that the uppermost curve in fig. 4, page 14, represents the normal state of the ionised mercury molecule, Hg$_2$, which dissociates into a normal atom, Hg, and an ionised atom, Hg . The possible vibrational levels associated with the ionised molecule are represented by the horizontal lines which converge to a limit as the vibrational quantum number increases. The energy of dissociation of the ionised molecule is equal to the energy difference between the lowest and the highest vibrational levels. The energy of dissociation can consequently be calculated from spectroscopic measurements, if a system of bands arising from transitions from all the vibrational levels can be found. The energy of dissociation is equal to h ($\nu_\infty - \nu_0$) ergs, where ν_0 and ν_∞ are the frequencies of the origin and the convergence limit of the band system. Let us also

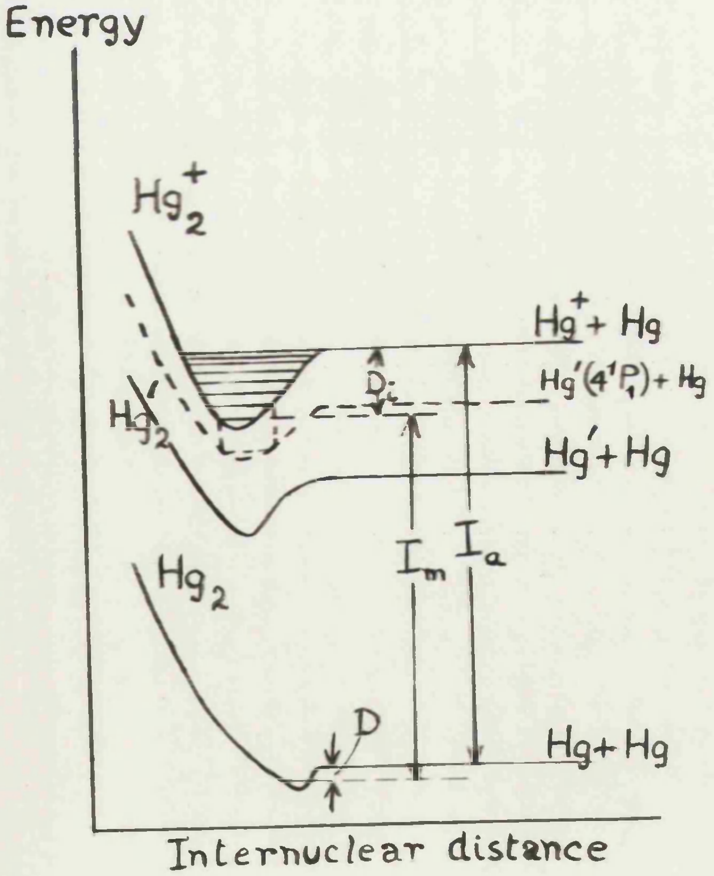

Energy
Hg_2^+
$Hg^+ + Hg$
D_i
$Hg'(4^1P_1) + Hg$
Hg_2'
$Hg' + Hg$
I_m
I_a
Hg_2
D
Hg+ Hg
Internuclear distance

FIG. 4.

suppose that the lowest curve in fig. 4 represents the normal state of the neutral molecule, Hg_2. This curve may have a slight minimum, due to van der Waals forces, at large internuclear distances. The minimum energy of the molecule in each state is just above the minimum of its curve by an amount equal to the energy of the lowest vibrational level.

It follows at once from the figure that the ionisation potentials of the molecule and the atom are connected by the relation

$$I_m + D_i = I_a + D \qquad (4)$$

where D and D_i are respectively the energies of dissociation of the normal molecule and the ionised molecule. The importance of this equation will be seen in the discussion of the experimental results in parts 2 and 3.

SECTION 2.

THE EXCITATION AND IONISATION OF ATOMS.

A normal atom can acquire the energy necessary for excitation and ionisation by colliding with an electron, with a photon, or with some other atom which is in an excited or ionised state.

It is only within the last fifteen years that the interchange of energy in these collision processes has been examined in detail. The results which have been obtained are invaluable for those engaged in an experimental investigation of ionisation processes, and they will be discussed in some detail in this section.

COLLISIONS BETWEEN ELECTRONS AND ATOMS.

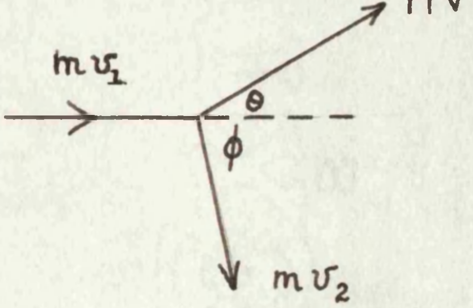


Fig. 5.

Suppose an electron of mass m, moving with velocity v_1 collides with an atom of mass M which is initially at rest. Let the velocities of the electron and the atom after the collision be respectively v_2 and V, in directions making angles ϕ and θ with the initial direction of the electron, and further let us suppose that during the collision the internal energy of the atom is increased by an amount p.

By the conservation of energy

$$\tfrac{1}{2}mv_1^2 = \tfrac{1}{2}mv_2^2 + \tfrac{1}{2}MV^2 + p \qquad (5)$$

By the conservation of momentum

$$mv_1 = MV\cos\theta + mv_2\cos\phi \qquad (6)$$

$$0 = MV\sin\theta - mv_2\sin\phi \qquad (7)$$

Eliminating ϕ from equations (6) and (7) we obtain

$$m^2v_2^2 = M^2V^2 - 2Mmv_1V\cos\theta + m^2v_1^2 \qquad (8)$$

Eliminating v_2 from equations (5) and (8) we have

$$M(M+m)V^2 - 2Mm\,v_1 \times V\cos\theta + 2pm = 0 \qquad (9)$$

Writing $\tfrac{1}{2}MV^2 = E_a$ and $\tfrac{1}{2}mv_1^2 = E_e$ equation (9) becomes

$$(M+m)E_a - 2\times\sqrt{MmE_aE_e}\cos\theta + pm = 0 \qquad (10)$$

This gives $$\sqrt{E_a} = \frac{\sqrt{M.m.E_e}}{M+m} \pm \sqrt{\frac{MmE_e\cos^2\theta}{(M+m)^2} - \frac{pm}{M+m}} \qquad (11)$$

Now for a hydrogen atom $\frac{m}{M} = \frac{1}{1840}$, and for heavier atoms this fraction is still smaller. Equation (11) can therefore be written

$$\sqrt{E_a} = \sqrt{\frac{m}{M}\times E_e}\cos\theta \pm \sqrt{\frac{m}{M}\times E_e\cos\theta - \frac{pm}{M}} \qquad (12)$$

Referring back to equation (10) we see that if $p = 0$ we immediately obtain for one value of E_a, $E_a = 0$, which can be discarded. We must therefore take the positive sign in equation (12) which shows that the maximum possible value for E_a occurs when $p = 0$ and $\cos\theta = 1$. That is for a head-on elastic collision.

i.e. $$(E_a)_{max} = \frac{4m}{M} \times E_e \tag{13}$$

The increase in the kinetic energy of translation of the atom is therefore negligible in all collisions, elastic (when $p = 0$) and inelastic (when $p > 0$).

The kinetic energy of translation of an atom at room temperature (20°C) is $6{\cdot}03 \times 10^{-14}$ ergs, this is equivalent to an energy of $3{\cdot}79 \times 10^{-2}$ electron-volts A2. We can consequently neglect the thermal energy of the atom in comparison with the energy of the colliding electron, and we can also neglect the increase in its kinetic energy due to any previous electron collision.

If E_e and E'_e are the kinetic energies of an electron before and after an inelastic collision, then we have from equation (5)

$$p = E_e - E'_e \tag{14}$$

Whenever an electron has sufficient energy to cause a transition in an atom it can only give up a definite amount of energy equal to the difference in energy between the initial and final states of the atomic electron. Any extra energy is carried away by the impacting electron as kinetic energy of translation, (equation 14). When the colliding electron causes ionisation of the atom it may give up an amount of energy greater than that which is required for complete removal of the atomic electron, since the latter once it is outside the atom can share in the carrying off of the excess energy.

The interesting feature of the excitation of atoms by electron impact lies in the way in which the probability of excitation changes as the energy of the electron is increased above the minimum value necessary for excitation. The problem can be investigated by two different experimental methods. The electrical method involves the measurement of the number of electrons which have lost the excitation energy of the state under investigation, as the initial energy of the electrons is increased above the excitation potential for that state. The optical method consists in measuring the intensity of the spectral lines emitted by the atoms in returning to the normal state after excitation by electrons of gradually increasing energy. The curve showing the probability of excitation to any state plotted against the energy of the exciting electrons is called the "excitation function" of that state.

Optical excitation functions have been obtained for helium by Hughes and Lowe (14), Lees and Skinner (15) and Hanle (16), and for mercury by Schaffernicht (17). Electrical excitation functions have been obtained for helium by Dymond (18) and Glockler (19), and for mercury by Arnot and Baines (20) and others. The results are interesting for they show that the excitation function for a triplet state rises to a sharp maximum just above the excitation potential and then falls off rapidly, whereas the excitation function for a singlet state rises to a broad maximum considerably above the excitation potential and then falls off slowly. This difference between singlet and triplet excitation is most marked for P states.

The theoretical excitation functions for helium have been calculated by Massey and Mohr (21) and for mercury by Penney (22). The agreement between the theoretical and experimental curves is very satisfactory.

It has already been mentioned on page 5, that in mercury and helium excitation of the triplet states from the ground state requires a rearrangement of the electron spins. This can only be brought about by an interchange

interchange of the atomic and colliding electrons. The exciting electron enters the higher orbit and the electron from the ground ($1'S_0$) state is ejected with the excess energy. This process has a maximum probability when the energy to be carried away by the ejected electron is small.

The probability of ionisation by electron impact for a number of gases has been investigated by Compton and Van Voorhis (23) and by Tate and Smith (24) and others. The results are in good agreement with the theoretical calculations of Massey and Mohr (25) and show that the probability of ionisation rises to a broad maximum for electron energies considerably above the ionisation potential.

When the energy of the colliding electron is above the minimum value necessary for the removal of one electron other types of ionisation processes may occur. The atom can simultaneously lose one electron and have another raised to a higher level, in which event an excited ion is formed. More than one electron may be removed from the atom giving a doubly or even trebly charged positive ion. In 1930 Bleakney (26) made a positive ion analysis of the ions formed in mercury vapour by electron impact and found critical potentials for the formation of Hg^{+}, Hg^{2+}, Hg^{3+}, Hg^{4+} and Hg^{5+} at 10.4, 30, 71, 143 and 225 electron-volts respectively.

COLLISIONS BETWEEN PHOTONS AND ATOMS.

We have seen that when an excited electron makes a transition to a lower level a photon is emitted with an energy, hv, equal to the difference in energy between the initial and final states of the atomic electron. The reverse process can take place, that is the atom can absorb the energy of a photon and be raised to a higher energy state. In gases at ordinary pressures the probability of a photon losing only a portion of its energy is small. A photon has no rest mass and consequently it can only excite an atom when it has exactly the required excitation energy, there being no particle set free to carry away the excess energy as kinetic energy of translation. The sharpness of the lines in an absorption spectrum shows that the probability of photo excitation is only appreciable when the energy of the photons is exactly equal to the excitation potential.

When a photon has sufficient energy to ionise an atom an electron is set free which can carry off any excess energy. The experiments of Lawrence and Edlesfen (27) on the photo-ionisation of the alkali metals, however, show that the probability of ionisation rises to a sharp maximum when the energy of the photons is equal to the ionisation potential and falls off sharply as the energy of the photons is increased above the ionisation limit. This indicates that for ionisation, as well as for excitation, the energy of the photons must be very nearly equal to the exact energy necessary for the electronic transition.

In 1926 Rouse and Giddings (28) carried out an investigation of photoionisation in mercury vapour. They found that ions were produced in the vapour when it was irradiated with its resonance radiation 2537 A. of which the photons have only 4.86 electron-volts energy. They observed that the resonance line and the resonance line only was essential for the formation of the ions. The ionisation was found to be proportional to the square of the intensity of the light. These results were checked by Foote (29) and Houtermans (30), and their significance will be discussed a few pages further on.

COLLISIONS BETWEEN ATOMS.

A collision in which an electron gives up some of its kinetic energy in exciting an atom to a higher state is called a "collision of the first kind." In 1921 Klein and Rosseland (31) showed that the converse of this process should be possible for an atom and an electron in thermodynamical equilibrium. This means that when an excited atom and an electron collide the atom may return to a lower state without the emission of a photon, the excitation energy of the atom appearing as an increase in the kinetic energies of translation of the atom and the electron.

In 1922 Franck (32) extended this theory to collisions between two atoms or molecules. When an excited atom, A, collides with another atom or molecule B, the excited atom may return to a lower state and the internal energy set free in the collision may be used up in several ways. It may be sufficient to excite or ionise the atom or molecule B, in which event any energy in excess of the excitation energy of B is used up in increasing the kinetic energy of translation of the two particles. When B is a molecule, part of the excitation energy of A may be employed in dissociation of the molecule, the balance of the energy appearing as kinetic energy of the products of dissociation.

All collisions of this type are known as "collisions of the second kind."

The transfer of the excitation energy from one atom to another has a maximum probability when there is close "resonance" between the excited states of the two atoms; that is when the amount of energy to be dissipated in the kinetic form is small.

Stuart (33) in 1925 investigated the quenching of the mercury resonance radiation by several different gases. He found that of a number of molecular gases hydrogen was the most efficient, this is due to the close resonance between the excitation energy of a 2^3P_1 mercury atom and the energy of dissociation of the hydrogen molecule. The addition of argon was also found to have a quenching effect.

A mercury atom excited to its resonance 2^3P_1 level possesses an excitation energy of 4.86 electron-volts. The heat of dissociation of the hydrogen molecule is 4.34 electron volts. Consequently nearly every collision between a mercury atom in the 2^3P_1 excited state and a hydrogen molecule results in dissociation of the molecule. The mercury atom returns to the ground state without the emission of a photon. The excess energy over that required for dissociation is 0.52 electron volts and it appears as kinetic energy of the products of dissociation.

The process can therefore be written

$$Hg'(2^3P_1) + H_2 \rightarrow Hg + H + H + K.E.(0.52\ e\text{-}v.) \qquad (A)$$

A metastable mercury 2^3P_o atom has an excitation energy of 4.66 electron volts and is also very effective in producing dissociation of a hydrogen molecule on collision. The process may be written

$$Hg'(2^3P_o) + H_2 \rightarrow Hg + H + H + K.E.(0.32\ e\text{-}v.) \qquad (B)$$

The quenching of the resonance radiation by the addition of argon is due to the fact that the excited mercury atom falls, not to the ground state, but to the metastable 2^3P_o state of 4.66 electron volts energy. This process can be written

$$Hg'(2^3P_1) + Ar \rightarrow Hg'(2^3P_o) + Ar + K.E.(0.2\ e\text{-}v.) \qquad (C)$$

The results of Rouse and Giddings for the ionisation of mercury vapour by its resonance radiation have been referred to on page 23. The fact that the ionisation is proportional to the square of the intensity of the light shows that <u>two</u> excited 2^3P_1 atoms take part in the formation of each ion.

The process

$$Hg'(2^3P_1) + Hg'(2^3P_1) \rightarrow Hg^+ + Hg + \varepsilon \qquad (D)$$

in which the combined energies of excitation result in the

[Foot-note. Throughout the thesis the symbol ' denotes an excited atom and the symbol ε a free electron.]

ionisation of one of the atoms is not energetically possible; since the energy of the left-hand side, which is 9.72 electron-volts, is less than that of the right-hand side by 10.39 - 9.72 i.e. 0.67 electron-volts. It was suggested that the ionisation might be due to the formation of ionised molecules by the process

$$Hg'(2^3P_1) + Hg'(2^3P_1) \rightarrow Hg_2^+ + \varepsilon. \qquad (E)$$

The energy available for the ionisation of the molecule in this process is 9.72 + D electron-volts, where D is the energy of dissociation of the <u>normal</u> molecule.

Houtermans (30), however, pointed out that the probability of a collision between two excited 2^3P_1 atoms each with a life of 10^{-8} seconds was very small, and he suggested that a collision between an excited 2^3P_1 atom and a 2^3P_0 metastable atom was a more likely explanation. This process may be written

$$Hg'(2^3P_1) + Hg'(2^3P_0) \rightarrow Hg_2^+ + \varepsilon \qquad (F)$$

The energy available for the ionisation of the molecule is now 9.52 + D electron-volts.

Since the vapour was excited by the photons from a mercury vapour lamp, any metastable 2^3P_0 atoms present in the vapour must have been produced by collisions of the second kind between excited 2^3P_1 atoms and normal atoms.

A photon cannot excite a normal atom into a metastable state, and therefore the process for the production of the 2^3P_0 atoms must be

$$Hg'(2^3P_1) + Hg \rightarrow Hg'(2^3P_0) + Hg + K.E.(0.2\ e\text{-}v.) \quad (G)$$

The formation of ionised molecules by the process F suggested by Houtermans will still show a dependence on the square of the intensity of the resonance radiation, since both the processes F and G are involved and in each of them a 2^3P_1 atom takes a part.

To test his suggestion Houtermans carried out a very ingenious experiment. After checking and confirming the results of Rouse and Giddings he examined the effect of the addition of hydrogen and of argon on the positive ion current in the vapour.

The addition of hydrogen resulted in a rapid decrease in the ionisation. This is due to the loss of both 2^3P_1 atoms and 2^3P_0 atoms by the processes A and C. Houtermans, however, was able to calculate the decrease in the number of 2^3P_1 atoms in his tube at different hydrogen pressures and hence to show that the ionisation was proportional to the number of 2^3P_1 atoms present.

The addition of argon gave an increase in the ionisation which was proportional to the first power of the argon pressure. Now the number of 2^3P_0 atoms formed by process B will increase with the first power of the argon pressure;

and therefore the ionisation must also be proportional to the number of 2^3P_0 atoms. This result is very important for it not only shows that a collision between an excited 2^3P_1 and a 2^3P_0, metastable, atom results in the formation of a molecular ion by the process F, but it also indicates that a collision between two metastable atoms does not result in ionisation.

If the process

$$Hg'(2^3P_0) + Hg'(2^3P_0) \rightarrow Hg_2^+ + \varepsilon \qquad (H)$$

is energetically impossible then we know that the ionisation potential of the mercury molecule must lie between the values 9.52 + D and 9.32 + D electron-volts, where D is the energy of dissociation of the normal molecule. This conclusion is of supreme importance in the development of the author's own experimental results on the formation of ionised molecules in mercury vapour.

There is yet another type of collision of the second kind which has not been discussed. This is ionisation by electron transfer which was first observed by Harnwell (34) and by Hogness and Lunn (35) in 1927. Suppose an ionised atom A collides with a normal atom B, then B may be ionised by an electron transfer from the atom B to the ion A provided the ionisation potential of A is greater than that of B. The energy difference between the ionisation potentials of the two atoms may be used partly in exciting one of the particles A or B and partly in increasing their kinetic energies of translation.

Harnwell observed processes of electron transfer of the type $He^{+} + Ne \longrightarrow He + Ne^{+}$ for various combinations of the rare gas atoms with each other and with hydrogen and nitrogen. In the example given the difference in the ionisation potentials of the two atoms is 3.0 electron volts, neither of the atoms has an excited state with energy as low as this and consequently the energy must be dissipated as kinetic energy of translation.

Hogness and Lunn discovered the effect with helium and argon ions in nitrous oxide.

The transfer process has been treated theoretically by Morse and Stueckelberg (36) and by Massey and Smith (37) on the basis of the new quantum mechanics. The theoretical results show that the probability of electron transfer is greater the smaller the amount of energy to be dissipated in kinetic form. This does not mean that the ionisation potentials of the colliding particles must be nearly equal for the electron transfer to take place. It will occur with a high probability if there is an excited state of one of the resulting particles with an energy just less than the difference between the ionisation potentials of the two atoms. The particle will then emerge from the collision in that excited state. This is in agreement with the experimental observations of such processes.

Electron transfer between doubly charged ions and neutral atoms was first observed by Henderson (38) in 1922. for α particles. This process has since been extensively studied for α particles by Rutherford, Chadwick and Ellis (39). These experiments indicate the transfer process gradually increases with the range of the α particle and then falls off sharply.

In 1930 Kallmann and Rosen (40) first observed a number of electron transfer processes between doubly charged ions and normal átoms of the type

$$Ar^{2+} + Ar \rightarrow Ar^{+} + Ar^{+}$$

$$Ar^{2+} + He \rightarrow Ar^{+} + He^{+}$$

$$Hg^{2+} + Hg \rightarrow Hg^{+} + Hg^{+}$$

These processes were studied by means of a mass spectro:
:graph. The distribution of the energy between the resulting ions was not examined in any detail, and has now been investigated by the author for the process

$$Hg^{2+} + Hg \rightarrow Hg^{+} + Hg^{+}$$

SECTION 3.

THE THEORY OF THERMIONIC EMISSION.

The thermal emission of electrons from a filament has been treated thermodynamically by Dushman (41). The problem may be regarded as equivalent to the evaporation of a monatomic gas and by applying the Clausius-Claperyon equation Dushman has shown that for any one particular surface the electron current emitted per unit area is given by the equation

$$i = AT^2 \varepsilon^{\frac{-b}{T}} \qquad (15)$$

where A and b are constants for the surface and T is the temperature of the emitter. In the derivation of this equation the effect of the mutual repulsions of the electrons has been neglected.

Let us now consider the passage of an electron current from a wire of radius r_w cms to a concentric cylinder of radius r_c cms when a potential difference of Vc volts is applied between the wire and the cylinder to draw the

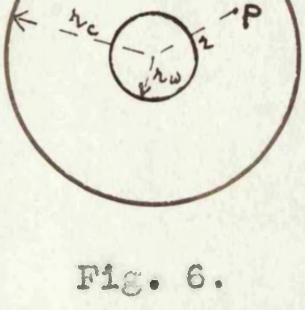


Fig. 6.

electrons away from the emitter. The electron density at a point P, r cms from the centre of the wire, will depend upon the current (i) emitted per cm length of the wire and the velocity (v) of the electrons at P.

For symmetrical cylindrical co-ordinates Poisson's equation

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -4\pi\rho \qquad (16)$$

can be written

$$\frac{1}{r}\frac{d}{dr}\left(r.\frac{dV}{dr}\right) = -4\pi\rho \qquad (17)$$

We also have $$-\rho = i\Big/2\pi r v \qquad (18)$$

and neglecting the initial velocity of the electrons

$$\frac{1}{2} m v^2 = Ve \qquad (19)$$

Eliminating v and substituting for ρ in (17) we obtain

$$r\frac{d^2V}{dr^2} + \frac{dV}{dr} = i\sqrt{\frac{2m}{eV}} \qquad (20)$$

The solution of this equation given by Langmuir (42) is

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\cdot\frac{V_c^{\frac{3}{2}}}{r_c\beta^2} \text{ amps per cm.}$$

$$= 14{\cdot}66 \times 10^{-6}\,\frac{V_c^{3/2}}{r_c\beta^2} \text{ amps per cm.} \qquad (21)$$

where β^2 is a function of the ratio r_c/r_w and is very nearly equal to unity for values of $r_c/r_w > 10$

We can now discuss the changes which take place in the emission from a heated filament under different conditions. If the applied potential between the filament and the collector is small then the value of the emission given by equation (21) will be less than the saturated emission given by equation (15). The electron current is then said to be limited by space charge, and raising the filament temperature will produce no increase in the emission. As the applied potential is gradually increased the emission will increase until its value given by equat: :ion (21) becomes equal to the saturated emission given by equation (15), further increase in the applied potential will then produce no increase in the electron current. That is, a saturated or temperature limited emission can only be increased by raising the temperature, while a space charge limited current can only be increased by raising the applied potential, or by admitting positive ions which will neutralise the negative space charge of the electrons.

Langmuir (42) was the first to point out the value of the space charge limited current as a detector of positive ions. A positive ion of mass M entering into the field between the filament and the anode will move with a velocity $\sqrt{m/M}$ times that of an electron of mass m, in the same field. The positive ion will consequently neutralise the space charge of at least $\sqrt{M/m}$ electrons. Actually the positive ion describes a number of spirals around the filament before striking it and can neutralise the space charge of as many as 10^4 to 10^6 electrons. The presence of a small number of ions can thus cause an appreciable increase in the filament emission.

In 1920, Found (43) verified the equation (21) obtained for the space charge limited emission. His apparatus consisted of a filament run at a high temperature and a surrounding anode. He showed that in the absence of any gas or vapour the current was accurately proportional to $V^{3/2}$, where V was the applied potential corrected for contact potentials. By admitting a number of gases and vapours to the tube, he obtained values for their ionisation potentials by determining the value of the potential V at which the current began to increase at a rate faster than that given by the 3/2 power law. He obtained values of 20.5 volts and 10.1 volts for the ionisation potentials of helium and mercury respectively.

The next improvement in the space charge method was made by Hertz (44) in 1923. His apparatus could be used to determine either excitation potentials or ionisation potentials by making a simple alteration in the external circuit. For the investigation of ionisation potentials he kept the potential between a filament and the surrounding anode constant at a value below the resonance potential of the gas under investigation. The filament was run at a high temperature to give a strongly space charge limited emission. The electrons from a second filament were accelerated up to a gauze in the anode surrounding the first filament. When the energy of the electrons, from the second filament, was sufficient to produce ions the emission from the detecting filament showed a marked increase. Although Hertz investigated the excitation and ionisation potentials in neon and argon, he has only reported an investigation of the excitation potentials in helium. This is unfortunate since any results, which he may have obtained, for ionisation in helium would have been interesting for comparison with those given in this thesis.

Hertz' method is an improvement over the original two electrode method used up to 1923, for the emission from the detecting filament is constant below the ionisation potential, and the break in the curve can be determined more accurately than when the curve is steadily increasing.

In both these methods, however, the <u>increase</u> in the emission must be measurable in comparison with the <u>actual</u>

emission before it can be detected. The sensitivity can be greatly increased by using two filaments arranged in parallel, one of which is exposed to any ions that may be formed, while the other is carefully shielded. By balancing the emissions from the two filaments, any fluctuations in the heating current can be eliminated, and the actual change in the emission of the detecting filament can be measured by a sensitive galvanometer. This is the method adopted by the author.

The space charge limited emission from a filament is unaffected by the presence of any electrons which may enter the region around the filament from any other source. This is a very great advantage as the effect of photo:electrons and secondary electrons which may be ejected from the electrodes and gauzes in the apparatus can be neglected, provided there are no fields present which can give these electrons an energy greater than that of the electrons used to excite or ionise the gas.

Actually because of the conduction of the heat by the filament leads, the emission from a filament is not space charge limited over its entire length. The emission from the central, or hottest, portion of the filament is space charge limited, but the emission from the cooler portion near the ends is temperature limited. Any electrons entering the region round the filament will reduce the saturated emission drawn from the ends, because of their negative space charge. This swinging over of the emission from a saturated to a smaller space charge limited value, will occur over a short length of the filament on either side of the centre, at the two points where the emission just ceases to be space charge limited.

If the temperature gradient at these two critical points is small, then the electrons approaching the filament from an external source will produce a greater effect than if the temperature gradient is large, since the emission from a greater length of filament will be affected. As the temperature of the central portion of the filament is increased the position of these two critical points, which are determined by a certain fixed temperature, will move towards the ends of the filament. Now the temperature falls off according to an exponential law as the distance from the centre is increased and therefore the temperature gradient decreases as we approach the ends of the filament. The effect of raising the temperature of the filament will therefore be to decrease the temperature gradient at the points where the swinging over of the emission occurs. This means that raising the temperature of the filament will make it more sensitive to the effect of external electrons.

The importance of this point will be discussed in the experimental section.

SECTION 4.

DISCUSSION OF SOME PREVIOUS WORK ON IONISATION IN HELIUM AND MERCURY VAPOUR.

Although a considerable amount of work was carried out between 1918 and 1923 with a view to determining the excitation and ionisation potentials of helium, no satisfactory explanation of the different results has so far been given.

The earliest workers were chiefly concerned with the obtaining of data by means of which the quantum theory of the atom could be checked. Until 1922, when Lyman (5) carried out his spectroscopic determination of the atomic ionisation potential which was found to be 24.5 electron-volts, the generally accepted value had been 25.2 electron-volts. In view of this correction the author has, where necessary, substracted 0.7 electron-volts from the values of the excitation and ionisation potentials given by workers before that date.

In 1920, Compton (45) using a modified Lenard method detected the first excitation potential at 19.8 volts and an ionisation potential at 24.5 volts. He also observed some ionisation for electron energies between 19.8 and 24.5 volts. This ionisation increased steadily as the pressure of the helium was raised. Compton suggested that the ions detected below the atomic ionisation potential were atomic ions formed by collisions between electrons and atoms in excited states. This process if it occurred with sufficient probability would certainly give rise to atomic ions below the atomic ionisation potential. Evidence will be put forward in the experimental section to show that the probability of such a collision is too small to account for the magnitude of the positive ion current detected.

Other workers who obtained similar results suggested that the effect was due to the ionisation of atoms of an impurity present in the helium, by collisions of the second kind with excited helium atoms.

An interesting investigation was that carried out by Horton and Davies (46) who used a modified form of Davis and Goucher's apparatus which had proved so satisfactory for a similar investigation with mercury (47).

Their apparatus is shown diagrammatically in fig. 7. The arrangement of potentials used for the detection of positive ions is given in the figure. Electrons from the filament F were accelerated up to the gauze G_1 by a variable potential V_0 and then retarded by a potential $V_1 > V_0$ applied between the gauzes G_2 and G_3. Ions formed in the field-free space between G_1 and G_2 were accelerated

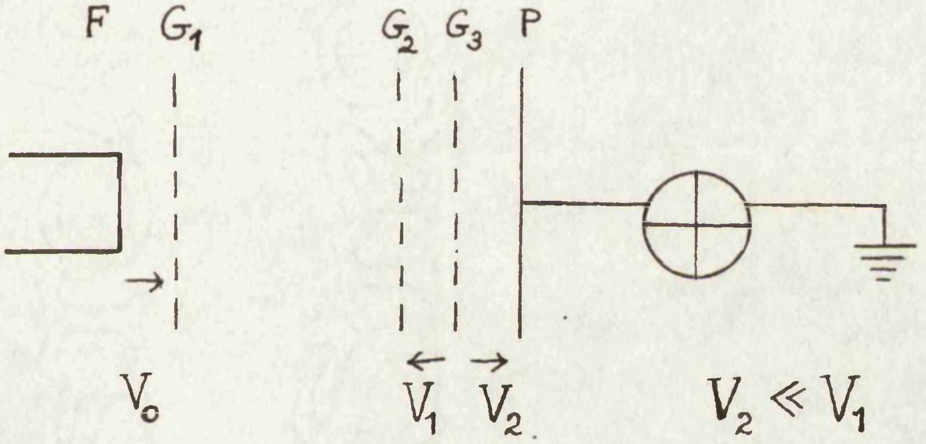


FIG. 7. Diagram to show arrangement of potentials in Horton and Davies' apparatus.

up to the gauze G_3 by the potential V_1 and were able to pass to the plate P against a small retarding potential V_2 which was applied between G_3 and P to prevent any electrons from leaving P. Electrons ejected from G_3 were accelerated up to P by the potential V_2.

With this arrangement of potentials as soon as the value of V_0 becomes equal to the first excitation potential a negative current due to the electron emission from G_3 should be detected by the electrometer connected to P. As soon as ions are formed the current should change from a negative to a positive value.

Horton and Davies detected a negative current which indicated an excitation potential when V_0 was equal to 19.8 volts. This was due to the ejection of electrons from G_3 by metastable 2^3S atoms. Oliphant (48) has since shown that metastable 2^3S helium atoms are singularly effective in bringing off electrons from metal surfaces with which they collide. When V_0 was increased to 20.5 volts, the resonance potential, Horton and Davies observed a strong positive ion current. They concluded that this was due to the ionisation of the metastable 2^3S atoms by the photons of the resonance radiation. In view of the work of Lawrence and Edlesfen referred to in section 2, we know that the probability of ionisation of a 2^3S atom by a photon of energy 20.5 electron-volts must be very small, since it only requires a further 4.7 volts energy for ionisation. This explanation cannot be correct.

Franck (49) has pointed out one source of error which is inherent in the use of this method. Electrons liberated from G_3 are accelerated by the potential V_1 and have energies which depend on their velocity of ejection and on the value of V_1. This energy may be far greater than the energy of the electrons from the filament and sufficient for them to be able to produce ions by collision with gas atoms.

There is however another much more serious source of error which does not appear to have been previously pointed out. The success of the method depends upon the fact that photoelectrons are prevented from leaving the plate P, if this is not so then it is impossible to distinguish between the arrival of a positive ion and the ejection of an electron. This means that the value of V_2 must be greater than the difference between the energy of the photons and the work function of the plate.

Horton and Davies used gauzes and electrodes of platinum which has a work function of 6.3 electron-volts (50). The value of V_2 should therefore not have been reduced below 18 volts. Unfortunately they do not give the precise value used, but they state that it was "very much smaller" than V_1 which was kept equal to $V_o + 4$. This suggests a value below 10 volts since a low value of V_2 increases the sensitivity to positive ions. No mention is made of any precaution taken to keep V_2 above 18 volts.

Metastable atoms are as effective as photons in liberating electrons from metal surfaces. The metastable atoms formed in the field-free space must pass through the gauzes G_2 and G_3 and reach the plate P before they can liberate electrons from it. The resonance radiation emitted by excited atoms in the field-free space can be absorbed and re-emitted by other atoms throughout the gas, and consequently will be more effective than the metastable atoms in liberating electrons from the plate P. This would account for the fact that Horton and Davies observed only excitation at 19.8 volts and ionisation at 20.5 volts.

In 1920, Goucher (51) used the same method and detected ionisation at about 20 volts, for a helium pressure as low as 0.01 mm. His value of V_2 was only 1.5 volts, which fully accounts for his result.

For work with mercury in which the photons of the resonance radiation have only 4.9 electron-volts energy, then a small potential of one or two volts is sufficient to prevent any photoelectric emission, and this method gave very satisfactory results.

The ionisation which occurs in helium for electron energies between 17 and 40 volts has now been investigated by the author, using a mass spectrograph, and some interesting results have been obtained.

In 1936 Arnot and Milligan (4) made a positive ion analysis of the ions formed in mercury vapour by electron impact. Their apparatus is fully described in Part 3 of this thesis, where an account of a similar investigation for helium ions is given. They obtained definite evidence which showed that ionised molecules are formed in mercury vapour by the attachment of excited atoms to normal atoms. Their curves indicate that an excited atom must possess about 9.5 electron-volts energy before it can combine with a normal atom to form an ionised molecule.

The energy level diagram for the mercury atom given in fig. 1b, shows that there are a large number of excited states having about this amount of energy. The following apparatus was designed to determine the appearance potential more precisely by the use of a balanced space-charge method. The high sensitivity of this method has been discussed on page 37.

PART 2.

AN INVESTIGATION OF THE FORMATION OF MERCURY MOLECULES BY A BALANCED SPACE-CHARGE METHOD.

THE APPARATUS.

The apparatus was contained in a large pyrex tube fitted with a 5 cm. ground glass joint, so that the whole apparatus could be withdrawn for adjustment and filament renewal.

The scale drawing of the tube in fig. 8 shows the advantage of this type of tube since it can be used for more than one piece of work. The dimensions of the apparatus are only restricted by the size of the joint. The diameter of the joint should not exceed about 5 cms if the glass is to withstand the high external pressure.

Low vapour pressure Apiezon grease "N" was used for the joint which was water cooled. It was found that the joint could be removed without difficulty if it was warmed with hot water to lower the viscosity of the grease. The removal of the joint was facilitated by the solid glass arms attached to the upper part of the tube. Any grease coming into contact with the apparatus on withdrawal was immediately removed, and the inside of the joint was carefully cleaned before re-insertion of the apparatus.

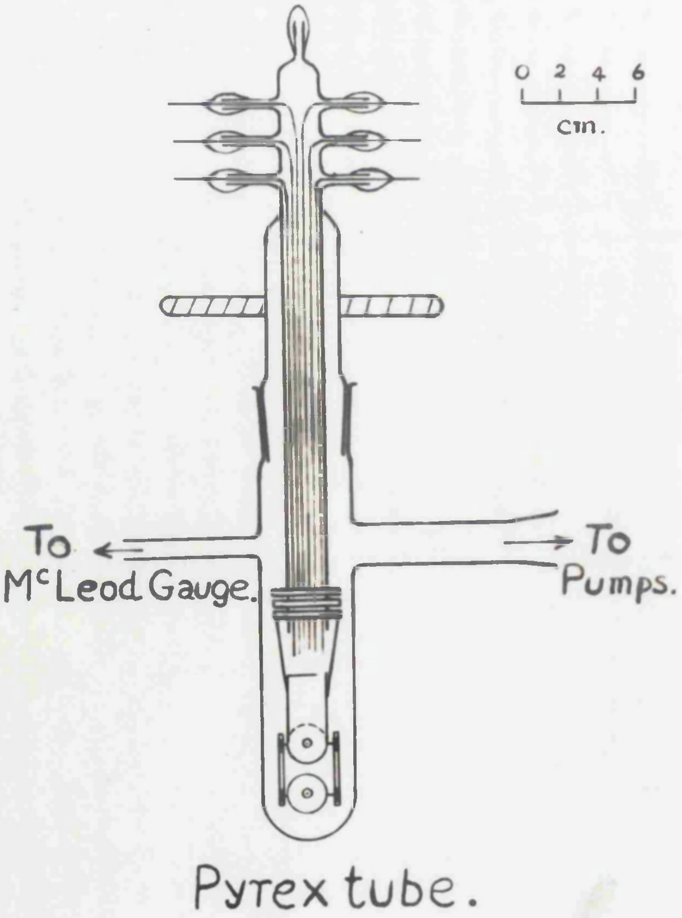


FIG. 8.

The filament leads and connecting wires, enclosed in fine quartz tubes, were led down the central tube. They were sealed into the pyrex tube by Lilliendahl's white vacuum wax.

The tube was supported on a wooden stand at an angle of 10° to the horizontal. The wider outlet tube was connected to a mercury diffusion pump backed by a Hyvac pump, the narrow tube was connected through a tap to the McLeod pressure gauge. A small quantity of phosphorus pentoxide was kept in a large air reservoir on the low vacuum side between the diffusion and backing pumps. The purpose of the reservoir was to give a large volume on the low vacuum side, so that in the event of a temporary failure of the Hyvac, the diffusion pump could continue to work for some time without the backing pressure becoming too great.

When it was necessary to let down the vacuum dry air was admitted by opening a tap between the reservoir and the Hyvac. The air which entered through the tap was first passed through a drying tube containing phosphorus pentoxide. The McLeod gauge was kept permanently evacuated by closing the tap between the gauge and the apparatus before the admission of the air.

The McLeod gauge was of the full length type, with a rubber tubing connection between the bulb and the mercury reservoir. It was found that by fitting an air trap between the rubber tubing and the bulb the troublesome effect of air bubbles was entirely eliminated.

A scale drawing of two forms of the apparatus together with a wiring diagram is shown in fig. 9. All metal parts, including gauzes, filament leads and connecting wires were made of gas-free nickel spot-welded where necessary. The cylinders C_1 and C_2 were similar except for a gauze window set into one side of C_1. The end-caps for the cylinders were pressed out of one piece of nickel so as to give a perfect fit. The holes, for the entry of the filament leads, were punched out of the nickel and then filed to the exact size of the short quartz insulating tubes. The iris formed in the filing process gave a good tight fit. The cylinder C_1 was fitted into a rectangular box folded out of one piece of nickel. The remainder of the box formed the space S and the shield round the filament F_1. In this way any electrons from F_1 were prevented from reaching the outside of the cylinder C_2. The cylinder C_2 was supported from C_1 by quartz rods which insulated it from the rest of the apparatus.

The filament F_1 was a straight tungsten wire 0.15 mm in diameter and 12 mm long. The filaments F_2 and F_3, which were connected in parallel, were of tungsten 0.1 mm in diameter and 12 mm in length. They were co-axial with the cylinders C_1 and C_2 and their leads were insulated from

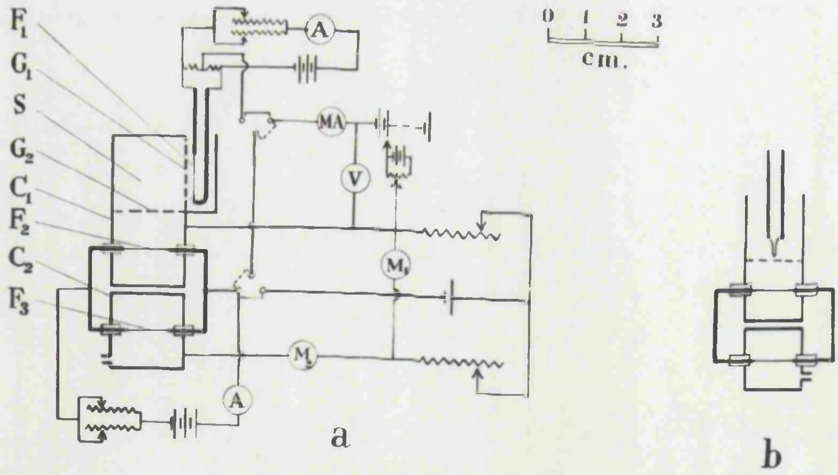


FIG. 9. Apparatus and wiring diagram for balanced space-charge method.

the end caps by short quartz tubes.

Three nickel-plated copper brackets were fitted round the central tube which passed through the joint. The apparatus was supported from the lowest bracket by means of short stout nickel wires spot-welded to the rectangular box as shown in fig. 8. The leads for the filament F_1 were kept permanently fixed to the other two brackets. The filament was supported by two short stout wires attached one to each bracket. The wires were fused into short pieces of thin pyrex tubing which were joined together side by side to give a rigid support for F_1. All wires were attached to the brackets by screws and washers. The quartz tubes which insulated the wires in the central tube were closely packed together, this gave sufficient rigidity for the other wires which could be led out and spot-welded directly to the different parts of the apparatus.

A pool of mercury was kept at the lower end of the tube which could be heated by a non-inductively wound electric furnace. A nickel-plated copper disc, just small enough to pass through the joint, was fitted between the apparatus and the outlets to the pumps and the McLeod gauge to prevent rapid diffusion of the mercury vapour at high pressures. The vapour pressure corresponding to different temperatures of the furnace was found by using an ionisation gauge of the external collector type.

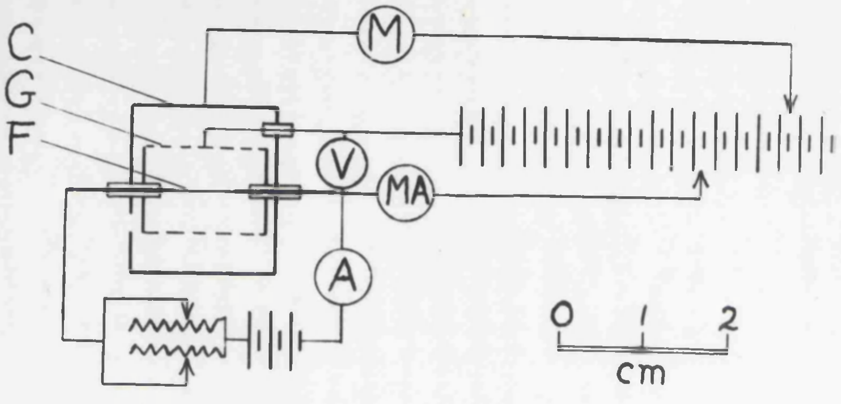


FIG. 10. IONISATION GAUGE.

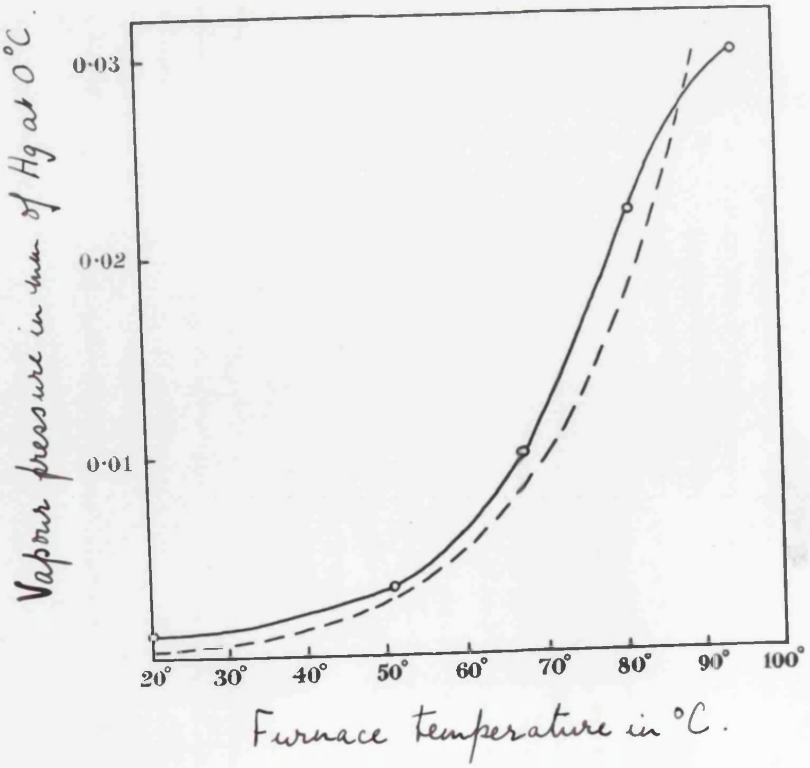


FIG. 11.

Broken curve is one-quarter of saturation vapour pressure.

The gauge which is shown in fig. 10 was substituted for the apparatus in the tube. The metal cylinder C and the cylindrical gauze G were made of nickel. The figure shows clearly the design of the gauge. Electrons from the filament F were accelerated up to the cylindrical gauze G by a potential V_0, and then were retarded by a potential $V > V_0$ applied between the gauze G and the concentric cylinder C. Positive ions formed in the space between G and C were drawn to C, and the positive ion current, which increases as the pressure of the gas or vapour in tube is raised, was measured by the galvanometer M. V_0 was set equal to 50 volts and V equal to 60 volts. The emission from the filament was held constant. Nitrogen was admitted to the tube, and the positive ion current measured at different nitrogen pressures as read on the McLeod gauge. The curve showing the positive ion current plotted against nitrogen pressure is the calibration curve of the gauge. When the nitrogen had been pumped out the furnace was switched on and the positive ion current was measured at different furnace temperatures and at room temperature,when the pressure of mercury vapour is 1×10^{-3} mm of Hg. The positive ion current was then plotted against furnace temperature and the ordinates reduced so that this curve at room temperature fitted the calibration curve at a nitrogen pressure of 1×10^{-3} mm of Hg. This correction is necessary because the positive ion current depends upon the relative probabilities of ionisation at a collision in mercury vapour and nitrogen, as well as on the pressure.

The actual vapour pressures at different furnace temperatures were then read off and the values of the vapour pressure were reduced to their values at 0°C. The full curve in fig. 11 shows the variation in vapour pressure with furnace temperature. The broken curve represents the saturation vapour pressures corresponding to the same furnace temperatures, the ordinates have been reduced by a factor one quarter. The values were taken from the "International Critical Tables" and reduced to 0°C. The curves show that the actual vapour pressure in the tube was about one quarter the saturated value at the same furnace temperature. The bend in the vapour pressure curve at a temperature of about 85°C indicated that some modification must be made in the apparatus for the use of higher pressures.

A second form of the apparatus shown in fig. 9a was constructed slightly smaller than the original so that it could be enclosed in a nickel cylinder 3 cm.in diameter and 6 cm.long. The cylinder was closed by a tight-fitting cap at each end, the only opening being a small aperture for the entry of the filament F_1. The other leads and connecting wires were brought out through quartz tubes which fitted tightly into the containing cylinder. When mercury was placed inside this cylinder, it was found that the heat radiated from the filaments was sufficient to produce a high vapour pressure. The vapour pressure was estimated by placing the ionisation gauge, without its outer cylinder C, inside the containing cylinder which took the place of C as the collector of positive ions. The vapour pressure inside the cylinder was found to be of the order of 0.1 mm of Hg at $0^{\circ}C$.

EXPERIMENTAL PROCEDURE.

The filament F_1 was first flashed to get rid of the gas in the tungsten. This was done by applying a potential of 60 volts between the filament and the gauze G_1, and then quickly raising the temperature of the filament until it gave a saturated emission of 100 milliamps. After ten seconds the heating current was reduced to zero and the gas given off was pumped out. The emission was read on a milliammeter with an internal shunt which gave the instrument ranges from 0-5, 0-50, and 0-500 milliamps. A very delicate wire which fused at 200 milliamps was kept in series with the milliammeter in case a short circuit, or an arc, occurred between the filament and the cylinder C_1. The heating current was adjusted to give a saturated emission of 2 milliamps and the filament was then run-in until the emission became steady and no more gas was given off.

The process was then repeated for the filaments F_2 and F_3. The same part of the external circuit could be used by short circuiting the galvanometers M_1 and M_2 and by making the dotted connections in the key, which was specially constructed for this purpose.

When the pressure of the residual gas, shown on the McLeod gauge, had fallen below 2×10^{-5} mm the heating current through the filaments F_2 and F_3 was adjusted to give a saturated emission from each filament of about 0.1 milliamp. The connections in the key were then changed to those represented by the full lines so that the potential between the filaments F_2 and F_3 and their respective cylinders was reduced to 2 volts. This resulted in their emissions becoming strongly space-charge limited to a value of about 0.01 milliamps. The emission from F_3 alone was read on the galvanometer M_2, which had a sensitivity of 9.7×10^{-9} amp/mm, so that its constancy during any one run could be checked. The emissions from F_2 and F_3 were then balanced by the bridge arrangement which incorporated two 10,000 ohm resistance boxes and the galvanometer M_1, which had a sensitivity of 7.8×10^{-11} amps/mm. Both galvanometers were provided with universal shunts so that their sensitivities could be suitably altered.

The heating current for the filament F_1 was adjusted to give a saturated emission of 0.2 milliamps, and then the potential between the filament and the gauze G_1 was reduced to a value of about 2 volts and gradually increased. The electrons from F_1 were accelerated up to the gauze by a potential V_o applied between the centre of the filament and the gauze. Two 100 ohm resistance coils were connected across the filament leads and the potential V_o was applied to the junction of the two coils as shown in fig. 9. Since the electrons are emitted from a short region in the centre of the filament this arrangement considerably reduces the effect of the potential drop along the filament.

V_o was altered by means of a potential divider, which was connected to earth, and the value of V_o was read on a Weston standard voltmeter.

Owing to the high sensitivity of the galvanometer M_1, the whole of the external circuit connected to the filaments F_2 and F_3 had to be carefully insulated. All the batteries, rheostats, resistance boxes etc. were mounted on wooden boards which rested on ebonite blocks with sulphur rings. It was found that if one stood on a wooden board, insulated from the floor by ebonite blocks, when adjusting the value of V_o no disturbance of the galvanometer occurred.

When V_o was raised to a value at which ions were formed in the field-free space S, some of the ions diffused through the gauze G_2 and by neutralising the space charge round the filament F_2 increased its emission.

If R_1 and R_2 are the values of the resistances taken out of the boxes to balance any inequalities in the emissions from F_2 and F_3 at the start of the run then

$$i_1 R_1 = i_2 R_2 \qquad (22)$$

where i_1 and i_2 are the actual emissions from F_2 and F_3. If δi is the <u>change</u> in the emission from F_2 due to the presence of positive ions, the actual current flowing in the galvanometer circuit is given by i where

$$i = \frac{(i_1 + \delta i) R_1 - i_2 R_2}{R_1 + R_2 + G} \qquad (23)$$

and G is the resistance of the galvanometer and the shunt. From equation (22) we have

$$i = \frac{R_1}{R_1 + R_2 + G} \cdot \delta i \qquad (24)$$

The current through the galvanometer is therefore proportional to the change in the emission from F_2.

With the apparatus shown in fig. 9b the ions were formed in the cylinder C_1 and were immediately drawn to the filament F_2. In this way the sensitivity was increased. The electrons from F_1 entering the cylinder C_1 were retarded by the potential of 2 volts applied between F_2 and C_1, and consequently a number must have made collisions when moving with an energy less than V_o.

The results obtained with the two forms of the apparatus show that the effect of removing the field-free space is unimportant, and the increase in the sensitivity enables the appearance potential to be determined with equal accuracy by either method. Theoretically, the original design of the apparatus is the better and without it one could not have been certain of the accuracy of the results obtained without the field-free space.

It is well known that in the absence of any positive ions the number of electrons passing through a gauze does not increase proportionally with the number of electrons coming up to the gauze. A preliminary test was therefore made by insulating the gauze G_1 from the rest of the apparatus, and then measuring the electron current to G_1 and to the box behind G_1 as V_o was increased. When V_o was below the ionisation potential the emission from F_1 was space-charge limited and consequently increased as V_o was increased up to the ionisation potential when saturation set in. It was found that when the emission from F_1 was kept constant, by altering the heating current after each change in V_o, the number of electrons entering the field-free space varied in an erratic manner. On the other hand when the emission was allowed to increase with V_o it was found that the number of electrons entering the field-free space steadily increased with V_o. The increase was linear up to the ionisation potential,

V_o = 10.4 volts, after which the rise became less steep as the emission approached its saturated value. It was therefore decided not to attempt to keep the emission from F_1 constant but to allow it to increase steadily as V_o was increased.

RESULTS.

MEASUREMENTS IN VACUUM.

The tube was temporarily rotated into a more vertical position and the lower end of the tube up to the two side outlets was immersed in a large Dewar flask containing a mixture of solid carbon dioxide and alcohol. V_o was increased from 0 to 12 volts at intervals of 0.5 volt and the change in the emission from F_2 was read on the galvanometer M_1. A number of runs were taken for different temperatures of the filament F_2. The results obtained are shown in fig. 12. The value of the saturated emission from F_2 is given to the right of each curve. The saturated emission, which is given by the equation $i = AT^2\varepsilon^{-\frac{b}{T}}$ on page 32, is a measure of the temperature of the filament. The curves, which have been slightly displaced in a vertical direction to separate the points at low values of V_o show that the emission from F_2 decreases steadily as V_o is increased. It is also seen that the rate of decrease increases with the temperature of the filament F_2. It was found that the decrease in the emission from F_2 increased when the emission from F_1 was increased.

We have seen on page 37 that owing to the cooling of the filament by the leads, the emission is not

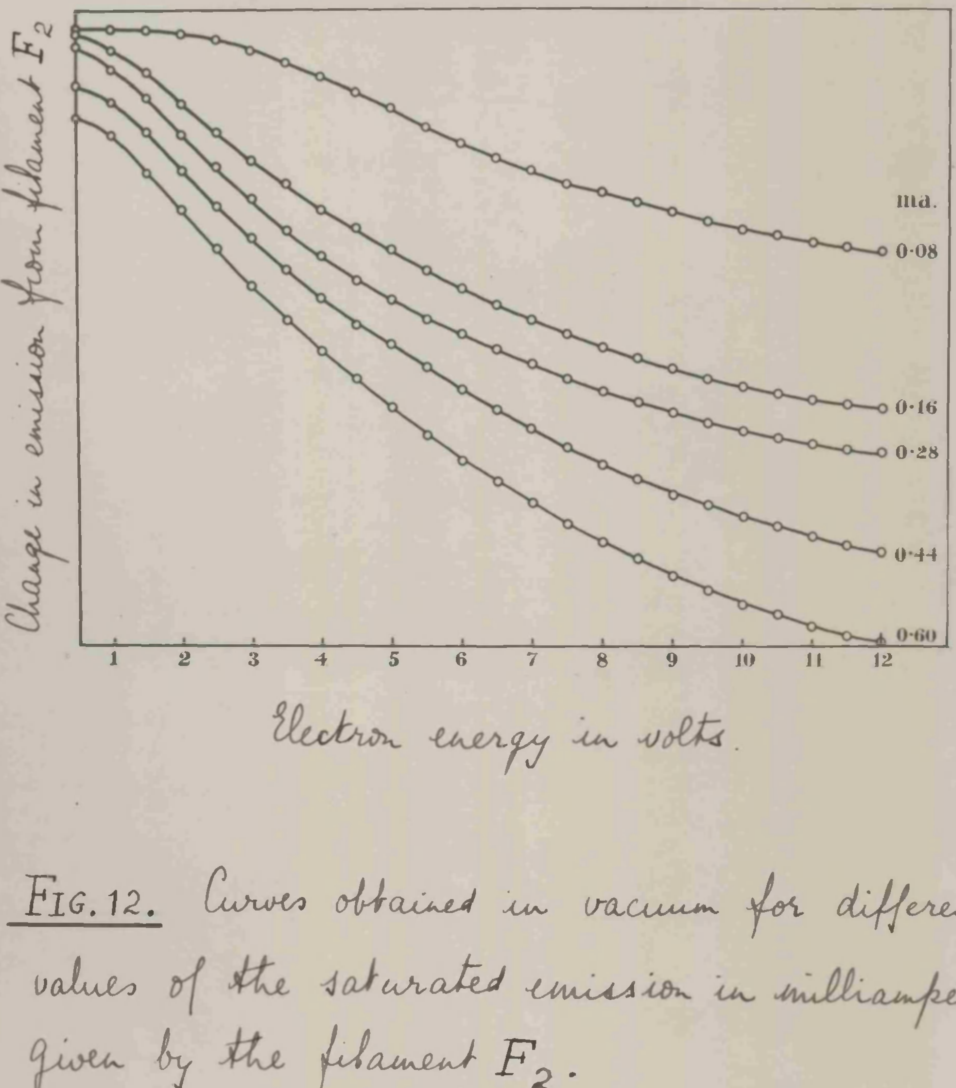


FIG. 12. Curves obtained in vacuum for different values of the saturated emission in milliamperes given by the filament F_2.

entirely space-charge limited and that the presence of any electrons from an external source will decrease the emission. Since the decrease in the emission from F_2 increases with V_o and with the emission from F_1 it must be due to the scattering of electrons from F_1 into the cylinder C_1 . It has also been shown from theoretical considerations that the effect of the scattered electrons will increase as the temperature of the filament F_2 is raised. This is borne out by the curves of fig. 12.

In the earlier runs with mercury vapour the heating current for the filaments F_2 and F_3 had been set to give a saturated emission of 0.1 m.A. To minimize the decrease in the emission from F_2 the filament current for F_2 and F_3 was subsequently reduced to give a saturated emission of 0.08 m.A. from each filament. The uppermost curve in fig. 12 shows that for this value of the saturated emission, the fall in the curve is very nearly linear. The curves obtained with mercury vapour showed a decrease in the emission from F_2 that was strictly linear as V_o was increased up to the point at which ions were formed. It was thus possible to make a more accurate determination of the ionisation potential than would have been the case for a non-linear fall.

MEASUREMENTS IN MERCURY VAPOUR.

Three curves obtained at different pressures of mercury vapour are given in fig. 13. The curves show the change in the emission from the filament F_2 as the energy V_o of the electrons from F_1 was increased. The pressure for curve (a) was 0.001 mm, for curve (b) 0.031 mm, and for curve (c) 0.11 mm of Hg at 0^oC.

The low pressure curve (a) shows a linear fall, similar to that obtained in vacuum, for electron energies below 10 volts. At 10.5 volts the curve begins to rise sharply, showing the presence of ions which neutralise the space charge around F_2 and increase its emission. The medium pressure curve (b) is similar to curve (a) except that ions now appear at about 9.5 volts. This movement, through about one volt, of the point where the curve begins to rise was found in all pairs of curves taken at pressures of the order of 0.001 and 0.01 mm.

A number of runs were taken at pressures ranging from 0.01 mm to 0.03 mm of Hg at 0^oC, V_o being gradually increased in steps of 0.1 volt. Two typical curves are shown in fig. 14. The curve (a) was obtained with the apparatus shown in fig. 9a, at a pressure of 0.026 mm of Hg, the curve (b) was obtained with the apparatus of fig. 9b at a pressure of 0.03 mm of Hg. All such curves showed a distinct increase in slope in the rising portion at a point about 1 volt above the bend in the curve. This change in slope did not appear

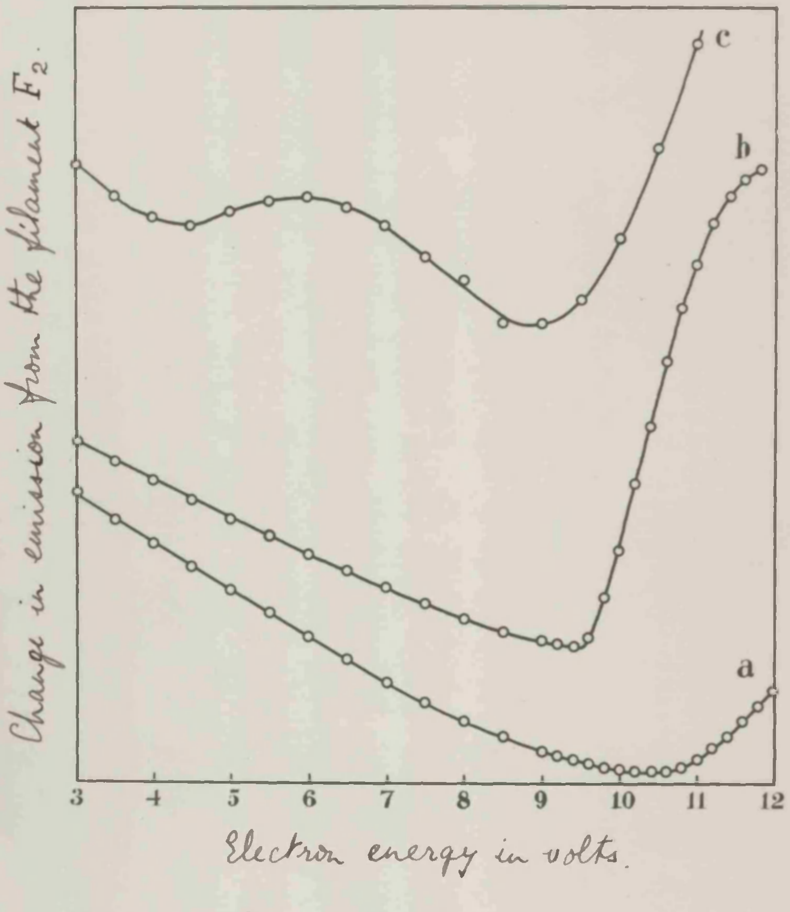


FIG. 13. Curves obtained in mercury vapour.
The vapour pressure for curve (a) was 0·001 mm.,
for curve (b) 0·037 mm. and for curve (c) 0·71 mm. at 0°C.

in the rising portion of any of the curves taken at a pressure of 0.001 mm of Hg at $0^{o}C$.

The formation of mercury molecular ions, as shown by Arnot and Milligan, requires a collision between an excited and a normal atom, that is it must occur within 10^{-8} seconds after the excitation of the atom. The probability of such a collision occurring at low pressures is very small. The value of V_o at which the low pressure curve (a) in fig. 13 starts to rise must therefore indicate the ionisation potential of the atom which is known from spectroscopic data to be 10.39 electron volts. The values of V_o given in these curves are uncorrected for contact potentials which will vary with the type of apparatus used and at each filament renewal. This accounts for the relative shift in the curves of fig. 14. It is to be noted that the curves (a) and (b) of fig. 13 were obtained consecutively and require equal corrections for the voltage scale.

The movement of the bend in the curves to a lower value of V_o when the pressure is increased by a factor of ten indicates the appearance of molecular ions. In the higher pressure curves the ionisation potential of the atom is indicated by the inflexion in the rising portion, which occurs at about one volt above the bend. The point at which these curves begin to rise is then the appearance potential of the molecular ion.

By determining the difference in energy between the point at which the curve begins to rise and the point at which the inflexion occurs the appearance potential of the molecular ion can be found, since the ionisation potential of the atom is known to be 10.39 volts. The value so obtained is independent of any contact potentials. Owing to the energy spread of the electrons from F_1 the bend is not sharp. By extrapolating the rising and falling portions of the curve as shown in fig. 14, the effect of the energy spread of the electrons from F_1 can be eliminated.

The following table gives seven values of the appearance potential determined from different curves obtained with the two forms of the apparatus shown in fig. 9. The pressure at which the curves were obtained is also given.

TABLE 1.

Apparatus of fig. 9 a.		Apparatus of fig. 9 b.	
Pressure in mm. of Hg at 0°C.	Appearance Potential electron-volts.	Pressure in mm. of Hg at 0°C.	Appearance Potential electron-volts.
0.026	9.71*	0.030	9.70†
0.020	9.62	0.027	9.64
0.017	9.77	0.020	9.65
0.009	9.68		

* From curve (a) fig. 14.   † From curve (b) fig. 14.

Three other curves obtained with the modified form of the apparatus shown in fig. 9 a gave values of 9.78, 9,82, and 9,64. The mean of these ten results is 9.70 ± 0.01.

An excited mercury atom must therefore possess a minimum energy of 9.70 ± 0.01 electron-volts before it can combine with a normal atom to form an ionised molecule by the process

$$Hg' + Hg \rightarrow Hg_2^+ + \varepsilon \qquad (A)$$

Houterman's explanation of the photoionisation of mercury vapour by its resonance radiation by the process

$$Hg'(2^3P_1) + Hg'(2^3P_0) \rightarrow Hg_2^+ + \varepsilon$$

has already been discussed on page 27. Since this process requires a collision between two excited atoms we would expect it to occur at higher pressures than are necessary for the occurrence of process (A) which involves only one excited atom.

The curve (c) in fig. 13, obtained at a pressure of 0.11 mm of Hg at 0°C with the modified apparatus enclosed in the nickel cylinder, definitely indicates the presence of ions for electron energies well below the appearance potential of the molecular ion at 9.7 electron-volts. Several similar curves were obtained at this high pressure. The curve (a) in fig. 15 shows this curve (c) of fig. 13 corrected for the fall in the emission from F_2, by the substraction of the results of a vacuum run. This fall has been shown to be due to the fact that the emission from F_2 is not entirely space charge limited, and is consequently decreased by the presence of electrons from F_1 which are scattered into the region round F_2.

In view of Houterman's evidence that a collision between two metastable 2^3P_0 atoms does not lead to ionisation, it follows that the rise in the curve (a) in fig. 15 cannot occur below the resonance potential 4.86 electron-volts. A correction of + 0.65 volts has consequently been made to the voltage scale in fig. 15 to make the rise begin at 4.86 volts. This correction can be accounted for by contact potentials existing in the apparatus. When the curve is corrected in this way the second upward rise due to the formation of molecular ions by the process (A) sets in at 9.7 volts, which is the mean value for the appearance potential already obtained.

For these high pressure curves V_0 was altered in steps of 0.5 volt, the primary object being speed, for owing to the rapid deterioration of the tungsten by the mercury vapour the emission from the filaments F_2 and F_3 tended to fluctuate. This was carefully checked by observing the galvanometer M_2, and any change in the

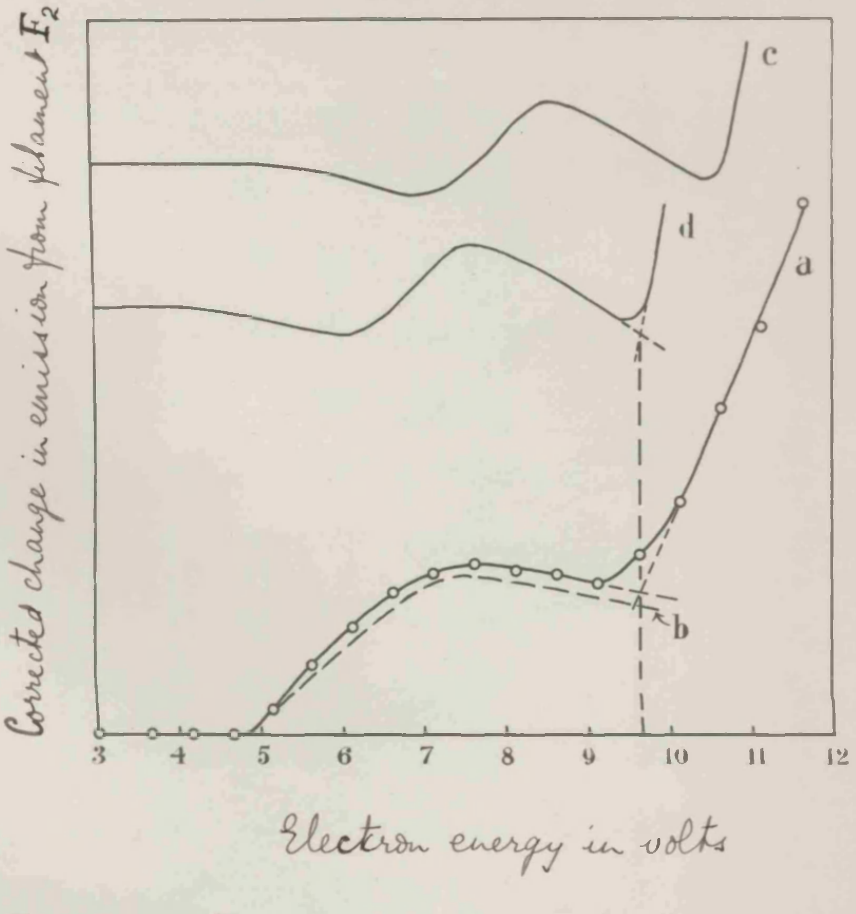


FIG. 15. Curve (a) is the curve (c) of fig. 13 corrected by the subtraction of a curve obtained in vacuum.
Curve (b) is Penney's theoretical excitation function for the 2^3P_1 state
Curve (c) is Snavely's original curve
Curve (d) is Snavely's curve with suggested correction for voltage scale.

emission from F_2 due to deterioration was easily distinguishable from a change due to the presence of positive ions. After any fluctuation the run was always restarted, and the experiment repeated until a sufficient number of complete curves had been obtained to confirm the result.

The broken curve (b) in fig. 15 represents the theoretical excitation function of the 2^3P_1 state given by Penney (22). The close agreement between the theoretical curve and the experimental curve below 9.7 volts confirms Houterman's conclusion. If a collision between two metastable 2^3P_0 atoms each with an energy of 4.66 electron-volts resulted in the formation of a molecular ion, we would have expected the ions to appear at a pressure more nearly equal to the pressure necessary for the process (A). Furthermore, if the curve (a) of fig. 15 had been corrected to give a rise beginning at 4.66 volts, instead of at 4.86 volts, then the second upward rise would have occurred at 9.5 volts, a value which is over 0.1 volt less than the lowest value of the appearance potential determined with a similar apparatus at a lower pressure.

DISCUSSION OF RESULTS.

While this piece of work was drawing to a conclusion a paper on the same subject was published by Snavely (52). His apparatus was similar to that shown in fig. 9 b. His published curve obtained at a pressure of 0.09 mm is reproduced in fig. 15 as curve (c). This curve can be compared with the author's curve (a). It is of approximately the same shape but is moved bodily to the right relative to the curve (a). Snavely corrected his voltage scale for contact potentials by moving the curve until the second minimum occurred at 10.39 volts, for he assumed that the steep rise was due to the onset of direct atomic ionisation. At the same time he remarked that an inflexion occurred in the upward rise of the corrected curve at 11.2 volts. The curves given in this thesis show that the inflexion marks the appearance of atomic ions, whose effect is superimposed on the already existing molecular ions. If Snavely's curve is now readjusted to bring the point of inflexion down from 11.2 to 10.39 volts, the curve takes the form of curve (d) in fig. 15. The steep upward rise now begins at 9.7 volts in agreement with the value of 9.70 volts for the onset of molecular ionisation by process (A).

The maxima of the two peaks in the curves (d) and (a) also occur at the same value 7.65 volts. The first rise in Snavely's corrected curve, however, does not set in until 6.1 volts, there being a slight fall between 4.1 and 6.1 volts. Snavely accounted for the fall in his curve by a process of negative ion formation discovered by Arnot and Milligan (53), who had shown that a mercury positive ion striking a filament or metal electrode captures two electrons from the metal surface and comes off as a negative ion. Snavely suggested that the presence of a large number of negative ions formed in this way increased the negative space charge round his filament and reduced the emission. Since Arnot and Milligan have shown that the probability of the conversion of a 4 volt positive ion into a negative ion is about 10^{-5} this explanation does not appear to be at all likely. Snavely does not report the result of any vacuum runs. The fall in his curve above 4 volts would probably have been much steeper in vacuum than in the curve (d) so that if his curve had been corrected by the substraction of a vacuum run the rise might have set in at 4.9 volts, in agreement with the curve (a) in fig. 15.

Since the appearance potential of the molecular ion is 9.70 ± 0.01 volts, the excited atom must possess at least 9.70 electron-volts energy before it can combine with a normal atom to form an ionised molecule. Reference to the energy levels of the mercury atom given in fig.

1 b page 4 shows that the excited state of the mercury atom having an energy nearest to this amount is the 6s.8p.4^1P_1 state which has 9.72 electron-volts energy. Just above this singlet state is the triplet state 6s.9p.$5^3P_{0,1,2}$ of which the energies are 9.79, 9.80 and 9.82 electron-volts. The values are taken from Bacher and Goudsmit (54).

Schaffernicht (17) gives an optical excitation function for the 4^1P_1 state which has a broad maximum at 45 volts. No excitation functions for the triplet 5P states are given, but since they are excited by electron exchange their excitation functions will rise to a sharp maximum just above their excitation potentials.

Arnot and Milligan (4) obtained a curve showing the probability of formation of these molecular ions as a function of the electron energy. Their curve showed a sharp maximum at 11.5 volts and a broad maximum at 47 volts. Their evidence for a maximum in the probability curve at 11.5 volts is confirmed by the presence of an inflexion in the curve (b) in fig. 13 at 11.5 volts. This inflexion appeared in all such medium pressure curves taken for electron energies up to 12 volts. Since the curve above 10.39 volts shows the efficiency of atomic plus molecular ionisation, the decrease in the molecular ionisation will only appear as an inflexion and not as a sharp maximum.

The molecular ions observed by Arnot and Milligan when mercury vapour is bombarded by electrons having energies between 9.7 and 200 volts can now be accounted for by the two processes

$$Hg'(4^1P_1) + Hg \longrightarrow Hg_2^+ + \mathcal{E} \qquad (a)$$

$$Hg'(5^3P) + Hg \longrightarrow Hg_2^+ + \mathcal{E} \qquad (b)$$

The process (a) accounts for the broad maximum observed in their probability curve at 47 volts, while the process (b) accounts for the sharp maximum at 11.5 volts.

It is impossible to say definitely that an excited atom in an S, D or F state above the 5^3P state cannot combine with a normal atom to form an ionised molecule. The processes (a) and (b) however fully account for the observations of Arnot and Milligan, and some evidence will be given later which suggests that an excited atom in an S, D or F state does not form an ionised molecule on collision with a normal atom.

The appearance potential of the molecular ion found experimentally to be 9.70 ± 0.01 volts, can now be fixed accurately as 9.722 volts, since this state has an energy value nearest to the experimentally determined value.

The ions produced by the processes (a) and (b) are definitely molecular since they have been detected by a mass spectrograph, but the ions formed by the process

$$Hg'(2^3P_1) + Hg'(2^3P_0) \longrightarrow Hg_2^+ + \mathcal{E} \qquad (c)$$

have not been analysed by this means. The results given here show quite definitely that a collision between an excited 2^3P_1 and a metastable 2^3P_0 atom leads to the formation of a positive ion. It has been assumed that the positive ions so formed are molecular. This assumption will now be justified.

The process

$$Hg'(2^3P_1) + Hg'(2^3P_0) \longrightarrow Hg^+ + Hg + \varepsilon \qquad (d)$$

is energetically impossible, since the energy of the left hand side is only 9.52 volts which is 0.87 volts less than the energy of the right hand side. An alternative process

$$Hg'(2^3P_1) + Hg'(2^3P_0) \longrightarrow Hg^+ + Hg^- \qquad (e)$$

is energetically possible since the electron affinity of mercury given by Glockler (55) is 1.79 volts. The energy of the right hand side is now 10.39 - 1.79 = 8.6 volts, which is less than the energy of the left hand side by 0.92 volts. This excess energy must be carried away in kinetic form by the resulting positive and negative ions. The process (e) involves an electron transfer from the one atom to the other. Massey and Smith (37) have shown that electron transfer does not become at all probable until the kinetic energy with which the particles collide is about ten times the excess internal energy which must be carried away by the particles as kinetic energy of translation after the collision. Now in the process (e) the kinetic energy of the particles before the collision is only their combined thermal energies of about 0.1 electron-volt. The excess energy to be carried away is 0.92 electron-volts which is about ten times the initial kinetic energy of the particles and not one tenth. The process (e) if it occurs at all must therefore have a very low probability.

This leads to the only possible conclusion that the ions which appear at the resonance potential are molecular and that they are formed by the process (c).

Since a collision between an excited 2^3P_1 atom and a metastable 2^3P_0 atom leads to the formation of an ionised molecule while a collision between two metastable atoms does not the ionisation potential of the mercury molecule must lie between the limits $9.52 + D$ and $9.32 + D$ electron-volts where D is the energy of dissociation of the normal molecule. This point has already been discussed on page 29.

A single atom excited to a state with 9.52 electron-volts energy has therefore sufficient energy to form an ionised molecule when it collides with a normal atom. The experimental results have shown however that the excited atom must possess at least 9.70 ± 0.01 electron-volts energy before an ionised molecule can be formed. The values given in Table 1 page 67 show that the maximum error could not reduce the value to 9.52 electron-volts. Reference to the energy level diagram in fig. 1 b shows that the excited states of the mercury atom lying between 9.52 and 9.72 electron-volts are all S, D or F states. The first P state having an energy greater than 9.52 electron-volts is the 6s.8p. 4^1P_1 state. Therefore although an excited atom in any one of the S, D or F states between 9.52 and 9.72 electron-volts has sufficient energy to form an ionised molecule none are observed until the atoms are excited into the 4^1P_1 state. Since the three processes (a), (b) and (c) which involve only excited atoms in P states are sufficient to account for all the experimental observations on the formation of mercury molecular ions, one is led to the conclusion that in mercury only atoms in excited P states can take part in the formation of molecular ions.

If this conclusion is correct we can now restrict the ionisation potential of the mercury molecule to narrower limits. We have seen that it lies between the limits 9.52 + D and 9.32 + D electron-volts. Since atoms in the triplet 5^3P state can form ionised molecules on collision with normal atoms, it is reasonable to suppose that excited atoms in the triplet 4^3P state could also do so provided their energy was sufficient. The energy of the triplet 4^3P state is 9.43 electron-volts. Since no ions are detected for electron energies as low as this, excited 4^3P atoms cannot have enough energy. The ionisation potential of the molecule is consequently fixed by the limits 9.43 + D and 9.52 + D electron-volts. The value of D the energy of dissociation of the normal molecule given by Winans (13) is 0.15 electron-volts. The ionisation potential of the mercury molecule therefore lies between the values 9.58 and 9.65 electron-volts.

The energy of dissociation of the ionised molecule is given by the relation obtained on page 15

$$I_m + D_i = I_a + D$$

I_m has some value lying between 9.43 + D and 9.52 + D electron-volts. I_a is known from line spectra observations to be 10.39 electron-volts. The energy of dissociation of the ionised molecule, D_i consequently lies between the limits (10.39-9.52) and (10.39-9.43) electron-volts i.e. between 0.87 and 0.96 electron-volts. It is to be noted that these values are independent of the energy of the dissociation of the normal molecule, a quantity for which very different values have been obtained. In 1932 Winans (56) observed certain bands in mercury vapour which only appeared in emission, they also had other properties which suggested that their origin was the mercury molecular ion Hg_2^+. From measurements of these bands he estimated that the energy of dissociation of the ionised molecule was greater than 0.5 electron-volts. The value given here is considerably higher.

THEORETICAL DISCUSSION OF THE FORMATION OF MERCURY MOLECULES

The formation of excited and ionised molecules in gases and vapours which are molecular in their normal state can be regarded as analogous to the excitation and ionisation of atoms.

In mercury there exist no molecules in the normal state and so the question arises as to how the excited and ionised molecules appear. It is generally assumed that an excited atom or ion can combine with a normal atom to form an excited or ionised molecule. A direct attachment process, as pointed out on page 10, requires the dissipation of an amount of energy equal to the energy of dissociation of the excited molecule. If there is no particle set free to carry off any excess energy it can only be radiated since a three body collision is very unlikely except at high pressures.

In the three processes

$$Hg'(4^1P_1) + Hg \longrightarrow Hg_2^+ + \varepsilon \qquad (a)$$

$$Hg'(5^1P_1) + Hg \longrightarrow Hg_2^+ + \varepsilon \qquad (b)$$

$$Hg'(2^3P_1) + Hg'(2^3P_0) \longrightarrow Hg_2 + \varepsilon \qquad (c)$$

which have been found to account fully for all the experimental observations on the formation of ionised molecules, an electron is set free which can carry off any energy in excess of that of a quantised state of the ionised ~~normal~~ molecule.

Arnot and Milligan could detect no trace of the formation of a molecular ion by the attachment of an atomic ion to a normal atom. This process which may be written

$$Hg^+ + Hg \longrightarrow Hg_2^+$$

would require the radiation of the excess energy which is about 0.9 electron-volts.

It is impossible to say that this process does not occur, but the non-radiative processes (a) and (b) have definitely a much higher probability.

Let us suppose the broken curve in fig. 4, on page 14, represents the potential energy curve for an excited 4^1P_1 atom and a normal atom. The formation of the ionised molecule may be considered in two ways. It may be represented by a horizontal movement to the left along the line representing the potential energy of the two atoms at large internuclear distances. On the other hand the formation of a molecular ion from an excited atom and a normal atom may be a two stage process. The excited molecule, whose potential energy curve is represented by the broken curve, may be formed and then immediately ionised by the excess energy. The ionisation process is then represented by the vertical lines, for according to the Franck-Condon principle the internuclear distance remains momentarily unchanged during an electron transition.

The fact that atoms in S, D or F states do not form ionised molecules, even when they have sufficient energy to do so, suggests that some such two-stage process is involved.

These suggestions are put forward very tentatively. There remains a great deal of work to be done on this part of the subject.

The satisfactory working of this apparatus suggested a similar investigation of the formation of ionised molecules in helium. This part of the research is described in the next section.

PART 3 (a).

AN INVESTIGATION OF THE FORMATION OF HELIUM MOLECULES BY A BALANCED SPACE-CHARGE METHOD.

THE APPARATUS.

At the conclusion of the work with mercury the whole tube, including the wires and the vacuum wax, was taken down and all traces of mercury were carefully removed. The tube was then set up again, with the necessary alterations for the use of the rare gases.

A liquid-air trap and a mercury cut-off, both of large diameter, were inserted between the pyrex tube and the mercury diffusion pump. The inner tube of the cut-off was drilled with a number of small holes of varying diameter arranged in a spiral. The rate of diffusion of the gas could be altered by raising or lowering the mercury level to cover any desired number of holes. An air-trap was joined to the cut-off to prevent air bubbles entering the apparatus as the reservoir was moved up and down. A smaller liquid-air trap was fitted between the tube and the McLeod gauge.

The rare gases were supplied by the British Oxygen Company in glass containers of 1¼ litre capacity, and were stated to be spectroscopically pure.

The gas container was connected through a mercury sealed tap to a manometer and a large glass bulb of 1 litre capacity. The bulb was joined by a tap to a fine capillary leak which was connected through a liquid-air trap to the pyrex tube. The capillary leak was short-circuited by a tap which could be opened when it was desired to evacuate the system behind the leak. This tap was always kept open when air was admitted to the experimental tube for filament renewal, to eliminate the risk of a particle of dust becoming lodged in the fine capillary.

Precautions had to be taken to ensure that the spectroscopically pure gases were not contaminated before reaching the apparatus. The mercury sealed tap prevented any possible leakage from the atmosphere into the container once the seal had been broken. Low vapour pressure Apiezon grease "L" was used for all taps and Apiezon grease "N" was used for all joints which were water-cooled.

After the entire vacuum system had been constructed, it was kept evacuated at a pressure below 10^{-5} mm of Hg for several days. Any gas from the low vacuum side was prevented from diffusing back into the apparatus when the pumping was discontinued, by closing the mercury cut-off when the diffusion pump was still running. The liquid-air traps were immersed in liquid-air to remove any traces of vapour, and when the pressure read on the McLeod gauge showed a "sticking vacuum", which is equivalent to a pressure below 10^{-6} mm of Hg, the seal of the container was broken. The gas was passed from the container to the large bulb, where it was stored at a pressure of a few centimetres of Hg as read on the manometer.connected to the bulb. When required the gas was admitted to the pyrex tube through the capillary leak and liquid-air trap. The pressure of the gas in the apparatus was controlled by adjusting the pressure in the bulb behind the leak and the level of the mercury in the cut-off. A circulating system was not employed and fresh gas from the reservoir was continually passing through the apparatus from which it was pumped away into the atmosphere.

The second form of the apparatus shown in fig. 9 b on page 50 was used. With mercury this had proved to be equally satisfactory and slightly more sensitive than the arrangement shown in fig. 9 a.

The hair-pin filament was surrounded by a small nickel cylinder 0.5 cm in diameter. This cylinder, which is not shown in the diagram, was connected to the negative lead of the filament and so focussed the electron beam passing up to the gauze.

The filaments were flashed and run-in and the pumping continued until the McLeod gauge showed a "sticking vacuum." The gas was then admitted to the apparatus and the experimental procedure carried out as for the work with mercury. The energy of the electrons from the filament F_1 was varied from a few volts below the first excitation potential to a few volts above the atomic ionisation potential, and the resulting change in the emission from the filament F_2 was observed. Several runs were taken at different pressures in each of the three gases, argon, helium and neon. They were used in this order.

RESULTS.

The curves obtained at various pressures in argon, neon and helium are shown in figs. 16, 17 and 18 respectively. As before the curves represent the change in the space-charge limited emission from the filament F_2 as the energy V_o of the electrons from F_1 was increased. The same linear fall, due to the fact that the emission from F_2 was not entirely space-charge limited, occurred as V_o was increased. The results for helium were obtained after the argon results and before those for neon. The curves in figs. 16 and 17 have been displaced in a vertical direction to separate the points below the atomic ionisation potential.

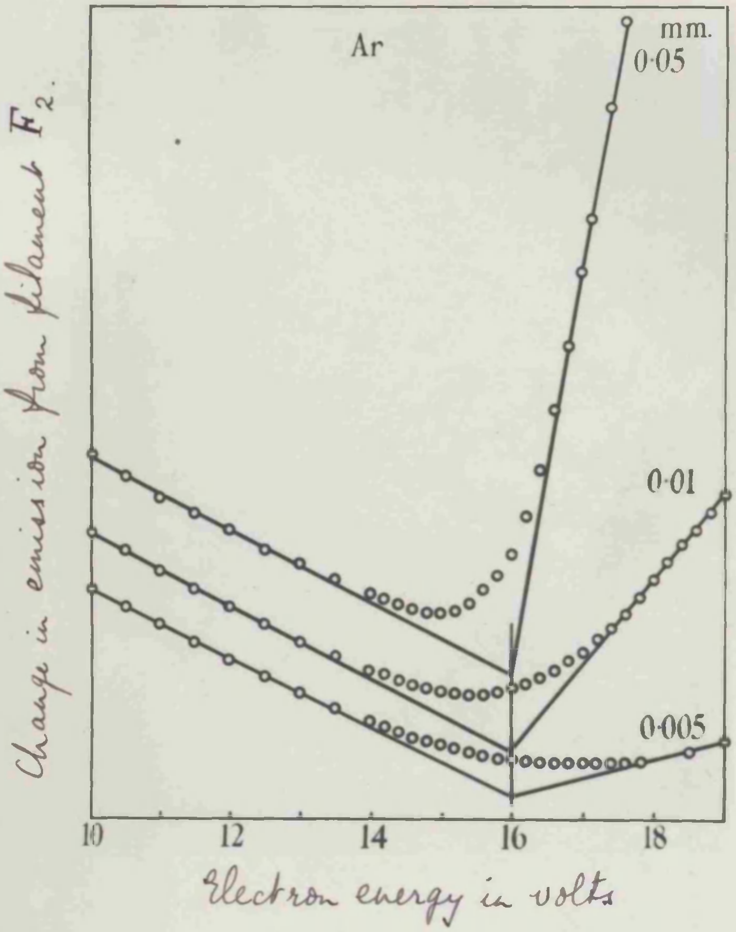


FIG. 16. Curves obtained in Argon.

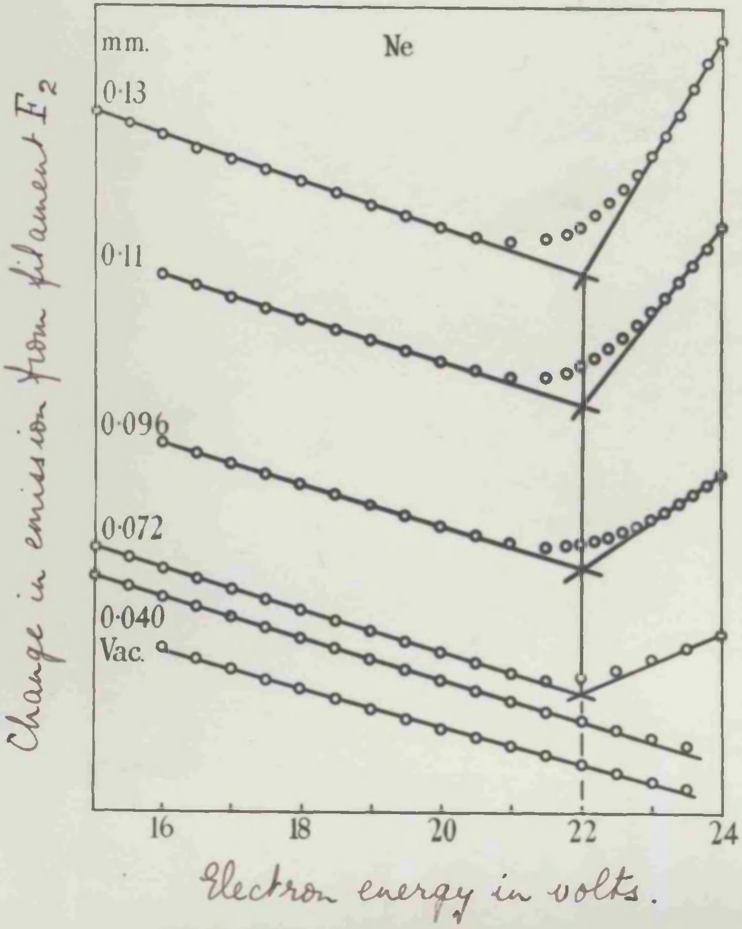


FIG. 17. Curves obtained in Neon.

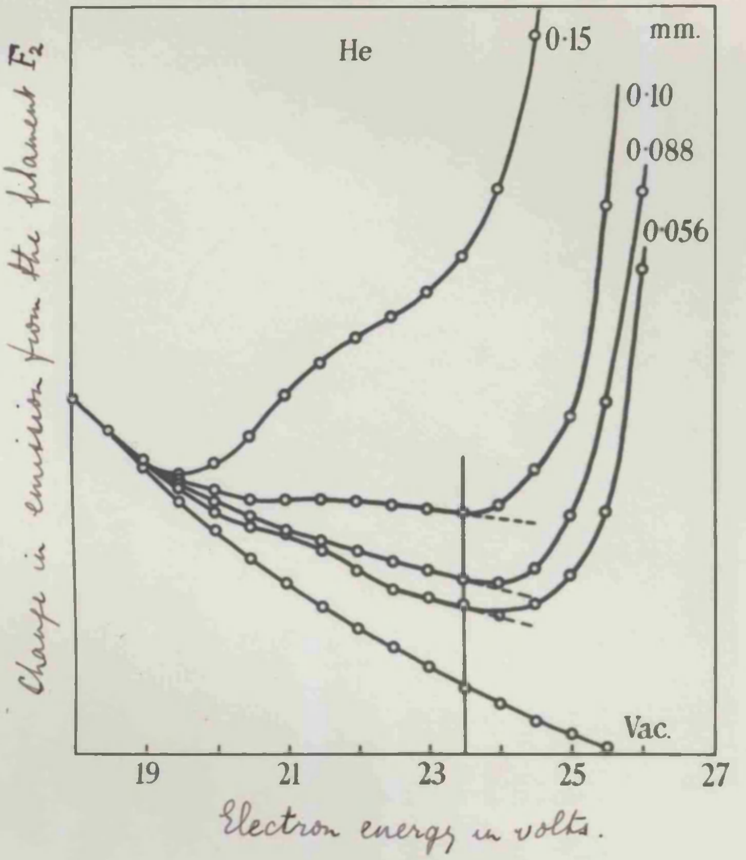


FIG. 18.

Curves obtained in helium.

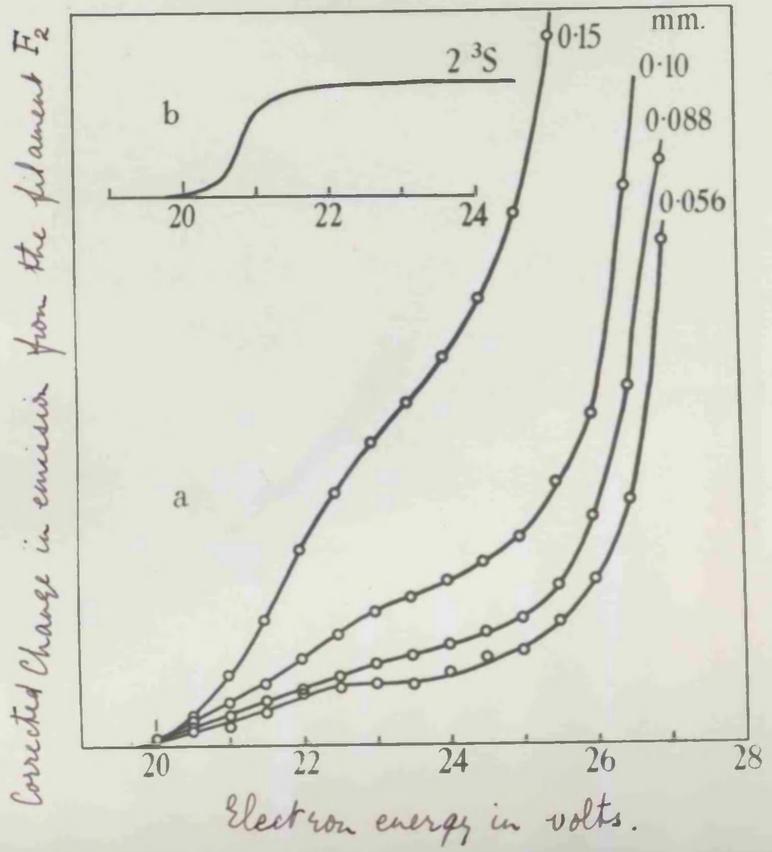


FIG. 19.

(a) The curves of fig. 18 corrected by the subtraction of the curve obtained in vacuum, and with the voltage scale adjusted by +1·0 volt to correct for contact potentials.

(b) Theoretical excitation function for 2^3S state.

The lowest curves in figs. 17 and 18 were obtained in vacuum.

The curves in figs. 16 and 17 show that in argon and neon ionisation sets in at the atomic ionisation potential for each value of the pressure used. The ionisation potentials for argon and neon obtained from line spectra measurements are 15.7 and 21.5 electron-volts respectively. This indicates a correction to the voltage scale for the argon curves of -0.3 volts, and for the neon curves of -0.5 volts. This correction has to be applied because of contact potentials. In argon and neon there is no evidence of any ionisation below the atomic ionisation potential. It is seen from the figs. 16 and 17 that the pressure of neon has to be about ten times that of argon to give the same change in the emission from F_2 when the value of V_3 is just above the ionisation potential. This is not due to any decrease in the sensitivity of the apparatus. It is due chiefly to the fact that the probability of ionisation at a collision is much greater in argon than in neon as was shown by Compton and Van Voorhis (23), and partly to the fact that the effective cross-section of an argon atom is greater than the effective cross-section of a neon atom.

The curves for helium in fig. 18 show definitely the appearance of ions below the atomic ionisation potential which is known from spectroscopic measurements to be 24.5 electron-volts. It is more difficult to decide from these curves the precise value of V_o at which the direct atomic ionisation sets in. All the curves except the one obtained in vacuum show a definite increase in the ionisation beginning at about 23.5 volts. This suggests a correction for the voltage scale of + 1.0 volt which is accounted for by contact potentials and by the energy spread of the electrons from F_1. The curves given in fig. 19 are the curves of fig. 18 corrected by the subtraction of a vacuum run and with the voltage scale adjusted by + 1.0 volt. These curves now show that ionisation sets in at 19.8 electron-volts.

The energy level diagram for the helium atom in fig. 2 page 6 shows that the lowest excited state of helium is the metastable triplet 2^3S state of 19.77 volts energy. The next state is the resonance level 2^1S_o of 20.55 volts energy. The curves of fig. 19 indicate that ionisation sets in when the atoms are excited to the lowest 2^3S state. Although the correction for the voltage scale is rather indefinite the curves in fig. 18 show that the error cannot be greater than ± 0.25 volts, and hence the correction cannot be greater than + 1.25 volts.

Ionisation must set in <u>either</u> at 19.8 volts <u>or</u> at 20.55 volts, for it cannot set in at some intermediate value. If the correct value were 20.55 volts, the correction to the voltage scale would have to be 1.8 volts, which is far above the limit of any possible error.

We can therefore only conclude that when helium is excited by electron impact positive ions are formed as soon as the energy of the electrons is sufficient to raise the atoms into the lowest excited 2^3S state. These ions may be molecular or they may be atomic, this point has yet to be decided.

This conclusion is simply a confirmation of the results of many other workers. However, by using the results obtained with neon and argon as an experimental control, a new interpretation can be given.

A trace of impurity in the helium might have produced a small positive ion current at the first excitation potential, since the atoms of the impurity could be ionised by collisions of the second kind with excited helium atoms. Owing to the precautions taken to maintain the purity of the helium, the only source of impurity could have been gas given off by the filaments or walls of the apparatus. If this were the cause then ionisation should have been observed also in neon at the first excitation potential which is 16.58 electron-volts, since the ionisation potentials of all the more common impurities are below this value.

The curves for neon in fig. 17 show no trace of ionisation below the atomic ionisation potential 21.5 electron-volts, and therefore there must be some other explanation.

A collision between an electron and an atom in a metastable state could produce an atomic ion. A collision of the second kind between two metastable atoms in which the energy of one atom was transferred to the other could also produce an atomic ion and a normal atom. The excess energy in this process is (39.54 - 24.47) electron-volts, i.e. 15.07 electron-volts and could be carried away by the ejected electron after the collision. However, we would expect any such process to occur in argon and neon as well as in helium, since argon and neon both have a metastable state as their lowest excited state, the energy of which is greater than half the ionisation potential.

No ions were detected below the atomic ionisation potential in argon and neon and so we must conclude that all of the above processes have too low a probability to give rise to a measurable positive ion current.

The helium metastable atoms bring off a large number of electrons from the metal surfaces in the apparatus. There is however no field present in the apparatus, which can give these electrons sufficient energy to enable them to produce atomic ions at a single collision.

The ions observed in helium at the lowest excitation potential must therefore be molecular. The existence of helium molecules is well known from band spectra evidence. No band spectra have been observed in argon and although a number of bands in the red in neon were reported by Dhavale (57) in 1930, this observation has not been confirmed.

The spectroscopic evidence for the existence of molecules in helium and for their non-existence in argon and neon is supported by the curves in figs. 16, 17 and 18.

The theoretical excitation function for the 2^3S state of the helium atom given by Massey and Mohr (21) is reproduced as curve (b) in fig. 19. This curve shows that the probability of excitation to the 2^3S state by electron impact rises to a maximum at about 22 volts and then remains practically constant for electron energies up to 24 volts. The lowest experimental curve obtained at a pressure of 0.056 mm of Hg also rises to a maximum at about 22 volts and then remains practically horizontal. This leaves little doubt that at low pressures molecular ions are formed from excited atoms in the 2^3S state. As the pressure is raised the experimental curves depart more and more from the form of the excitation function of the 2^3S state. This suggests that at higher pressures atoms in higher excited states take part in the formation of the molecular ions. Since the atoms in the higher excited states are not metastable, a higher pressure is necessary in order that they may make an effective collision before they have time to radiate.

These results show definitely that helium molecules are formed by a collision of an excited atom in the 2^3S state with either a normal atom or another atom in the 2^3S state. The former process will have a much larger probability, and is probably the effective process <u>provided</u> it is energetically possible, that is if the ionisation potential of the helium molecule is <u>less</u> than 19.77 electron-volts.

In the first paper on this subject, published by Dr. F.L. Arnot and the author (58), we assumed the correctness of a value of the ionisation potential of the helium molecule given by Jevons (10). The value given was 18.58 electron-volts which was based on observations made by Hopfield (8). After publication it was brought to our notice by Dr. Herzberg that Hopfield had subsequently decided that the bands, which he had assigned to helium, were due to nitrogen. This fact was not published by Hopfield but was apparently mentioned in a conversation between Hopfield and Mulliken, and is given as a foot note by Mulliken (9) in a paper on the nitrogen bands.

The ionisation potential of the helium molecule is therefore not known, and so we cannot say definitely from these results whether the effective process is a collision between two excited atoms or a collision between an excited atom and a normal atom.

The only way in which this point can be decided is to investigate the way in which the number of molecular ions increases as the filament emission from F_1 is raised.

The balanced space-charge method is invaluable for making a precise determination of the appearance potential of positive ions, but it is not suitable for making any quantitative measurements. It was therefore decided to investigate the problem using a mass spectrograph, which should establish definitely the existence of the molecules, and to see what conclusions could be drawn from the results of the two methods considered as a whole.

PART 3 (b).

AN INVESTIGATION OF THE FORMATION OF HELIUM MOLECULES BY A MASS SPECTROGRAPH METHOD.

THE APPARATUS.

The same apparatus as had been used by Arnot and Milligan (4) for their work with mercury vapour was employed. The apparatus which consisted of an ionisation chamber and a magnetic analyser is shown in fig. 20 a. The only alteration was in the design of the ionisation chamber, this is shown in fig. 20 b.

The analyser, with the exception of the soft iron tube T, was made of brass soldered where necessary. After construction the analyser, the soft iron tube and the Faraday cylinder A were copper-plated and then nickel-plated. The copper surface was necessary to make the nickel adhere. The nickel coating ensured that the analyser was vacuum tight and prevented amalgamation of mercury with the solder and brass of the analyser. As an additional precaution the analyser was coated on the outside with an even coat of porcenam paint. The analyser was set in a gap of 1 cm between the poles of a large electromagnet. The pole pieces were firmly bolted down to prevent any movement at large fields.

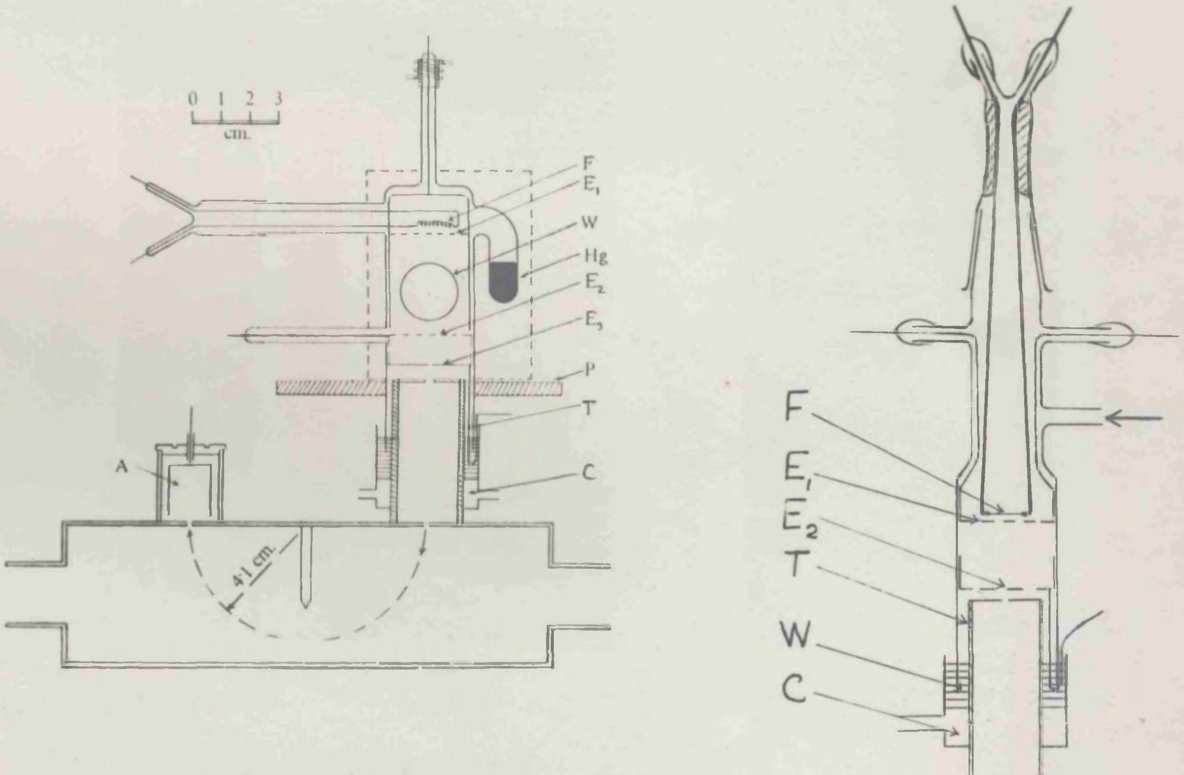


FIG. 20. (a) The ionisation chamber and analyser used by Arnot and Milligan for work with mercury.
(b) The modified ionisation chamber used for work with helium.

The Faraday cylinder was supported by a quartz tube which passed through an ebonite block with a sulphur ring. The shield of the Faraday cylinder and the wire connecting the Faraday cylinder to the electrometer were enclosed in a brass cylinder, which was connected to earth and insulated from the top of the analyser by a ring of ebonite.

The electronmeter, enclosed in an earthed metal box, was mounted on a stone slab just above the Faraday cylinder to keep the connection as short as possible. The box was provided with a gauze window for the entry of the light from the lamp and scale. The electrometer needle was connected through a water resistance to the positive terminal of a 200 volt battery the negative terminal of which was earthed. The quadrants connected to the Faraday cylinder could be either insulated, or connected to earth through one-tenth part of a megohm resistance, by raising or lowering a key inside the electrometer box. The key was connected to the table at which the observations were made by a fine silk thread, the tension in which could be altered at will to raise or lower the key. The other quadrants were connected to earth.

The sensitivity of the electrometer was measured daily. A 2-volt cell was connected across the whole of the megohm resistance so that the quadrants connected to the Faraday cylinder were raised to a potential of 0.2 volts. The resulting deflection on the scale was observed and the sensitivity calculated. Throughout the work the sensitivity was found to be 1180 ± 10 volts/mm.

The right-hand outlet tube of the analyser was connected through a liquid-air trap of large diameter to a mercury diffusion pump backed by a Hyvac pump. The left-hand outlet tube was connected through another liquid-air trap to a McLeod gauge. The gauge was of the short-length type with an evacuated reservoir and a calibrated scale. This is a much more convenient form than the full-length type used with the other apparatus. An evacauated double-walled rubber tube connection between the reservoir and the gauge prevented the entry of air bubbles.

The ionisation chamber which is shown in fig. 20 b was made of quartz. It was cylindrical in shape and open at the lower end. A ground glass joint was provided for removal of the filament. The gauzes E_1 and E_2 were made of nickel, spot-welded to nickel bands which fitted tightly into the open end of the tube. Two alternative connecting wires for the gauze E_1 were brought out through the two upper side tubes. The connecting wire for the gauze E_2 was brought out through the lower end of the ionisation chamber. The filament leads, of stout nickel wire, were kept rigid by two rolls of nickel sheet which fitted tightly into the upper part of the ionisation chamber. The filament was a straight tungsten wire 0.15 mm in diameter and 10 mm in length. The filament leads and the connecting wires were sealed into the tube by Lilliendahl's vacuum wax.

A trough containing vacuum wax, W, was fitted round the soft iron tube T, and was provided with a water cooling system C. The slits in the soft iron tube and in the analyser were 2 mm wide by 8 mm long.

When the entire ionisation chamber had been assembled, steam was passed through the cooling system of the trough to soften the wax. The ionisation chamber was then carefully lowered into the trough and held in position with the filament vertically over the slit in the top of T and with the wire from the gauze E_2 kept from touching the side of the trough, while cold water was passed through the cooler to set the wax.

The glass tubing connecting the ionisation chamber to the helium reservoir was then fixed in position. The vacuum system was similar to that used with the other apparatus. The helium was passed from a reservoir, through a capillary leak and a liquid-air trap, to the ionisation chamber. The pressure in the apparatus was adjusted by altering the pressure in the reservoir.

The ideal arrangement is to have a high pressure in the ionisation chamber and as high a vacuum as possible in the analyser to prevent loss of ions by scattering. This apparatus was designed for work with mercury vapour in which the conditions can be much more easily controlled. The soft iron tube was cooled to reduce diffusion of the vapour through the slits to a minimum. The air traps connected to the analyser then gave a very low vapour pressure in the analyser, even at high pressures in the ionisation chamber.

For work with gases, a system of differential pumping can be employed. The ionisation chamber may be divided into two parts by a narrow slit, gas passing through the slit from the high pressure side is removed by a fast pump to reduce diffusion through the lower slits into the analyser. A second fast pump is connected to the analyser as in this apparatus.

Since this apparatus is about to be taken down and entirely rebuilt it was decided not to make any alterations, and it was found that it could be worked very satisfactorily for pressures up to 4 x 10^{-3} mm of Hg.

EXPERIMENTAL PROCEDURE.

After the filament had been flashed and run-in, a potential of V_0 volts was applied between the centre of the filament and the gauze E_1 to accelerate the electrons from the filament. A potential V_1 volts was applied between the gauzes E_1 and E_2 to retard electrons, and to accelerate ions formed between E_1 and E_2 through the gauze E_2. A potential V_2 volts was applied between E_2 and the slit in the iron cylinder, to accelerate the positive ions into the analyser with an energy $V_1 + V_2$ electron-volts. The values of V_o, V_1 and V_2 were read on a standard Weston voltmeter. The value of V_o could be adjusted to any desired fraction of a volt by means of a potential divider. V_1 and V_2 were set equal to 10 and 190 volts respectively. These values were maintained throughout the work. High resistance sphagetti resistances were placed in the external circuit between the filament and E_1, between E_1 and E_2 and between E_2 and the iron cylinder, to prevent the setting up of an arc at high pressures. A fine fuse wire was placed in series with the milliammeter used to measure the emission from the filament, to prevent any possible damage to the instrument.

The two slits in the iron cylinder defined the beam of positive ions which entered the analyser with an energy of 200 electron-volts.

A positive ion of mass m after acceleration by a potential V volts will enter the analyser with a velocity υ given by the relation

$$\tfrac{1}{2} m \upsilon^2 = Ve \times \frac{c^2}{300} \qquad (25)$$

where c is the velocity of light and e is the charge on the ion in e.s.u.

A magnetic field H gauss applied in a direction perpendicular to the path of the ions will cause them to travel in a circular path of radius given by the relation

$$Hev = \frac{mv^2}{\rho} \qquad (26)$$

Eliminating v from equations (25) and (26) we obtain

$$H^2\rho^2 = \frac{2Vmc^2}{300e} \qquad (27)$$

The field required to bring a 200-volt helium molecular ion into the analyser by causing it to move in a circular path of radius 4.1 cms calculated from this equation, is found to be 1461 gauss. This required a current of 0.515 amps in the magnet coils.

The magnet was calibrated by means of a search coil and a Grassot fluxmeter. The field was found to be accurately proportional to the current in the coils up to 10,000 gauss, except at very small fields where the calibration curve showed a slight deviation from the straight line and failed to pass through the origin. The field produced by a given current was found to be always the same provided the current was first taken to a higher value and then reduced to the required value.

The analysis of the ions was made by varying the magnet current. An alternative method is to vary the accelerating potential V. The method adopted has the advantage that the energy of the ions is unaltered and so the loss by scattering and neutralisation is constant throughout the analysis. The magnet current was taken up to 0.6 amps and reduced in steps of 0.01 amp. The rate of drift of the spot of light reflected from the electrometer mirror was observed for each value of the magnet current. The rate of drift is proportional to the number of ions entering the Faraday cylinder.

The analyser was maintained at a potential of - 40 volts, to prevent the ejection of electrons from the Faraday cylinder by metastable helium atoms. Until this potential was applied the positive ion analysis curves showed an apparent background of positive ions for all values of the magnet current. This potential, which was applied between the Faraday cylinder and the analyser, had no effect on the value of the magnet current required to bend the ions into the Faraday cylinder, since they only encountered the retarding field after completing their semi-circular path and were still moving with their initial energy of 200 electron-volts which was more than sufficient to enable them to reach the Faraday cylinder.

The pressure of residual gas shown on the McLeod gauge, before the admission of the helium, was below 10^{-5} mm of Hg.

RESULTS.

ANALYSIS OF THE IONS.

Three positive ion analysis curves for different values of V_o, the electron accelerating potential, are shown in fig. 21. The lowest curve was obtained in vacuum and the three upper curves at a helium pressure of 3×10^{-3} mm of Hg. The filament emission was held constant at 1.0 milliamp for the two upper curves, and at 0.9 milliamp for the two lower curves.

The large peak in the uppermost curve at a magnet current of 0.35 amps shows the helium atomic ion He^+. The ordinates for this peak have been reduced by a factor of 1/200.

The smaller peak at a magnet current of 0.514 amps shows the presence of a singly-charged ion of atomic mass $4 \times (0.514 \div 0.35)^2$, i.e. of atomic mass 8.5. This is the helium molecular ion He^+_2.

The atomic mass is calculated from the equation (27) on page 103, which shows that for two groups of singly-charged ions of atomic mass m_1 and m_2

$$\frac{H_1^2}{H_2^2} = \frac{m_1}{m_2} \tag{28}$$

A strictly linear relation between the field and the magnet current is assumed. The apparent error in the atomic mass

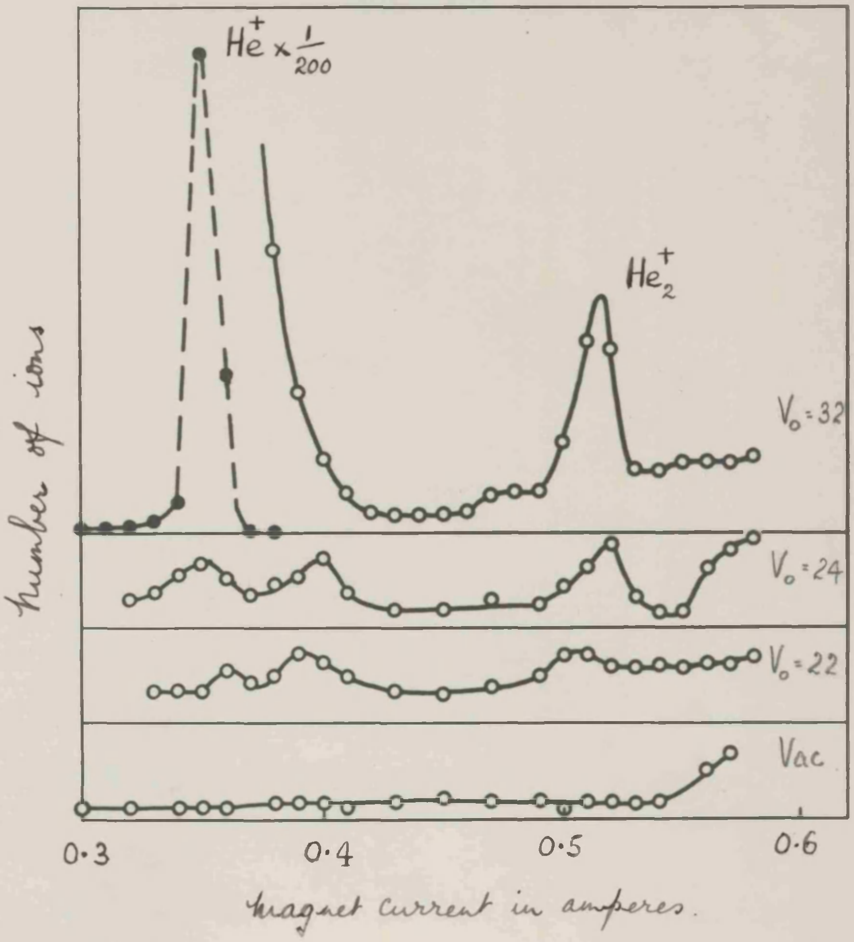


FIG. 21. Positive ion analysis curves.

calculated from equation (28), arises from the fact that the calibration curve of the magnet, as mentioned on page 103, was not strictly linear for very small fields. Consequently by substituting the values of the magnet current, instead of the actual values of the field, into the equation (28) we obtain too large a value for the atomic mass, since the current has to be increased by a factor just greater than $\sqrt{2}$ to produce a field $\sqrt{2}$ times as great. For work with the lighter elements this error becomes more appreciable than for the heavier elements. There is, however, no doubt as to the origin of this peak.

The very small peak at a magnet current of 0.40 amps, and the larger peak at a magnet current of 0.58 amps correspond respectively to singly-charged ions of atomic masses 5 and 10. They are probably due to the presence of impurities, such as gas given off by the filament or the walls of the analyser which could not be baked out. These peaks were not examined and are of no importance here, although certain features of the peak at 0.40 amps suggest that the effect of the addition of hydrogen might prove interesting. The author hopes to try this very shortly.

The great advantage of this method is that we can neglect the presence of any impurities, and by setting the magnet current to bring any desired type of ion into the Faraday cylinder we can examine the effect of changing the pressure, the filament emission, or the energy of the electrons for that type of ion alone.

It will be noticed that for values of V_0 below the atomic ionisation potential, 24.5 volts, there is evidence of a few atomic ions, but that the atomic peak is now much smaller than the molecular peak. The presence of atomic ions below the ionisation potential can be accounted for by the fields existing in this apparatus. The metastable helium atoms, as shown by Oliphant (48), bring off a large number of electrons from the gauzes and metal parts of the apparatus. Electrons ejected from the nickel cap in the top of the iron cylinder are accelerated by the potential of 190 volts applied between the cap and the gauze E_2. These electrons may produce quite an appreciable number of atomic ions on collision with atoms. There are however other possible processes, such as a collision between an electron and an atom in an excited state or a collision between two excited atoms, which could give rise to atomic ions. This point therefore requires investigation.

The total potential drop across the filament and its leads was measured and found to be 1.3 volts. The potential drop across the emitting portion of the filament must therefore have been small, so that the atomic ions observed below 24 volts cannot have been due to a large energy spread in the electrons from the filament.

To determine the processes involved in the formation of the molecular ions and in the formation of atomic ions for electron energies below the ionisation potential the following tests were carried out.

VARIATION IN THE HEIGHTS OF PEAKS WITH PRESSURE.

Fig. 22 shows the variation in the heights of the atomic and molecular peaks with helium pressure for electron energies above the atomic ionisation potential. For the atomic peak the electron energy was 28 volts and for the molecular peak it was 32 volts. The helium pressure is given in mm. of Hg at 0°C.

Several readings were taken over the top of each peak at slightly different magnet currents. When the exact position of the top of the peak had been determined the run was started. The magnet current was small, the coils therefore soon settled down to a steady temperature, and no shift of the peaks due to a change in the permeability of the iron was observed. The tap connecting the helium reservoir to the capillary leak was closed. The space between the tap and the leak was small, so that as the helium was pumped out of the apparatus the pressure behind the leak fell fairly rapidly. Readings were taken as quickly as possible at gradually decreasing pressures in the apparatus.

The curves in fig. 22 show that at very low pressures the atomic peak increases with pressure and then starts to fall off. This decrease is caused by multiple scattering and absorption of the ions in the analyser. The molecular peak, on the other hand, increases steadily with the pressure. This shows that the number of molecular ions formed is proportional to a higher power of pressure than that which governs the formation of the atomic ions. The molcular ions cannot be due to direct ionisation of helium molecules but must be formed by some attachment process, which will be discussed later. These curves are very similar to the curves obtained by Arnot and Milligan (4) for the Hg^+ and Hg_2^+ ions formed in mercury vapour.

The curves in fig. 23 show the variation in the heights of the atomic and molecular peaks with pressure for electron energies below the atomic ionisation potential. The electron energy was 22 volts and the filament emission was 1.0 milliamp for both curves.

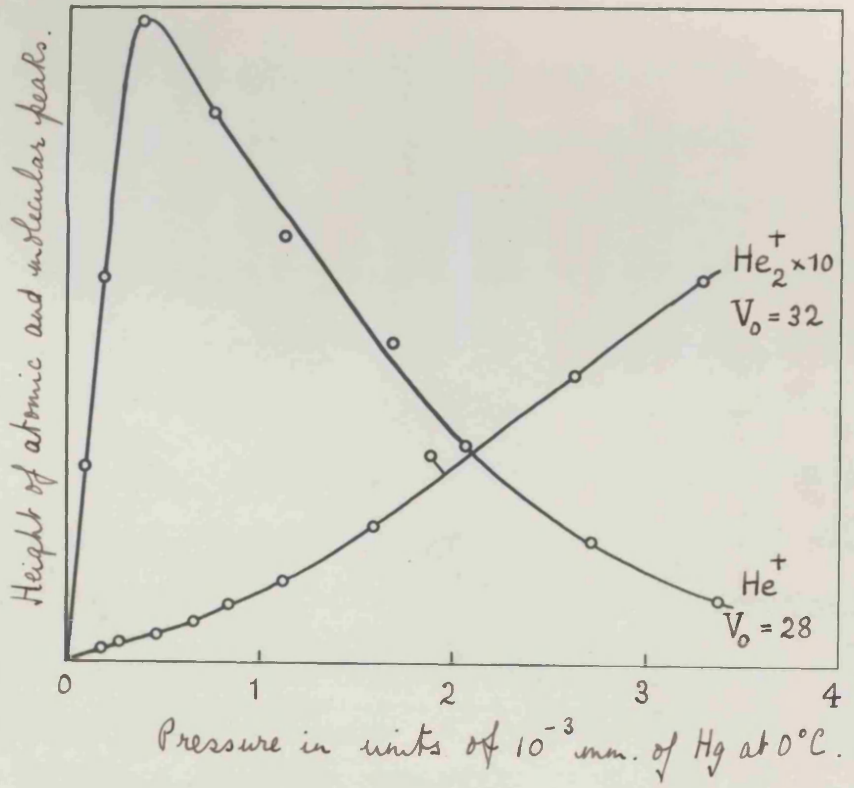

Height of atomic and molecular peaks.
$He_2^+ \times 10$
$V_0 = 32$
He^+
$V_0 = 28$
0
1
2
3
4
Pressure in units of 10^{-3} mm. of Hg at 0°C.

FIG. 22.

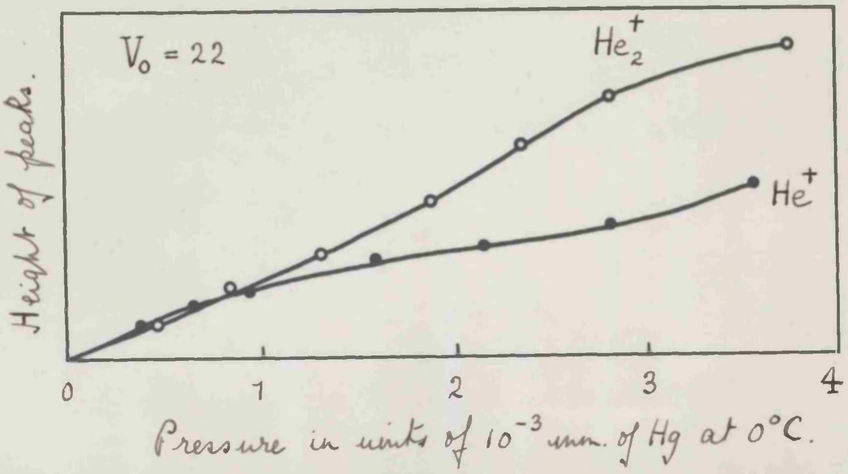

Height of peaks.
$V_0 = 22$
He_2^+
He^+
0
1
2
3
4
Pressure in units of 10^{-3} mm. of Hg at 0°C.

FIG. 23.

The number of atomic ions and the number of molecular ions both increase throughout the pressure range, which is the same as for the curves in fig. 22. The form of the curve for the He_2^+ ions is similar to that in fig. 22. This indicates that the molecular ions are formed by the same process for electron energies of 22 and 32 volts respectively. The form of the curve for the He^+ ions is now quite different from the corresponding curve in fig. 22. This shows that the process involved in the formation of atomic ions for electron energies below the atomic ionisation potential is fundamentally different from the single electron collision which is known to occur above the ionisation potential. The atomic ions observed below 24 volts are clearly not due to a large energy spread in the electrons from the filament. This point was mentioned on page 108 where it was suggested from a measurement of the total potential drop across the filament and its leads, that the potential drop across the emitting portion must have been very small.

VARIATION IN THE HEIGHTS OF PEAKS WITH FILAMENT EMISSION.

A number of curves showing the variation in the heights of the peaks with filament emission for different electron energies are given in fig. 24. The pressure in the apparatus was 3 x 10^{-3} mm of Hg at 0°C.

The curves show that for all values of the electron energy used, the number of atomic ions and the number of molecular ions is always a linear function of the filament emission.

This is to be expected for the atomic ions when the energy of the electrons is above the ionisation potential. That the He^+ curve is also linear for electron energies below the atomic ionisation potential is in agreement with the suggestion, on pages 108 and 109, that the ions are formed by collisions between normal atoms and electrons which are ejected from the metal parts of the apparatus by metastable atoms. The number of electrons which are formed in this way will be a linear function of the filament emission. The ejected electrons acquire the energy necessary for ionisation at a single collision in the fields existing in the ionisation chamber. The linear form of the curve definitely shows that the atomic ions observed below the ionisation potential are not due to collisions between electrons and excited atoms, or to collisions of the second kind between two excited atoms.

The number of molecular ions formed is also a linear function of the filament emission. This shows that in the attachment process, suggested by the curves

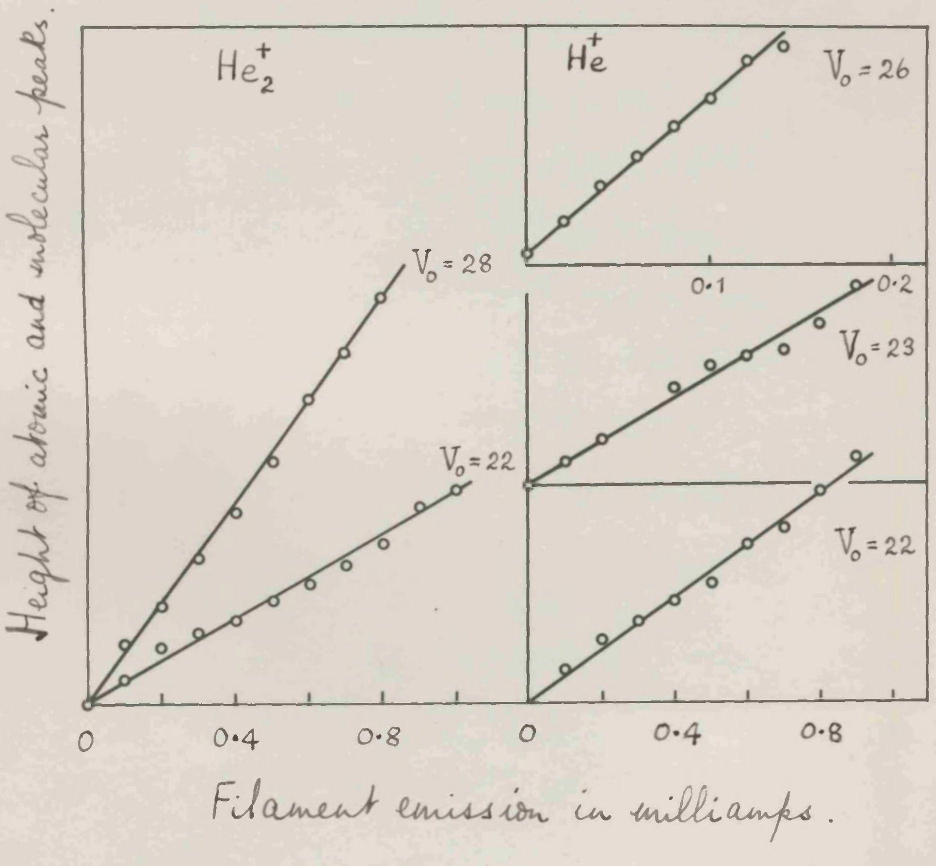


FIG. 24. The number of atomic and molecular ions plotted as a function of the filament emission.

of fig. 22, only one of the atoms taking part in the formation of the molecular ion is in an excited state, the other atom must be a normal atom. If the effective process were the formation of a stable neutral molecule by the attachment of an excited atom to a normal atom, followed by ionisation of the stable molecule by electron impact, then the number of molecular ions should be a function of the square of the filament emission. Such an attachment process is unlikely since a three-body collision is very improbable at low pressures and radiation of the excess energy is the only means of its disposal. The curves in fig. 22 indicate that such a process does not take place at pressures below 3 x 10^{-3} mm.

VARIATION IN THE HEIGHTS OF PEAKS WITH ELECTRON ENERGY.

Two curves showing the variation in the heights of the atomic and molecular peaks with electron energy are given in fig. 25. The curve shown in the inset is the curve for the atomic ion He^+ reduced by a factor of 1/10. The filament emission was held constant at 1.0 milliamp for both curves which were obtained at a pressure of 3 x 10^{-3} mm of Hg.

As the energy of the electrons is increased from 17 volts the curve for the atomic ion He^+ remains horizontal until the electron energy is about 19.5 volts, it then starts to increase slowly and at an electron energy of about 24 volts it suddenly increases rapidly showing the onset of direct atomic ionisation at a single electron collision with a normal atom.

The curve for the molecular ion He_2^+ also starts to rise when the energy of the electrons is about 19.5 volts, it then increases steadily to a maximum between 28 and 29 volts. The subsequent rise and fall in the He_2^+ curve beyond 29 volts appeared in all similar curves and will be discussed later.

The voltage scale in fig. 25 has not been corrected for any contact potentials or energy spread in the electrons from the filament. It is difficult to decide the exact value of V_o at which direct atomic ionisation sets in, because of the formation of atomic ions by the secondary process. The He^+ curve, however, rises sharply just above 24 volts, which shows that the correction must be small. The He_2^+ curve in fig. 25 shows that the appearance potential of the molecular ion is close to 20 volts.

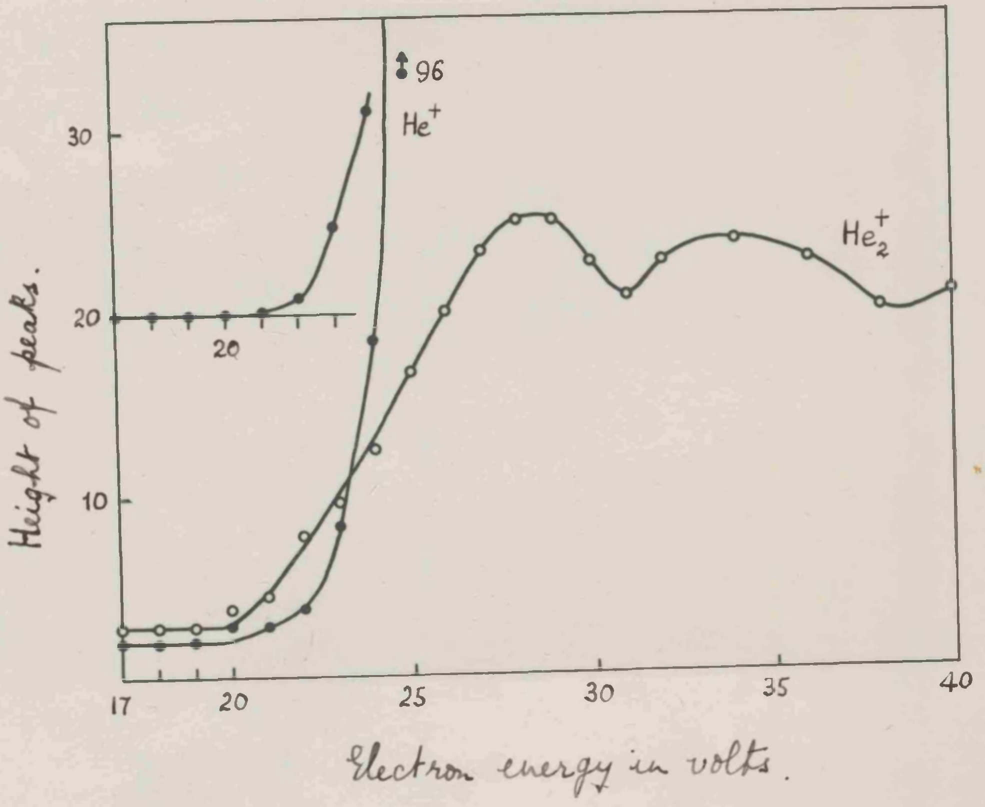


FIG. 25. Curves showing the number of atomic and molecular ions as a function of the electron energy.

DISCUSSION OF RESULTS.

THE FORMATION OF ATOMIC IONS FOR ELECTRON ENERGIES BELOW THE ATOMIC IONISATION POTENTIAL.

We will consider this point first and leave the more interesting and important question of the formation of the molecular ions till later.

It has been shown on pages 112 and 113 that the atomic ions observed below the ionisation potential are not due to a large energy spread in the electrons from the filament, or to any form of accumulative process. They can only be accounted for by the ejection of electrons from the metal parts of the apparatus by the metastable helium atoms. The ejected electrons can acquire as much as 200 volts energy in the fields in the ionisation chamber and so can produce atomic ions on collision with normal atoms. This explanation, which follows from the curves in figs. 22, 23 and 24, is also supported by the He^+ curve in fig. 25, which shows that atomic ions are formed as soon as the energy of the electrons from the filament is equal to about 19.77 volts, the excitation potential of the metastable 2^3S state.

The relative probabilities of the different types of collision, which may occur in the ionisation chamber, can be estimated roughly as follows.

The kinetic mean free path of a helium atom at a pressure of 1 mm of Hg at $0^{\circ}C$ is given in the Landolt-Bornstein tables to be 0.0176 cms. The mean free path at a pressure of 3×10^{-3} mm. is therefore 5.86 cms. A large number of metastable atoms will consequently diffuse to the walls without making any collisions and so the concentration of metastable atoms will be very small. The number of collisions between two metastable atoms will therefore be negligible compared with the number of collisions between a metastable and a normal atom.

If N electrons, moving with a velocity v cms/sec. cross unit area per second. The electron density ρ is given by the relations

$$\rho = N/v = i/e.v. \qquad (29)$$

where i is the electron current in e.m.u. and e is the electronic charge also in e.m.u. When the filament emission is 1 milliamp and the energy of the electrons is 20 electron-volts we have:-

$i = 10^{-4}$ e.m.u.

$e = 1.59 \times 10^{-20}$ e.m.u. ^{A_1}

$v = 5.94 \times 10^{7} \times 20^{\frac{1}{2}}$ cms/sec. ^{A_2}

From these values it follows that $\rho = 2.37 \times 10^{7}$. The number of normal atoms per cc at a pressure of 3×10^{-3} mm of Hg is 1.07×10^{14}. ^{A_1} The probability that a metastable atom will collide with a normal atom is therefore approximately 10^7 times greater than the probability that it will collide with a fast electron before reaching the walls.

No double collision process leading to the formation of atomic ions could be expected to occur with a measurable probability under these conditions.

The curves in fig. 23 are interesting. It will be shown later that the molecular ions are formed by the attachment of metastable atoms to normal atoms. As the pressure is raised the number of metastable atoms making collisions with normal atoms will increase more rapidly than the number of metastable atoms reaching the walls of the apparatus. Consequently the curve, showing the variation in the number of molecular ions with pressure, should increase more rapidly than the curve showing the variation in the number of atomic ions below the ionisation potential. This is borne out by the curves in fig. 23.

It is impossible to say from these curves what might occur at higher pressures. In 1922, Davies (59) observed all the lines of the arc spectrum in helium at the first excitation potential, when the pressure was above 2 mm. This suggests that as the concentration of metastable atoms increases, some form of cummulative process occurs.

The results given here, however, show that the probability of formation of a molecular ion at the first excitation potential, is much greater than the probability of formation of an atomic ion by some double collision process. At low pressures, with an apparatus which has no fields sufficient to give secondary electrons an energy greater than 24.5 volts, the ions observed below the atomic ionisation potential must be molecular. This confirms the conclusion drawn from the results of the investigation by the space-charge method.

The ions observed by Compton (45) at pressures ranging from 0.001 mm to 0.17 mm, and by Found (43) at a pressure of 0.49 mm when the energy of the exciting electrons was about 20 volts, were not analysed and most probably were molecular.

THE FORMATION OF HELIUM MOLECULAR IONS.

The curve in fig. 25 showing the variation in the number of molecular ions with electron energy indicates a steady decrease in the number of molecular ions as the electron energy is reduced below 22 volts. There is, however, no sharp break in this, or in any other similar curve not shown, at about 22 volts. The curve runs perfectly smoothly, which shows that there can be no change in the effective process as the energy of the electrons is reduced below 22 volts. Therefore any conclusion, which may be drawn as to the formation of the molecular ions when the atoms are bombarded by electrons of energy 22 volts, must hold for electron energies down to the appearance potential, which is seen from the He_2^+ curve in fig. 25 to be between 19.5 and 20 volts.

Owing to the low values of V_0 used the emission from the filament was space-charge limited, and could not be raised higher. It was therefore necessary to work at 2 volts above the appearance potential of the molecular ion, in order to obtain positive ion currents of sufficient intensity.

The pressure variation curves in fig. 22 indicate that the number of molecular ions formed is proportional to a higher power of the pressure than the number of atomic ions. This shows that the molecular ions are not formed by direct ionisation of a normal molecule, but that they are produced by some secondary or attachment process.

The linear relation between the number of molecular ions and the filament emission shown in the curves of fig. 24, proves quite definitely that only one of the atoms taking part in the formation of the diatomic molecular ion is excited or ionised. The other atom must therefore be in the normal state.

There are therefore two possible processes, depending on whether the atom is excited or ionised. These processes may be written

$$He' + He \rightarrow He_2^+ + \varepsilon \qquad (a)$$

$$He^+ + He \rightarrow He_2^+ \qquad (b)$$

The He_2 curve in fig. 25 shows the presence of molecular ions as soon as the energy of the electrons becomes equal to the first excitation potential. This suggests that the process (a) occurs, but since there are also present a number of atomic ions for electron energies between 20 and 24 volts, the curves must be further examined to decide whether the molecular ions are not due to the occurrence of the process (b).

If the molecular ions are produced by the process (b), then the curve showing the variation in the number of molecular ions with the energy of the electrons should be similar in form to the curve showing the variation in the number of atomic ions over the same range of electron energies. The He^+ and He_2^+ curves in fig. 25 show quite definitely that this is not so for electron energies below 25 volts. The sudden rise in the atomic ion curve above 24 volts, which shows the onset of direct atomic ionisation, is not accompanied by any corresponding increase in the molecular curve. Bleakney (60) has shown that the number of atomic ions formed in helium by electron impact increases steadily with the energy of the electrons up to 150 volts. The molecular curve in fig. 25 remains almost horizontal for electron energies between 30 and 40 volts. There is thus no evidence for the occurrence of process (b). This is similar to Arnot and Milligan's conclusion for the formation of molecular ions in mercury vapour. It is to be expected, since a three body collision is highly improbable at a pressure of 3 x 10^{-3} mm of Hg and there is no particle set free to carry off any excess energy above a quantised state of the molecular ion. Radiation of the excess energy is considered to be very unlikely.

We have now two independent results from which to determine the appearance potential of the molecular ion, which must be formed by the attachment of an excited atom to a normal atom according to the process (a).

The molecular curve in fig. 25 shows that the appearance potential is between 19.5 and 20 volts. The mass spectrograph results have only served to confirm the conclusion, drawn from the results of the balanced space-charge method, that the ions observed at the first excitation potential are molecular. It has already been pointed out that there were no fields existing in the space-charge apparatus which could give any secondary electrons an energy greater than 24 volts. Prior to the magnetic analysis of the ions it was necessary to have the argon and neon results as an experimental control. The high sensitivity of the balanced space-charge method enabled the appearance potential of the molecular ions to be determined more precisely, and the value of 19.8 electron-volts is definitely established.

The use of the mass-spectrograph apparatus has also shown quite definitely that the molecular ions are formed by the attachment of excited atoms to normal atoms.

We can therefore only conclude that molecular ions are formed in helium by the attachment of metastable atoms, in the 2^3S state of 19.77 volts energy, to normal atoms. This conclusion is supported by the similarity between the molecular curve below 30 volts in fig. 25, and the theoretical excitation function of the 2^3S state given by Massey and Mohr (21). The rise and fall in the molecular curve between 30 and 40 volts suggests that atoms in other excited states may also attach themselves to normal atoms to form molecular ions. This is in agreement with the conclusion drawn from the curves in fig. 19 obtained with the space-charge apparatus.

It is impossible to analyse this curve in terms of the different excitation functions, for we do not know in what proportion to combine the various excitation functions which have maxima corresponding to the maxima in the molecular curve.

Arnot and Milligan, in their work with mercury vapour, found that the curves showing the variation in the number of molecular and atomic ions with electron energy changed in a very marked way with the design of the ionisation chamber. The one used here, and shown in fig. 20b, is similar to their ionisation chamber "Number 2" which gave an extension of their curves in the direction of the V_o axis at high values of the electron energy. It is therefore not advisable to lay too much stress on the form of the curve at the higher values of the electron energy.

The importance of these results, however, lies in the fact that they show definitely that a metastable 2^3S atom can combine with a normal atom to form an ionised molecule by the process

$$He'(1s\,2s,{}^3S) + He(1s^2,{}^1S_0) \longrightarrow He_2^+(1s\sigma^2\,2p\sigma,{}^2\Sigma_u^+) + \varepsilon \text{ ---(c)}$$

The first term on the left-hand side represents the excited atom in the metastable 2^3S state of 19.77 electron-volts energy, and the second term represents the normal atom in the ground state 1^1S_0. The first term on the right-hand side represents the normal state of the ionised helium molecule He_2^+.

The energy available for ionisation of the molecule in this process is (19.77 + D) electron-volts, where D is the energy of dissociation of the normal molecule, which may be taken to be zero. The ionisation potential of the molecule is consequently equal to or less than 19.77 electron-volts. Since this is the energy of the lowest excited state of the helium atom, the ionisation potential cannot be determined any more precisely by this method, and the exact value will have to be deduced from band spectra measurements.

The ionisation potential of the molecule can be estimated from band spectra data. The lowest stable state of the helium molecule is the $1s\sigma^2, 2p\sigma, 2s\sigma, {}^3\Sigma_u^+$ state of energy ($I_m - 4.233$) electron-volts, where I_m is the ionisation potential of the molecule. This is the value given by Jevons (10). A molecule in the lowest stable state is supposed to dissociate into a normal helium atom and a metastable atom in the 2^3S state of 19.77 volts energy. Dr. G. Herzberg has informed Dr. F.L. Arnot that the most recent determination of the energy of dissociation of a helium molecule in the lowest stable state, reckoned in wave numbers, is about 20,000 cm^{-1}. This is equivalent to an energy of 2.47 electron-volts.[A2] The ionisation potential of the molecule is consequently (19.77 - 2.47 + 4.23) electron-volts, i.e. 21.53 electron-volts. This is considerably higher than the upper limit, of 19.77 electron-volts, obtained by the author.

Using the relation $I_m + D_i = I_a + D$ obtained on page 15, we see that the energy of dissociation of the ionised molecule is equal to or greater than (24.47 - 19.77) electron-volts, i.e. 4.7 electron-volts. This value is nearly double that obtained by Weizel (61) from band spectra measurements, the value found being 2.5 electron-volts.

Pauling (62) in 1933, and Weinbaum (63) in 1935, calculated the energy of dissociation of the ionised helium molecule and obtained values of 2.47 and 2.22 electron-volts respectively. These results are in good agreement with Weizel's value to which they both refer. Pauling and Weinbaum were compelled to assume functions for the field of the atoms in the molecule, and justify their choice of function by the close agreement between the theoretical and experimental values. This is a very usual method of obtaining a solution of a problem, which cannot otherwise be solved. Too much importance however cannot be attached to the result.

This recent value of the energy of dissociation of the helium molecule in its lowest stable state given by Dr. Herzberg, leads to the value (24.47 - 21.53) electron volts, i.e. 2.94 electron-volts for the energy of dissociation of the ionised molecule. This is above Weizel's value and is the highest estimate so far obtained. It suggests a tendency for the spectroscopic value to increase with improved experimental technique.

Let us now reconsider these curves and see if there is any possible source of error in one or more of the curves, arising from some peculiarity in the apparatus, which could account for the discrepancy between the numerical values for the ionisation potential of the molecule.

Reference to the energy level diagram for the helium atom on page 6 shows that if the ionisation potential of the molecule is actually close to this value of 21.53 electron-volts, then no molecular ion can be formed by the attachment of an excited atom to a normal atom, until the atoms are excited into the 3^3S state of 22.6 volts energy. The He_2^+ curve in fig. 25 shows quite definitely that molecular ions are formed for electron energies down to 20 volts. This result is confirmed by the curves, in fig. 19, obtained with the space-charge apparatus, and must therefore be correct.

The only explanation which could bring the results into line, is that the molecular ions are formed by collisions between two metastable atoms. The linear relation between the number of molecular ions and the filament emission shown in fig. 24 for three different values of the electron energy cannot be spurious, since we obtain a strictly linear relation between the number of atomic ions and the filament emission when the energy of the electrons is 26 volts. It is therefore quite definite that only <u>one</u> of the atoms taking part in the formation of the molecular ion is in an excited state.

The consideration of the conditions in the ionisation chamber given on page 119 shows that a collision between two metastable atoms is very unlikely compared with the probability of a collision between a metastable and a normal atom. From theoretical considerations a collision of the second kind between two metastable atoms could lead to the formation of an atomic ion. The fact that no atomic ions formed in this way were detected in this work supports the supposition that a collision between two metastable atoms is very unlikely at such a low pressure.

Although this conclusion as to the formation of molecular ions in helium is in conflict with the numerical values of the band spectroscopists, it suggests a very satisfactory explanation for certain other experimental observations, which will now be briefly discussed.

Davies (59) in 1922, observed that when helium at a pressure of 10 mm was excited by electron impact, all the bands appeared when the energy of the electrons was 19.8 volts. This can now be accounted for by the formation of molecular ions by the non-radiative process (c). The molecular ions may capture an electron into different excited states, giving rise to the bands.

That the metastable helium atoms play an important part in the formation of helium molecules has been shown by Eméleus and Duffendack (64), and more recently by

McCallum and Wills (65). Emeléus and Duffendack based their conclusions on observations of the intensity of the lines and the bands in the different parts of a helium discharge. They conclude, however, that the metastable atoms combine with normal atoms to form stable neutral molecules, and suggest the occurrence of a three-body collision for the disposal of the excess energy.

Three potential energy curves for the helium molecule, based on the results given in this thesis, are shown in fig. 26. The lowest curve is for the completely unstable helium molecule He_2, the middle curve is for the lowest stable state $1s\sigma^2, 2p\sigma, 2s\sigma, {}^3\Sigma_u^+$, and the uppermost curve is for the normal state of the ionised molecule. The ionisation potential of the molecule has been taken to be 19.77 volts, the maximum possible value, and the minimum of the curve for the lowest stable state has been drawn 4.23 volts below the ionisation potential. The curves are now all much steeper, indicating larger values for the energies of dissociation, than in the scheme of potential energy curves given by Mulliken (66). The values of the internuclear distance are taken from Mulliken's paper.

The formation of the helium molecular ion can be regarded in the same way as the formation of the mercury molecular ion on page 81. It may be a two-stage process,

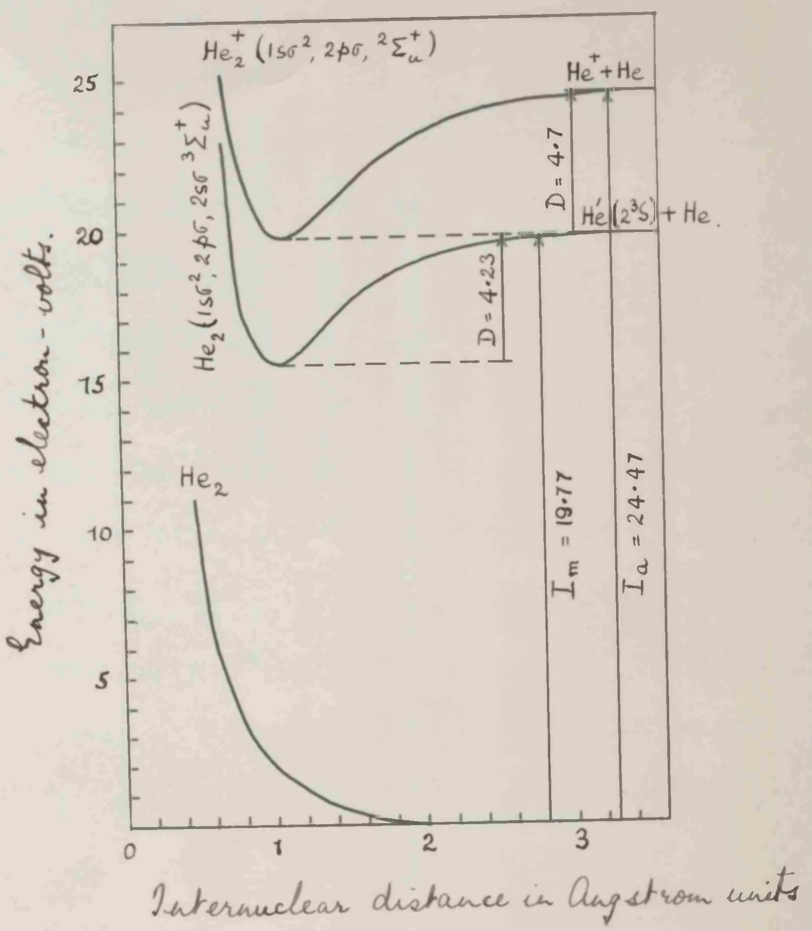


FIG. 26. Approximate potential energy curves for helium molecule.

in which a molecule in the $1s\sigma^2 . 2p\sigma , 2s\sigma \, {}^3\Sigma_u^+$ state is formed and then immediately ionised by the excess energy. This non-radiative process in which the excess energy is carried off by the ejected electron appears to be a much more likely process, although it does not preclude the possibility of a three-body collision at higher pressures as suggested by Emeléus and Duffendack.

McCallum and Wills made observations on the rate of decay of the lines and bands when helium at a pressure of 27.5 mm was excited in such a way as to produce the lines and the bands with approximately equal intensity. They found that 1/600 seconds after the discharge had been interrupted, the lines had disappeared, but that the bands were of almost the same intensity. They suggest that either the helium molecules have a life of 1/600 seconds, or that more probably the molecules are formed in the gas after the excitation has ceased by collisions between metastable atoms and normal atoms. This latter suggestion is in agreement with the results given in this thesis.

If a collision between a metastable atom and a normal atom can only give rise to a molecule in its lowest stable state, as suggested by Emeléus and Duffendack, then the bands must originate from collisions between electrons and the stable molecules, whereby the latter are raised to higher states from which they return to lower states with the emission of photons. But if a collision between a metastable atom and a normal atom gives rise to a molecular ion, then the bands can be accounted for by the capture of electrons by the molecular ions into their different excited states. This latter would seem to be a more likely process in the absence of any source of excitation, as found by McCallum and Wills, and can be accounted for by the results of this experimental research.

SUMMARY OF RESULTS ON THE FORMATION OF HELIUM MOLECULES.

The formation of molecules in helium has now been shown to be very similar to the formation of molecules in mercury vapour, which was discussed on page 80.

The attachment of a metastable atom to a normal atom to form an ionised molecule has been definitely shown to occur. This non-radiative process which may be written

$$He'(2^3S) + He \rightarrow He_2^+ + \varepsilon \qquad (c)$$

can account for various observations on the helium bands, and also for the ionisation which was observed below the atomic ionisation potential by the earlier workers on critical potentials. This effect, which was peculiar to helium, attracted considerable attention at the time, it was generally ascribed to the presence of impurities or to atomic ionisation by some accumulative process. The formation of ionised molecules does not appear to have been considered.

The occurrence of the process (c) shows a maximum value of 19.77 e-volts for the ionisation potential of the molecule, this is 1.7 e-volts below the spectroscopic value of 21.5 e-volts. The energy of dissociation of the ionised molecule has consequently a minimum value of 4.73 e-volts, this is 1.8 e-volts above the spectroscopic value of 2.9 e-volts.

It has been shown that in mercury vapour excited atoms in states other than P states do not form ionised molecules by attachment, even when they have more than sufficient energy to do so. The helium atom is similar to the mercury atom in that it has two outer electrons, but the outer shell of the helium atom is complete while the outer shell of the mercury atom is incomplete. This difference apparently allows the formation of ionised helium molecules from excited atoms in S states.

PART 4.

ELECTRON TRANSFER IN MERCURY VAPOUR.

INTRODUCTION.

During the course of an experiment involving the acceleration and subsequent retardation of positive ions in mercury vapour, it was found that the retarding potential had to be just greater than twice the accelerating potential in order to stop completely the passage of any positive ions.

Retarding potential curves for the positive ions were obtained and differentiated to give the energy distribution of the Hg^+ ions. A typical energy distribution curve found for positive ions which had been accelerated by a potential V_1 volts is shown in fig. 27. This curve is merely a sketch, the actual curves will be given later. It is apparent that the majority of the ions have an energy equal to that acquired in moving through the accelerating field, while a smaller group of ions have double this amount of energy. Practically no ions have energies between these two values.

This suggested the occurrence of the process of electron transfer which was first observed by Kallmann and Rosen (40) in 1930, and which has been discussed together with other similar processes in Part I, Section 2 of this thesis.

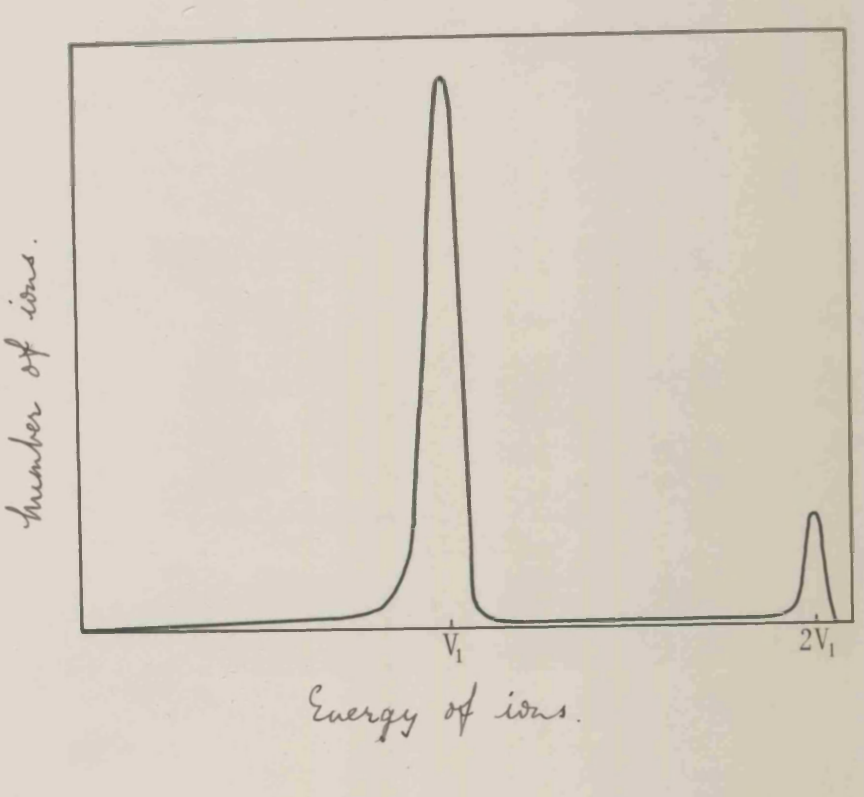


FIG. 27. A typical energy distribution curve obtained for Hg^+ ions accelerated by a potential V_1 volts.

The effective process, which may be written

$$Hg^{2+} + Hg \longrightarrow Hg^{+} + Hg^{+}$$

involves the transfer of an electron from a neutral Hg atom to a doubly-charged Hg^{2+} ion. An Hg^{2+} ion in passing through an accelerating potential V volts acquires an energy 2eV electron-volts. If the fast Hg^{2+} ion then makes a collision with a neutral atom and if one, or other, of the resulting Hg^{+} ions moves on with the whole of the kinetic energy 2eV electron-volts, then a retarding potential of 2 V volts will be required to reverse it.

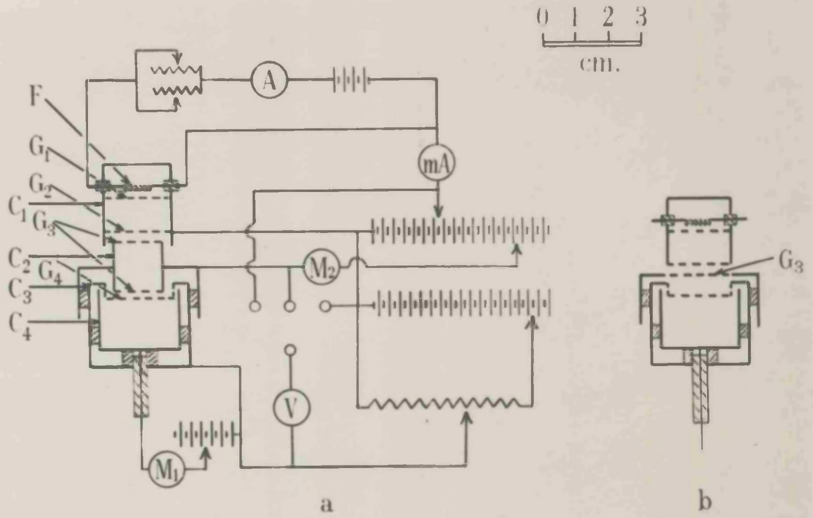
Kallmann and Rosen assumed that the effective collision was a grazing one in which the Hg^{2+} ion in passing close to a normal atom extracted an electron and moved on as a fast Hg^{+} ion. The distribution of the energy between the resulting Hg^{+} ions was not however examined in any detail.

The following apparatus was accordingly designed to investigate this point. The results obtained indicate that the assumption made by Kallmann and Rosen was incorrect. The transfer process was investigated for Hg^{2+} ions having energies from 140 to 400 electron-volts.

THE APPARATUS.

The apparatus, which is shown in fig. 28 together with a wiring diagram, was mounted in the same pyrex tube (fig. 8, page 47) as had been used for the investigation of the formation of helium and mercury molecules by the space-charge method.

The metal parts and gauzes were made of nickel spot-welded where necessary, and the end caps for the cylinders were pressed out of one piece of nickel so as to give a perfect fit. The large Faraday cylinder C_4 was supported inside and insulated from the shielding cylinder C_3 by two tight-fitting sindanyo rings. The cylinder C_3 was supported rigidly on one of the quartz tubes which passed down the centre of the pyrex tube. The connecting wire inside this quartz tube was spot-welded to the Faraday cylinder, and it is clear from the diagram that the Faraday cylinder and its connecting wire were completely shielded from any electrons or ions except those which passed through the gauze G_4. This gauze G_4, which was spot-welded to the end-cap of the cylinder C_3, was made cylindrical in shape so that ions leaving the cylinder C_2 at wide angles could enter into the Faraday cylinder. The cylinder C_2 was tightly spot-welded into the end cap of a cylinder open at its other end. The containing cylinder supported the cylinder



<u>FIG. 28.</u> Apparatus and wiring diagram for investigation of ionisation by electron transfer.

C_2 by fitting tightly over the sindanyo ring round C_3, and also shielded the gauze G_4 from any ions or electrons except those which passed through the lower gauze G_3. The cylinder C_1, which contained the close-coiled tungsten filament F and the two gauzes G_1 and G_2, was supported and insulated from the cylinder C_1 by short quartz rods. The filament was of tungsten 0.15 mm in diameter and its length before coiling was 2 cms. The filament leads were insulated from the cylinder C_1 by short quartz tubes which fitted tightly into holes punched in the sides of the cylinder.

The high-vacuum system was the same as for the earlier work. No liquid mercury was kept in the tube. The vapour which diffused from the McLeod gauge and the diffusion pump gave a pressure of 10^{-3} mm at 0^{o}C. This was high enough to give sufficiently large positive ion currents.

EXPERIMENTAL PROCEDURE.

The apparatus was baked out by means of an electric furnace at a temperature of 350^{o}C. This had to be continued for some time before the pressure fell below 2×10^{-5} mm owing to the large amount of gas present in the sindanyo. The filament was then flashed and run in.

The electrons from the filament were accelerated up to the gauze G_1 by a potential V_0 which was set equal to

60 volts. This value lies between the critical potentials for the formation of Hg^{2+} and Hg^{3+} given by Bleakney (26) as 30 and 71 volts respectively. Any Hg^{2+} and Hg^{+} ions formed in the field-free space between the gauzes G_1 and G_2 were accelerated up to the gauze G_3 by a potential V_1 applied between G_2 and G_3. The potential V_1 , which had values ranging from 70 to 200 volts for different runs, also served to reverse all electrons from the filament F and consequently it could not be reduced below a value just greater than V_o. A retarding potential V_2 was applied between the lower gauze G_3 and the gauze G_4 to reverse the ions leaving the field-free space inside the cylinder C_2. Any ions emerging from C_2 with an energy greater than V_2 passed through the gauze G_4 and were drawn into the Faraday cylinder by a potential of 20 volts, applied between the Faraday cylinder and the shield. The positive ion current entering the Faraday cylinder was read on the galvanometer M_1, which had a sensitivity of 7.8×10^{-11} amps per mm.

All parts of the external circuit connected to the galvanometer M_1 were insulated by mounting them on ebonite blocks with sulphur rings. A preliminary test was made by setting $V_o < 30$ volts so that no Hg^{2+} ions could be formed. V_1 was set equal to 200 volts, the maximum value used, and the retarding potential V_2 was varied from 200 up to 400 volts. No current through the galvanometer could be detected, which showed that the insulation of the Faraday cylinder circuit was complete.

The values of V_0, V_1 and V_2 were all read on the same standard Weston voltmeter by means of the key shown in fig. 28. The positive ion current to the field-free cylinder C_2 was read on a unipivot galvanometer, M_2, which had a sensitivity of 3.1×10^{-7} amps per scale division.

Sphagetti resistances were included in the external circuit to prevent the establishment of an arc at high potentials. The galvanometers and the milliammeter were protected from possible damage by fine fuse wires, which fused at 200 milliamps.

The first part of the work consisted in measuring the energy distribution of the ions entering the field-free space C_2. These ions will be called the "incident" ions, those leaving it will be called the "emergent" ions. The apparatus shown in fig. 28b, which is simply that of fig. 28a with the field-free cylinder C_2 replaced by a single gauze G_3, was used. When this had been done the apparatus was changed to the form shown in fig. 28a, and the energy distribution of the emergent ions was measured.

RESULTS.

THE ENERGY DISTRIBUTION OF THE INCIDENT IONS.

V_o was set equal to 60 volts and the filament heating current adjusted to give an emission which was held constant at 1.0 milliamp. Positive ions, formed by electron impact, were accelerated up to the gauze G_3 by a potential V_1 applied between G_2 and G . The retarding potential V_2, applied between G_4 and G_3, was altered in small steps of one or two volts from a value of about 30 volts below the value of V_1 to a few volts above V_1. The positive ion current entering the Faraday cylinder for each value of V_2 was read on the galvanometer M_1, which was worked at a sensitivity of 7.8×10^{-9} amps/mm. The curve showing the positive ion current plotted against the value of V_2 is the retarding potential curve for the incident ions. The slope of the curve at any value of V_2, say V_2', gives the number of ions having an amount of energy equal to V_2'. The energy distribution curve was obtained by differentiating the retarding potential curve and plotting the slope at a large number of different points against the corresponding values of the retarding potential V_2.

Retarding potential curves were obtained for incident ions accelerated by values of V_1 equal to 70, 110, 150 and 200 volts. The energy distribution curves obtained by differentiation of the reatrding potential curves are shown in fig. 29. These curves give the energy spread for all positive ions formed between G_1 and G_2. According to Bleakney (26) 90% of these ions are Hg^+ and 10% are Hg^{2+} when V_o is 60 volts. The Hg^{2+} ions and the Hg^+ ions cannot be separated in this apparatus. The curves will however represent the energy distribution of the Hg^+ ions, which is given by the lower abscissa scale in fig. 29 .

There are two factors which introduce inhomogenity into the incident ion beam. Firstly some of the ions lose kinetic energy in elastic collisions with other atoms, and secondly electrons from the filament penetrate into the region between G_2 and G_3 before they are reversed. Any ions formed in this region will not receive the full accelerating potential.

To reduce the number of electrons which passed through the gauze G_2, a magnetic field was applied at right angles to the axis of the cylinder. The field was provided by two large bar magnets set up, one on each side of the tube, so as to give a field only over the region of the cylinder C_1. The strength of this field was measured by using a search coil and a Grassot fluxmeter. It was found to be about 50 gauss, which was sufficient to make the electrons describe circular paths in the field-free space between G_1 and G_2. This field

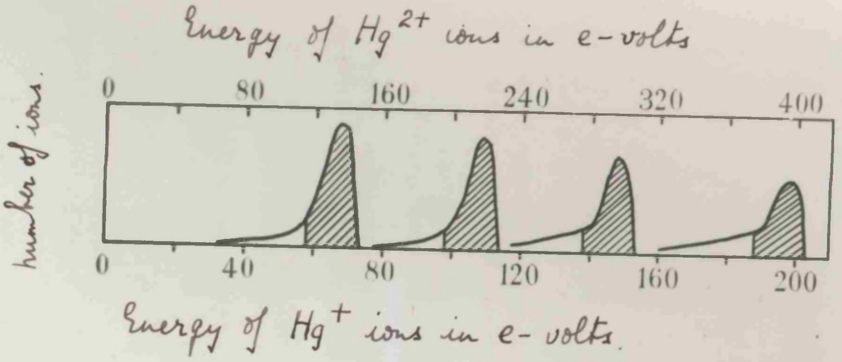


FIG. 29. Energy distribution curves for incident ions.

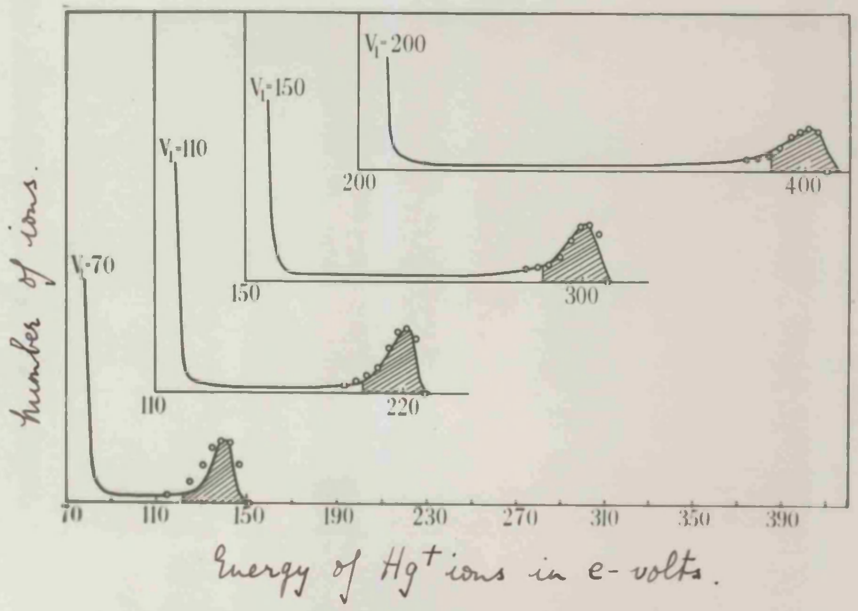


FIG. 30. Energy distribution curves for emergent ions.

was too small to have any appreciable effect on the motion of the heavy mercury ions.

The curves in fig. 29 show the energy distribution of the incident ions with this field present. Curves obtained without it showed greater inhomogenity. The field was therefore retained for the remainder of the work.

The factors, which introduce this inhomogenity in the energy distribution of the Hg^+ ions, must also affect the energy distribution of the Hg^{2+} ions. The curves shown in fig. 29 will therefore represent the energy distribution of the incident Hg^{2+} ions provided the abscissa scale is multiplied by a factor of 2, since the Hg^{2+} have an energy double that of the Hg^+ ions in virtue of their double charge.

The upper scale in fig. 29 consequently gives the energy distribution of the incident Hg^{2+} ions. The reason for the shaded portion of each curve will be seen later.

THE ENERGY DISTRIBUTION OF THE EMERGENT IONS.

The apparatus was changed to the form shown in fig. 28a. The value of V_0 was kept equal to 60 volts, and the heating current for the filament was adjusted to give a constant emission of 8 milliamps. The retarding potential V_2 applied between the lower gauze G_3 and the gauze G_4 was altered in small steps from a value just greater than V_1 to a value above 2 V_1. The object of this part of the work being to investigate the small peak due to fast Hg^+ ions with an energy 2 V_1 shown in fig. 27. The sensitivity of the galvanometer M_1 was increased by a factor of 100, to 7.8×10^{-11} amps/mm.

Retarding potential curves for the emergent ions were obtained for different values of V_1 between 70 and 200 volts. Four of the energy distribution curves obtained by differentiating the retarding potential curves are shown in fig. 30. The significance of the points shown on the peaks will be explained later.

The steep fall at the start of each curve in fig. 30 is due to a few of the incident Hg^+ ions having energies considerably in excess of the value V_1. It might seem that the energy spread of the incident ions with this form of the apparatus is greater than that given in fig. 29 for the apparatus of fig. 28b. However it is to be noted that the sensitivity of the galvanometer is increased by a factor of 100, and that the filament emission is increased by a factor of 8. This fall is therefore the "tail" of the energy distribution curves in fig. 29 magnified 800 times and it does not vitiate the form of the energy distribution curves obtained for the Hg^{2+} ions in fig.29 .

Owing to the design of the apparatus it was not possible to investigate the transfer process for Hg^{2+} ions of energy below 140 electron-volts. To obtain positive ion currents of sufficient intensity the energy of the electrons could not be reduced below 60 volts. Since the same field was used to accelerate the Hg^{2+} ions and to reverse the electrons from the filament, the minimum accelerating potential had to be above 60 volts.

The introduction of another gauze between G_2 and G_3 would have enabled the process to be investigated for lower energy values. The ions could have been accelerated up to the additional gauze and then retarded before entering the field-free space. However, the beam of Hg^{2+} ions entering the field-free cylinder without the insertion of an extra gauze had a fairly wide range of energies. This modification in the design of the apparatus would certainly have increased the inhomogenity in the energy of the ions, and for this reason it was not made.

THE VARIATION IN THE NUMBER OF FAST Hg IONS WITH ELECTRON ENERGY.

So far it has been assumed that the group of fast ions which appears in every curve in fig. 30 originates from the production of fast Hg^+ ions by the process

$$Hg^{2+} + Hg \rightarrow Hg^+ + Hg^+$$

Three curves showing the variation in the number of fast Hg^+ ions as the energy of the electrons was increased from 20 to 60 volts are given in fig. 31. The curves, which are for three different values of V_1, have been displaced in a vertical direction to separate the points. The critical potential for the formation of Hg^{2+} obtained from spectroscopic data is given by Bacher and Goudsmit (54) as 29.06 volts. It is clearly shown by the curves in fig. 31 that no fast Hg^+ ions appear for electron energies below 29 volts. This justifies the assumption that the fast Hg^+ ions are produced by Hg^{2+} ions.

The variation in the number of fast Hg^+ ions with filament emission was also examined and found to be strictly linear.

The significance of the energy distribution curves in fig. 30 can now be discussed.

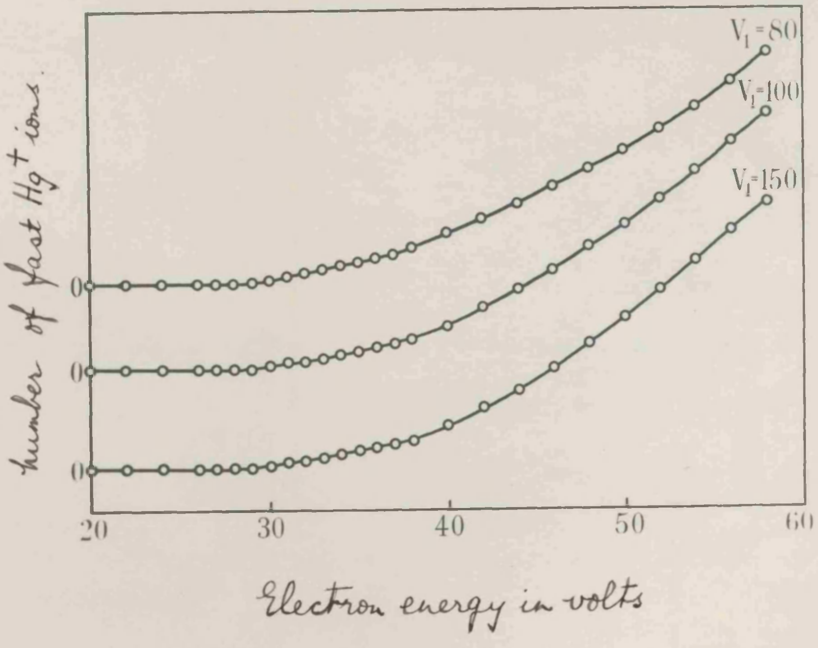


FIG. 31. Curves showing the number of fast Hg^+ ions as a function of the electron energy.

DISCUSSION OF RESULTS.

If the kinetic energy of the Hg^{2+} ion, which is $2\ V_1$ electron-volts, is shared in a random way between the two Hg^+ ions which are formed by the transfer process, then the energy distribution curve should show Hg^+ ions with a wide range of energies between V_1 and $2\ V_1$ electron-volts. A sharp peak at $2\ V_1$ indicates that the process is far more probable for a head-on collision or for a collision in which the Hg^{2+} ion just grazes the normal Hg atom. In a head-on collision the normal atom becomes the fast Hg^+ ion, in a grazing collision the Hg^{2+} ion becomes the fast Hg^+ ion. It is therefore of interest to see if we can determine from these curves the exact nature of the effective collision.

The peaks showing the energy distribution of the fast Hg^+ ions in fig. 30 indicate an energy spread of about 30 volts. If this spread can be accounted for by the energy spread of the incident Hg^{2+} ions then the effective collision must be either a head-on or a grazing collision.

Points from the energy distribution curves for the incident Hg^{2+} ions in fig. 29 were taken and reduced to fit the peaks of fig. 30 at their maxima. These points are plotted on the peaks in fig. 30. They show that for each value of V_1 the energy spread of the fast Hg^+ ions is fully accounted for by the energy spread of the incident Hg^{2+} ions.

The process $Hg^{2+} + Hg \rightarrow Hg^{+} + Hg^{+}$ is therefore more probable and perhaps only possible for a head-on or a grazing collision, in which one of the resulting Hg^{+} ions carries off all the kinetic energy of the incident Hg^{2+} ion.

THE CLASSICAL MECHANICS OF THE COLLISION PROCESS.

The internal energies of an Hg^{2+} and an Hg^{+} ion ~~atom~~ are respectively 29.06 and 10.39 electron-volts. There is therefore set free in the collision process an amount of internal energy equal to (29.06 - 20.78) i.e. 8.28 electron-volts. This internal energy may be entirely converted into kinetic energy of translation, or some of it may be used to excite one of the Hg^{+} ions into one of its excited states.

If the internal energy set free for conversion into kinetic energy is denoted by p, then the effective transfer process can be written more definitely as

$$Hg^{2+}(2\ V_1\ e.v.) + Hg \rightarrow Hg\ (2\ V_1 e.v.) + Hg^{+} + p$$

where p is equal to or less than 8.28 electron-volts.

The question of the distribution of this internal energy between the two Hg^{+} ions will now be investigated for both types of collision, head-on and grazing.

HEAD-ON COLLISION.

Suppose an Hg^{2+} ion moving with a velocity V_o makes a head-on collision with a normal atom which may be considered at rest, since it has only thermal energy which is equivalent to about 1/30 electron-volts at room temperature.[A1] Let the velocities of the resulting Hg^+ ions be v_1 and v_2.

By the Conservation of energy, we have

$$\tfrac{1}{2} mv_o^2 + p = \tfrac{1}{2} mv_1^2 + \tfrac{1}{2} mv_2^2 \qquad (29)$$

By the Conservation of momentum

$$mv_o = mv_1 + mv_2 \qquad (30)$$

Squaring (30) and subtracting (29) we obtain

$$v_1 v_2 = -\frac{p}{m} \qquad (31)$$

Eliminating v_2 from equation (29) we have

$$\tfrac{1}{2} mv_o^2 + p = \tfrac{1}{2} mv_1^2 + \frac{p^2}{2\, mv_1^2}$$

$$\text{i.e. } E_o + p = E + \frac{p^2}{4E} \qquad (32)$$

where $E_o = \tfrac{1}{2} mv_o^2 = 2\, V_1$

$E = \tfrac{1}{2} mv_1^2$

$$\therefore E^2 - (E_o + p)E + \frac{p^2}{4} = 0 \qquad (33)$$

$$\text{i.e. } E = \tfrac{1}{2}(E_o + p) \pm \tfrac{1}{2}\left[(E_o + p)^2 - p^2\right]^{\frac{1}{2}}$$

$$= \tfrac{1}{2}(E_o + p) \pm \tfrac{1}{2}E_o\left(1 + \frac{2p}{E_o}\right)^{\frac{1}{2}}$$

$$\tfrac{1}{2}(E_o + p) \pm \tfrac{1}{2}E_o\left(1 + \frac{p}{E_o}\right)$$

since $p \leqslant 8.28$ e.v. and $E_o \geqslant 140$ e.v.

The solutions are therefore

$$\left.\begin{aligned} E &= E_o + p = 2V_1 + p \\ \text{and} \quad E &= 0 \end{aligned}\right) \qquad (34)$$

This means that one Hg^+ ion travels on with kinetic energy equal to that of the incident ion plus any internal energy set free in the collision. The other ion remains at rest.

GRAZING COLLISION.

When an Hg^{2+} ion just grazes a normal Hg atom any internal energy set free will affect the relative motion of the Hg^+ ions only in a direction at right angles to the direction of motion of the Hg^{2+} ion. The Hg^{2+} ion will retain its original kinetic energy in the forward direction and must be the fast ion.

If v_1 and v_2 are the velocities of the resulting Hg^+ ions in a direction perpendicular to the direction of motion of the Hg^{2+} ion

By the conservation of energy

$$p = \tfrac{1}{2} m v_1^2 + \tfrac{1}{2} m v_2^2 \qquad (35)$$

By the conservation of momentum

$$0 = m v_1 + m v_2 \qquad (36)$$

As for head-on collision, we obtain

$$v_1 v_2 = -\frac{p}{m} \qquad (37)$$

Eliminating v_2 from (35), we have

$$p = E + \frac{p^2}{4E}$$

i.e. $4E^2 - 4Ep + p^2 = 0$

i.e. $(2E - p)^2 = 0$

i.e. $E = \tfrac{1}{2}p$ (38)

Therefore in a grazing collision the internal energy set free in the process is shared equally between the two Hg^+ ions. This produces a motion of the Hg^+ ions perpendicular to the direction of motion of the incident Hg^{2+} ion and consequently it has no effect on the component of the velocity of the fast Hg^+ ion in the direction of motion of the incident Hg^{2+} ion.

The equations (34) and (38) show that the resulting fast Hg^+ ion should have a component velocity in the direction of the retarding field which is equivalent to an energy of $2V_1 + p$ electron-volts if the collision is a head-on one, and of only 2 V_1 electron-volts if the collision is a grazing one. It should therefore be possible to determine from the energy distribution curves whether the effective collision is a head-on or a grazing collision.

The following table shows the energy of the fast Hg^+ ions for different values of V_1. These energy values are the energies of the maxima of the fast Hg^+ peaks shown in fig. 30 and in other curves not given in this thesis. The final column gives the energy of these ions in excess of 2 V_1.

TABLE 2.

V_1 e-volts.	Energy of fast Hg^+ ions. e-volts.	Energy in excess of 2 V_1. e-volts.
x 70	140	0
90	183	3.0
x 110	222	2.0
130	262.5	2.5
x 150	301	1.0
176	353.5	1.5
x 200	402	2.0

x Values obtained from curves in fig. 30.

This table shows that the fast Hg^+ ions have an energy of about 2 electron-volts in excess of the energy 2 V_1. Consequently the collision cannot be a grazing one, nor can it be a head-on one in which the whole of the internal energy is converted into kinetic energy. The collision must be a head-on one in which part of the internal energy is used in exciting one of the resulting Hg^+ ions, the energy required for excitation is apparently about 6.23 electron-volts. There are two excited states of the Hg^+ ion having energies close to this amount, the $5d^9 . 6s^2 . {}^2D_{1\frac{1}{2}}$ state of 6.23 electron-volts energy and the $5d^{10} . 6p . {}^2P_{\frac{1}{2}}$ state of 6.35 electron-volts energy. The values are given by Bacher and Goudsmit (54).

The process first observed by Kallmann and Rosen can now be described much more definitely. An Hg^{2+} ion moving with an energy V_1 electron-volts on making a head-on collision with a normal Hg atom, captures an electron into an excited state, which may be either the $5d^9 . 6s^2 . {}^2D_{1\frac{1}{2}}$ state or the $5d^{10} . 6p . {}^2P_{\frac{1}{2}}$ state, and comes to rest. The normal atom loses an electron and becomes a normal Hg^+ ion and moves on with a kinetic energy equal to that of the incident Hg^{2+} ion plus the internal energy set free in the transfer process. This is about 2 electron-volts.

This process can be written as follows

$$\begin{array}{ccccccc} Hg_{a}^{2+} & + & Hg_{b} & \longrightarrow & Hg^{+}_{a}({}^{2}D_{1\frac{1}{2}}) & + & Hg^{+}_{b} \\ eV & & 0 & & 0 & & eV+2 \end{array}$$

The kinetic energies of the particles are given below the equation, and the suffices are used to distinguish the ion and atom before and after the transfer process.

It has already been mentioned on page 30 that from theoretical considerations the probability of electron transfer is only appreciable when the excess energy, to be carried away by the colliding particles as kinetic energy, is small compared with the kinetic energy of the particles before the collision.

The results given here for electron transfer in mercury vapour are in agreement with the theoretical prediction, since the greater part of the excess energy is used in raising one of the particles into an excited state leaving only a small amount of energy to be carried away as kinetic energy. The variation in the probability of the transfer process as the energy of the incident Hg^{2+} ions is increased is of interest to theoretical workers for comparison with the theoretical curves. This can be determined from the experimental curves of figs. 29 and 30 as follows.

THE PROBABILITY OF ELECTRON TRANSFER PROCESS.

The probability of any specified collision process is usually given in terms of the effective cross-section of the atom for that process. The effective cross-section is the imaginary area of the atom that must be struck in order that the process may take place with certainty. The probability can be obtained by dividing the effective cross-section by the kinetic theory cross-section. The kinetic theory cross-section for any collision is independent of the velocity of the colliding particles, whereas the effective cross-section varies with the velocity of the colliding particles.

To determine the effective cross-section for the electron transfer process it is necessary to know the number of Hg^{2+} ions entering the field-free space C_2, and also the number of fast Hg^+ ions leaving the same space.

For any one value of V_1 let A be the area of the peak representing the emergent fast Hg^+ ions in fig. 30, and let a be the area of the peak representing the incident Hg^{2+} ions. The results given by Bleakney (26) show that the ratio of the number of Hg^{2+} ions to the number of Hg^+ ions formed by electrons of 60 volts energy is 0.10. The area a is therefore one-tenth of the area of the peaks in fig. 29 which were obtained for the incident Hg^+ ions. The scale factor for the peaks in fig. 29 is the same as for the peaks in fig. 30. The areas A and 10a are therefore the shaded portions of the peaks in figs. 29 and 30, and they cover an energy spread of 30 electron-volts in both figures.

The fraction of the total number of incident Hg^{2+} ions which on collision with neutral atoms in the field-free space produce fast Hg^{+} ions is given by the relation

$$N = \left(\frac{A}{a}\right) S.I.F. \qquad (39)$$

where S is a factor introduced to correct for the change in the sensitivity of the galvanometer used for the measurement of the energy distribution of the incident and emergent ions. As stated on page 149, $S = 1/100$. I is a factor which corrects for the change in the filament emission, which was 1.0 milliamp for the results of fig. 29 and 8.0 milliamps for the results of fig. 30 I is therefore 1/8. This correction is only possible because of the linear relation between the number of ions and the filament emission mentioned on page 150. The factor F, which is equal to 1/0.71, is introduced since the number of gauzes in the apparatus of fig. 28a which was used to give the results of fig. 30 was one more than the number of gauzes in the apparatus of fig. 28b used to give the results of fig. 29. The transmission area of each gauze was 71% of its total area.

The <u>effective</u> cross-section for the electron transfer process is therefore given by Q where

$$Q = N/\ n\ x\ p \tag{40}$$

n is the number of atoms per cc at a pressure of 1 mm of Hg at 0°C and is equal to 3.56×10^{16} A_1, p is the pressure of mercury vapour in C_2, and is equal to 1×10^{-3} mm of Hg at 0°C, x is the distance (1.5 cms) which the Hg^{2+} ions travel in the field-free space. N is given by equation (39).

We have, therefore,

$$Q = \frac{S.I.F.}{n.x.p.} \cdot \frac{A}{a}$$

$$= 3.3 \times 10^{-17} \cdot \frac{A}{a} \tag{41}$$

The effective cross-section for the electron transfer process $Hg^{2+} + Hg \rightarrow Hg^{+} + Hg^{+}$ was calculated from equation (41) by measuring the areas A and a. The effective cross-section is shown in fig. 32 as a function of the energy of the incident Hg^{2+} ions. The kinetic theory cross-section for collision between two neutral Hg atoms obtained from viscosity measurements is given in the Landolt-Börstein Tables to be 57.7×10^{-16} cm^2. The effective cross-section for the electron transfer process over the energy range 140 to 400 electron-volts is therefore of the order of one-tenth the gas kinetic cross-section for collision. The probability of the electron

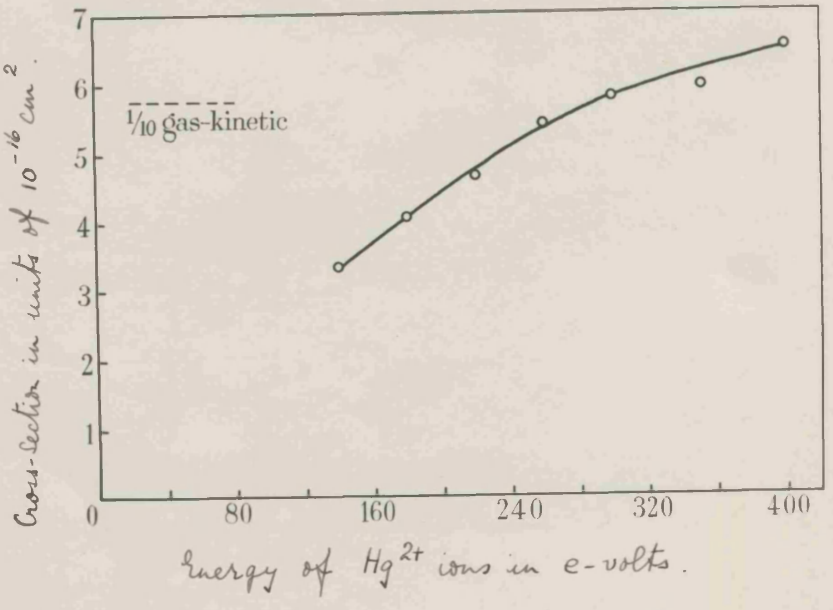


FIG. 32. Curve showing the probability of the transfer process as a function of the energy of the Hg^{2+} ions.

transfer process at a collision is consequently of the order of 0.1. Throughout the energy range investigated the probability of the transfer increases with the energy of the incident Hg^{2+} ions. The form of the curve in fig. 32 suggests a possible maximum above 400 volts.

In conclusion I should like to express my sincere thanks to Professor H. Stanley Allen, F.R.S. for the keen interest he has shown throughout the course of these investigations and to Dr. F.L. Arnot, Ph.D. for his many invaluable suggestions and helpful criticisms. I am also indebted to Mr. Gerrard for his kind assistance in the preparation of the diagrams.

APPENDIX 1.

THE VALUES OF CERTAIN CONSTANTS USED THROUGHOUT THESIS.

Electronic mass	9.042×10^{-28} grams.
Mass of hydrogen atom	1.662×10^{-24} grams.
Planck's constant (h)	6.547×10^{-27} erg-secs.
Electronic charge	4.774×10^{-10} e.s.u. 1.591×10^{-20} e.m.u.
Number of atoms or molecules per cc at N.T.P.	2.705×10^{19}
Number of atoms or molecules per cc at a pressure of 1 mm at 0°C	3.56×10^{16}
Kinetic energy of translation of one atom or molecule at 20°C.	6.03×10^{-14} ergs. 3.792×10^{-2} e-volts.

A_2

APPENDIX 2.

The electron-volt is a unit of energy, equal to the energy acquired by an electron in falling through a potential difference of 1 Volt.

The energy acquired by an electron in falling through a potential difference of V volts $= \frac{eV}{300}$ ergs

$$\therefore \; 1 \text{ electron-volt} = \frac{4.774 \times 10^{-10}}{300} \text{ ergs}$$

$$= 1.591 \times 10^{-12} \text{ ergs}$$

If v cms/sec is the velocity acquired by an electron in falling through a potential difference of V volts

$$\tfrac{1}{2} mv^2 = 1.591 \times 10^{-12} \; V$$

$$\therefore \; v = \left(\frac{3.182}{9.042}\right)^{\frac{1}{2}} \times 10^8 \times V^{\frac{1}{2}} \text{ cms/sec}$$

$$= 5.94 \times 10^7 \times V^{\frac{1}{2}} \text{ cms/sec.}$$

The energy of a photon of wavelength λ Angstrom units

$$= \frac{h \times c}{\lambda} \times 10^8 \text{ ergs}$$

$$= \frac{12336}{\lambda} \text{ electron-volts.}$$

APPENDIX 3.

SPECTROSCOPIC NOTATION USED THROUGHOUT THESIS.

For Atoms.

n, l and s: the principal, azimuthal and spin quantuum numbers for individual electrons. s is always equal to $\frac{1}{2}$.

s,p,d,f ... electrons: electrons with $l = 0,1,2,3$ .....

$6\,p^x$: x electrons with $n = 6$, $l = 1$.

L and S: the azimuthal and spin quantuum numbers for the resultant orbital and spin angular momenta of the individual electrons in the atom.

J: the inner quantuum number for the atom is the vector sum of L and S.

S,P,D.F ... states: atomic electronic states with $L = 0,1,2,3$ .....

$^{2S+1}P_2$: An atomic state of multiplicity $2S+1$, with $L = 1$, $J = 2$. For a singlet state $S = 0$, for a triplet state $S = 1$.

The electron configurations of the valency electrons are sometimes given in front of the atomic state e.g. $6s.8p.4\,^1P_1$.

For Molecules.

λ: the quantuum number for the component, parallel to the internuclear axis, of the angular momentum of the individual electron.

$\sigma, \pi, \delta, \phi$ ..... electrons: electrons with $\lambda = 0,1,2,3$ ......

Λ : the quantuum number for the component, parallel to the internuclear axis, of the resultant orbital angular momenta of the individual electrons.

Σ, Π, Δ ..... states: molecular electronic states for which $\Lambda = 0,1,2,$ .....

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