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IONS, ELECTRONS,

AND

IONIZING RADIATIONS

BY

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PREFACE TO SIXTH EDITION

In the preface to the first edition of Ions, Electrons, and Ionizing Radiations the volume was described as a text-book from which students who have been grounded in the more elementary portions of Physics might obtain a systematic knowledge of its later developments. This purpose has been kept strictly in view in each of the succeeding editions, and it is the purpose of this sixth edition. The extraordinary progress which has been made in the past five years, not only on the experimental but also on the theoretical side of Atomic Physics, has necessitated a very complete revision of the text, if the book were to continue adequately to serve its purpose.

A text-book, unhappily, cannot be brought up to date by a process of simple accretion. The acquisition of new knowledge inevitably alters the relative importance of the old, and a balance between the two must be maintained. Moreover a text-book should be written from a definite standpoint, and it is desirable that this standpoint should not be too far removed from that of current scientific thought. The reader will, in many cases, pass on to more advanced treatises on some of the subjects dealt with, and it is desirable that he should have as little as possible to unlearn.

Accordingly, the text for the new edition has been very drastically revised. Two new chapters have been added, and several have been rewritten. A considerable number of new illustrations have been provided, both in the text and in the form of Plates. Descriptions of the earlier work, however, have generally been allowed to stand after careful revision, as they appeared to have some of the freshness which is often associated with contemporary accounts. Certain matters of relatively minor importance have been deleted, as no longer appropriate to a first course.

In making the revision, I have borne in mind the fact that there is a growing tendency to introduce the study of Atomic Physics at a comparatively early stage in the student's university

course, and I have tried to select and arrange my material so that a student in the second year of a pass degree course should have no difficulty in following the argument of the book. Similarly I have simplified the mathematical treatment of the subject wherever possible, and where it was not possible (as in the case of the whole wave mechanical theory) I have contented myself with quoting the necessary results without formal proof. This, however, is not merely a concession to weakness. I have found in practice that even with students who are mathematically reasonably well equipped, a real understanding of the argument and of the underlying physical principles is more readily attained if their attention is not distracted either by the beauties or the difficulties of complicated mathematical analysis.

In short, my aim has been to provide a firm outline of the whole subject, its principles and its methods, and to make as clear as possible the relation between its different parts. The outline can be filled in from the special treatises mentioned in the General References. A number of numerical examples are appended to the volume, in the hope that they may give the student some facility in finding his way about the realm of Atomic Physics.

My thanks are due to the Council of the Royal Society for permission to reproduce Figs. 88, 99 and 104; to Dr F. W. Aston for Fig. 43; to Dr G. Shearer for Fig. 68; to Sir J. J. Thomson for Fig. 41; to Professor C. T. R. Wilson for Figs. 16, 17, 18, 18a and 59; to Sir William Bragg and Messrs Bell and Sons, Ltd. for Fig. 61 from *The Crystalline State*; to Lord Rutherford, Dr J. Chadwick and Dr C. D. Ellis and the Cambridge University Press for Fig. 80 from *Radiations from Radio-active Substances*; and to Professor G. P. Thomson and the Cambridge University Press for Fig. 94 from Sir James Jeans' *The New Background of Science*. I also wish to express my thanks to Dr W. N. Bond, who supplied some, and has verified the answers to all, of the numerical examples, and to Dr Paul White for his assistance with the proofs.   J. A. C.

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CHAPTER I

INTRODUCTION

1. Electrons. Historically the subject dealt with in the present text-book may be said to have taken its origin in experiments on the discharge of electricity through gases at low pressure contained in some form of discharge tube. When a high tension discharge is sent through a gas at low pressure (say some fraction of a millimetre of mercury) the gas becomes luminous shewing a series of glows and striae (see Fig. 28), which are often very beautiful, but which, at the time of their discovery, were very difficult to explain on the current theories of the time. If the pressure is sufficiently low, a series of streamers known as the cathode rays can be observed proceeding in straight lines from the cathode and crossing the other glows in the tube. The experiments of Sir William Crookes led him to the conclusion that these rays were material in nature, consisting of some new manifestation of matter to which he gave the term *radiant matter*. On the other hand there existed, especially in Germany, a large school of thought which was inclined to assign the effects to some sort of wave motion in the ether, probably of very short wave length, and thus analogous to ultra-violet light.

The controversy raged hotly and somewhat inconclusively for nearly twenty years. It was not until 1895 that Sir J. J. Thomson following up the work of Perrin proved conclusively that the cathode rays consisted of negatively charged particles. These experiments may be said to mark a new epoch in physical science. The method evolved enabled him to measure not only the velocity of the particles but also the ratio of the mass of an individual particle to the charge upon it. It was found that the velocity of the particles was a function of the difference of potential across the terminals of the discharge tube. In

C I   I

general its value lay between 10^9 and 10^{10} cm. per second, or roughly between one-thirtieth and one-third of that of light. The ratio of the mass of a cathode particle to the charge upon it was, however, within the limits of experimental error, perfectly constant and independent of all the circumstances of the experiment. It was found to have the same value no matter what the potential across the tube, no matter what the chemical nature of the substance used as the cathode, and no matter what the nature and pressure of the residual gas within the tube. It was in fact a universal constant. These particles can be produced from and thus are contained in all chemical substances.

It was later found possible to determine separately both the mass and the charge on these particles or *electrons* as they are now called. It was found that the mass of an electron was very small compared with that of the lightest known atom, being only about 1/1839th of that of a hydrogen atom. The mass of an electron has been found to be $9{\cdot}0 \times 10^{-28}$ gm. and its charge $4{\cdot}77 \times 10^{-10}$ electrostatic units or $1{\cdot}59 \times 10^{-20}$ electromagnetic units of charge. The radius of the electron has been estimated at approximately $1{\cdot}9 \times 10^{-13}$ cm. The radius of an atom is about 10^{-8} cm. The radius of an electron is thus about 1/50,000th of that of the atom. Such electrons must, as we have already seen, form a part of every known kind of matter.

No charge has yet been observed which is smaller than that on the electron. Every charge observed, which is sufficiently small to be directly compared with that of the electron, has been found to be an exact integral multiple of it. We are thus led to the conclusion that *electricity is atomic in structure*; the smallest possible unit of charge being that of the electron, which thus constitutes our fundamental unit of electricity. It is generally supposed that the "mass" of the electron is entirely an electrical effect, and is due solely to the charge which it carries. The electron therefore constitutes a real atom of electricity.

Quite recently a *positively* charged counterpart to the negative electron has been discovered. The term electron, however, has been used for so long as signifying a negative electron that it will

be convenient to continue to use it in this sense, and to find a new name for the positively charged particle. It is proposed to call the latter a *positron*.

2. **Conduction through gases.** The investigation of the electron and its properties was given a further stimulus by the discovery, which followed hard upon it, that gases which ordinarily are among our best insulators of electricity can be rendered partially conducting by the action of certain agents upon them. The discovery of X-rays by Röntgen in 1895 was quickly followed by the observation that charged bodies rapidly lost their charge when an X-ray bulb was worked in their vicinity. This loss of charge was shewn to take place through the surrounding air, which became temporarily conducting. It was shewn that the conductivity of the gas was due to the creation in it of positively and negatively charged systems, which by analogy with the carriers in electrolytic conduction were termed *gaseous ions*. These ions must, on the electron theory, consist of molecules of the gas which have lost or gained one or more electrons. Further investigation shewed that similar properties could be conferred upon a gas by the action of cathode rays. Owing partly to the small number of the carriers, partly to the great simplicity in the structure of gases, a study of these carriers has thrown considerable light on some obscure parts of science.

The existence of these gaseous ions was controverted for some little time, but no other explanation has been found adequate to explain the phenomena. Their objective reality was placed beyond all reasonable doubt by the experiments of C. T. R. Wilson, who shewed that these ions could serve as nuclei for the condensation of drops of water in a supersaturated space. The ions were thus rendered visible by the deposition of the water upon them, and could readily be observed, and even photographed. Photographs such as that of Fig. 17, which represents the track of a cathode particle through air, make it certain that the production of conductivity in a gas by these ionizing radiations is due to the formation in the gas of definite charged systems.

3. Radio-active substances and their radiations. The discovery of X-rays and the somewhat startling manner in which these rays were able to penetrate considerable thicknesses of materials which were opaque to ordinary light naturally led to an exhaustive search among natural substances to see if any of these emitted radiations having properties at all resembling those of X-rays. The research was pursued with vigour by Becquerel and afterwards by the Curies, and led to the discovery that radiations possessing the properties of penetrating opaque substances and of causing conductivity in gases were emitted by the salts of uranium and thorium. The subsequent observation that naturally occurring ores of uranium were several times more active than the metal itself led to the isolation of polonium, radium, and subsequently of other similar substances which were found to possess these properties in a very remarkable degree. Substances which are capable of emitting spontaneously these ionizing radiations are classed together under the title *radio-active substances*.

It has been shewn that each radio-active substance is a definite chemical element, and that its activity is due to a spontaneous decomposition or disintegration as it is usually termed of the radio-active atom into one of smaller weight, the process taking place according to definite laws which have been determined. This naturally leads us to the view that the atoms of the various chemical elements are not essentially different in kind but represent complex systems built up out of one or two elementary forms according to certain definite laws.

On further investigation it was found that the rays given out by these radio-active substances were of three kinds, which were denoted by the non-committal symbols α, β, and γ. All three types possess in common with X-rays the properties of converting a gas into a conductor, of affecting a photographic plate, and of causing luminescence in a fluorescent screen. In other respects however they differ very markedly in their properties.

The α-rays were found to be positively charged and were of the mass of atoms. They have been proved to consist of helium atoms which have lost two electrons and thus possess

a positive charge of $2 \times (4 \cdot 77 \times 10^{-10})$ or $9 \cdot 54 \times 10^{-10}$ e.s.u. They are very easily absorbed in matter being completely stopped by 1/10th mm. of aluminium or a few centimetres of air at atmospheric pressure. They produce very intense ionization in the gas through which they pass. Their velocity depends on the substance from which they are ejected; their nature is always the same.

The β-rays on the other hand carry a negative charge. They can penetrate much greater thicknesses of matter than the α-rays, producing measurable effects through a thickness of even a centimetre of aluminium. The ionization they produce in a gas is however small compared with that of the α-rays. Their nature is found to be identical with that of the cathode rays. They consist of electrons, carrying the universal electronic charge, and differ from the cathode rays only in velocity. Whereas it is difficult to obtain cathode rays with a velocity much greater than one-half that of light, the β-rays from radium possess velocities which range up to within one or two per cent. of that of light itself.

The γ-rays are exceedingly penetrating, those from radium producing quite measurable effects through a thickness of 20 or 30 cms. of iron. Their ionizing power is small, as the fraction of their energy which can be absorbed by any reasonable thickness of gas is minute. They are now known to be pulses in the ether of very short wave length (less than 10^{-9} cm.). X-rays are also ether pulses but of longer wave length; those most commonly employed ranging between 10^{-9} cm. and 10^{-8} cm. With modern improvements in X-ray production, the X-ray spectrum now overlaps that of the γ-rays. The γ-rays and X-rays thus represent the extreme short wave length end of the electromagnetic wave scale; they are, in fact, ultra-violet rays of extremely short wave length. The shortest ultra-violet waves produced and investigated by optical methods have a wave length of about 10^{-5} cm. Radiations of intermediate wave lengths have, however, been produced in high vacua, and the gap between ordinary X-rays and the ultra-violet has now been completely covered. We shall see later that ordinary ultra-violet rays have many properties in common with X-rays.

CHAPTER II

PASSAGE OF A CURRENT THROUGH AN IONIZED GAS

4. Conductivity of gases in the normal state. A gas in its normal state is one of the best insulators of electricity known. It was indeed for a long time a moot point whether gases conducted electricity at all, and whether the gradual loss of charge which always occurs with charged bodies might not be due to slight defects in the insulating qualities of the solid materials used to support the body. The matter was settled by C. T. R. Wilson using the ingenious apparatus shewn in Fig. 1. The gas is enclosed in a large spherical vessel which is silvered inside to make it conducting. The charged system takes the form of a brass rod carrying a pair of thin gold leaves. In this way the charged body is made to serve as its own electroscope. Since the electrical capacity of a system such as this is very small, a very small loss of charge will be sufficient to produce a large fall of potential, and hence a considerable movement of the gold leaves, which were closely observed with a long focus microscope having a micrometer scale in the eye-piece. The apparatus was thus exceedingly sensitive.
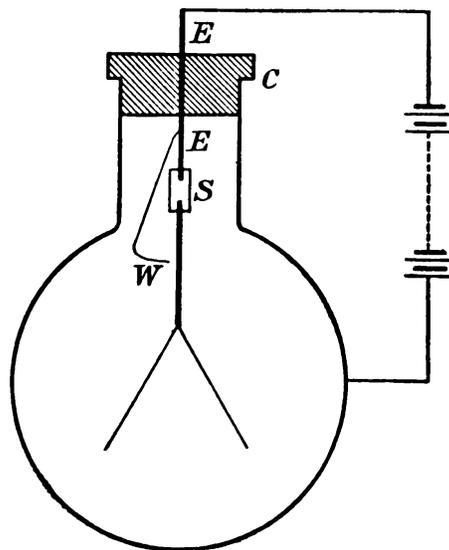
The end of the rod carrying the gold leaves was fused into a block of sulphur S; sulphur when carefully prepared being an exceedingly good insulator. The sulphur block was supported

Fig. 1

by another brass rod E passing through an ebonite cork in the neck of the vessel.

The rod E is charged to some suitable potential (about 400 volts) and is maintained at this potential throughout the experiment, most conveniently by connecting it to one end of a cabinet of small accumulator cells, the other terminal of which is connected to the silver coating of the vessel. Contact between E and the gold leaves can be made, when required, by means of the fine iron wire W which can be attracted by a magnet so as to touch the gold leaf system, and then allowed to fly back leaving the latter perfectly insulated. The gold leaves are then at the potential of E.

Since the latter remains at the same potential throughout, any leak across the sulphur plug will only tend to keep the deflection of the leaves at their original value. Any loss of charge must take place therefore across the gas. Even under these circumstances it was found that the leaves gradually became discharged, the loss of charge per second being about 10^{-8} V electrostatic units of charge where V is the volume of the vessel.

We see therefore that even in its normal state a gas allows the passage of a small current of electricity. Under certain circumstances, however, the gas acquires a conductivity many times greater than the normal, and these currents have acquired considerable importance in the development of modern electrical theory.

If, for example, a quantity of radium is brought near the electroscope of Fig. 1, the leaves collapse with considerable rapidity and similar effects are observed if an X-ray tube is worked in the vicinity. Gases drawn from a Bunsen flame also possess temporarily the power to discharge a conductor, and this capacity is enormously increased if the flame is fed with a volatile salt such as sodium or potassium chloride.

The power to discharge a conductor persists in the gas for some little time after the active agent has been removed, and is transferred from place to place with the air. Thus if air from a Bunsen flame (Fig. 2) is drawn in a continuous current into an electroscope, the latter will be discharged.

If, however, the gas is filtered through tightly packed glass wool or passed through water the effect disappears, and it can also be removed by subjecting the gas to a strong electric field. It disappears spontaneously if the gas is allowed to stand for a few minutes.
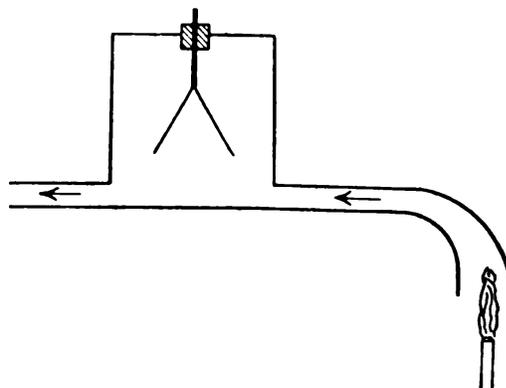
5. Ionization theory of gaseous conduction.

The phenomena of the passage of electricity through gases can best

Fig. 2

be explained by assuming that charged systems are set up in the gas by the action of the various agencies, and that these charged systems or gaseous ions, as they are called, convey the current across the gas by moving in opposite directions through the gas under the action of the electrostatic field set up by the charged body, in much the same way that a current is conveyed through the solution of an electrolyte by the motion of the positively and negatively charged electrolytic ions.

Thus if the body has a positive charge and is surrounded by a gas containing gaseous ions the negative ions will be attracted to the body, and giving up their charges to it will gradually bring about its discharge. The difference between electrolytic and gaseous conduction which experimentally is very marked is due to two principal causes. In the first place the electrolytic ions are formed by the mere process of solution and persist so long as the salt remains dissolved, while the gaseous ions are only formed by the action of an external agency, which we may call the *ionizing agent*, and gradually disappear when the latter is removed. In the second place the number of charged systems present in a gas under the most intense ionizing agent is only a very small fraction of those present even in very dilute electrolytic solutions.

6. Methods of measuring the current through a gas. Before proceeding to describe the phenomena attending the passage of an electric current through gases it will be convenient to explain briefly the methods available for measuring such currents. The discharge through a normal gas is as we have seen about 10^{-8} electrostatic units (e.s.u.) per unit volume. If the volume of gas is one litre this corresponds to a current of 10^{-5} e.s.u., since current is the rate of flow of electricity. The current through the gas is thus equal to $10^{-5}/3 \times 10^{10}$ in absolute electromagnetic units (e.m.u.), that is $\frac{1}{3} \times 10^{-15}$ e.m.u. or about $3\cdot3 \times 10^{-15}$ amperes. This is about one ten thousandth of the smallest current which could be detected on our most sensitive galvanometers. Thus even if the conductivity of the gas is increased a thousand fold by the ionizing agent the current will still be beyond the range of a galvanometer.

Let Q be the charge at any instant on an electrical conductor of capacity C. The potential V of the conductor is given by the equation
$$Q = C \cdot V.$$
The current i through the gas at any instant is given by the rate of loss of charge of the conductor. Thus

$$i = dQ/dt = C \cdot dV/dt \quad . \quad . \quad . \quad . \quad (1)$$

since the capacity C is constant.

Thus if the rate of loss of potential can be measured, as for example by measuring the rate of collapse of the leaves of an electroscope, the current through the gas can be calculated when the capacity of the charged system is known. This method was employed by Wilson in his measurements on the conductivity of a normal gas already described.

In this form of measurement the potential across the gas must be adjusted to suit the instrument used. Thus if the gold leaf electroscope requires a potential difference of, say, 100 volts to produce a sensible deflection of the leaves we cannot work with potential differences of less than this amount. It is often, therefore, more convenient to measure the rate at which an insulated conductor receives electric charge from the gas under the action of a field supplied by another electrode immersed

in the gas. The current will clearly be measured by $i = C \cdot dV/dt$ as before, where C is the combined capacity of the receiving electrode and the measuring instrument, and dV/dt the rate at which the potential of the latter increases.

7. Measuring instruments. The instruments used in practice are either the electrometer or some form of
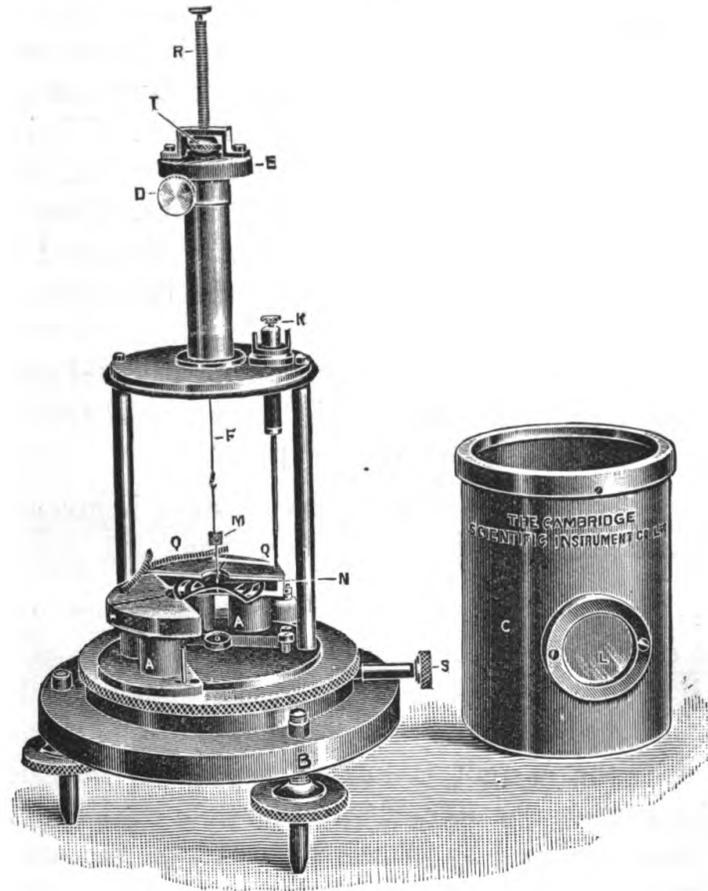
Fig. 3

electroscope. The **Dolezalek electrometer** (see Fig. 3) is an improved form of the quadrant electrometer described in the text-books on electrostatics, in which special attention is paid to obtaining not only a high degree of sensitiveness but also a small capacity. The quadrants are small and are carefully insulated on amber supports. The needle is made as light as possible and supported by a fine strip of phosphor

bronze. The instrument is used heterostatically, the needle being kept at a constant potential of about 120 volts by means of a high tension battery. One pair of quadrants of the electrometer is connected to the electrode at which the current is to be measured, the other pair being permanently earthed. If the collecting electrode is initially earthed, the rate of increase of deflection of the needle is proportional to the rate of rise of potential of the insulated quadrants, that is, to dV/dt.

To Electrode.

To Cells
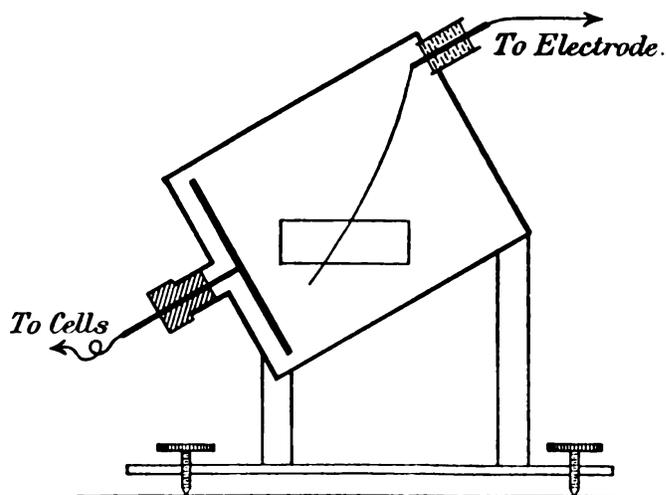
Fig. 4

If the deflection is measured by a reflected beam of light in the usual way, a deflection of 1000 mm. per volt can be obtained on a scale placed one metre from the instrument. The capacity of the electrometer is generally of the order of 50 e.s.u. An improved form of this instrument, introduced by Compton, with a still smaller capacity gives a sensitivity under similar conditions of 10,000 mm. per volt.

The gold leaf electroscope. One form of electroscope has already been described and is still largely employed for certain classes of measurement. A more sensitive form, also due to C. T. R. Wilson, is the tilted electroscope (Fig. 4). In this instrument the gold leaf which is initially at zero potential is attracted outward from the vertical position by a plate which is charged to some constant potential, usually about 160 volts, by a cabinet of cells. If the plate is positively charged

a small negative potential on the leaf will cause it to be attracted still further towards the plate, while a small positive potential will cause it to move towards the vertical position. The position of the gold leaf is read by a microscope with micrometer eyepiece. For certain potentials of the plate, and for a certain position of tilt of the instrument, generally about 30° as in the figure, the leaf becomes almost unstable and in this state is very sensitive to slight changes in potential. A sensitivity of 500 divisions per volt can be obtained, and the capacity can be made very small; it need not exceed one or two electrostatic units. The instrument can be still further improved by substituting a gilded quartz filament for the gold leaf.

The Lindemann electrometer combines some of the merits of both instruments. It consists of a vertical gilded quartz fibre nn (Fig. 5), which is supported by stretched horizontal quartz fibres, so that it lies symmetrically between four parallel brass plates, $ABCD$. The plates are charged oppositely, in pairs, as shewn in the diagrams, to a potential of approximately $\pm$ 30 volts. The small potential to be measured is applied to the quartz needle. As the potentials of its plates are gradually raised a position of instability is reached, just as in the case of the tilted electroscope, and just below this point the instrument is very sensitive. The quartz needle makes an ideal object for a high power magnification, and owing to the mode of suspension the instrument is insensitive both to vibrations and tilt.
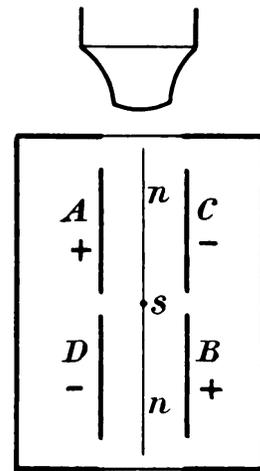
Fig. 5

Comparison of the relative sensitiveness of the electrometer and electroscope. A comparison of the two instruments affords a useful exercise in the principles of the method of measurement. Let us assume that the electrometer gives a deflection of 1000 divisions per volt, and the electroscope 200, and that in each case a rate of deflection of one division in 10 seconds can be measured. In the case of the electrometer

this corresponds to a value of dV/dt of 10^{-4} volts per second. The capacity of the instrument is, say, 50 e.s.u., or since one farad or practical unit of capacity is equal to 9×10^{11} e.s.u. the capacity of our electrometer is $\dfrac{50}{9 \times 10^{11}}$ or approximately 6×10^{-11} farads. The smallest current which can be measured with accuracy is therefore $6 \times 10^{-11} \times 10^{-4}$, that is 6×10^{-15} amperes.

For the electroscope the rate of change of potential is on the same assumptions 1/2000 volt per sec., while the capacity is, say, 2 e.s.u., or about $2 \cdot 2 \times 10^{-12}$ farads. The smallest measureable current is thus $2 \cdot 2 \times 10^{-12} \times \frac{1}{2000}$ or $1 \cdot 1 \times 10^{-15}$ amperes. Thus, although the electrometer is more sensitive as regards potential, the electroscope is more sensitive to current, owing to its smaller electrostatic capacity.
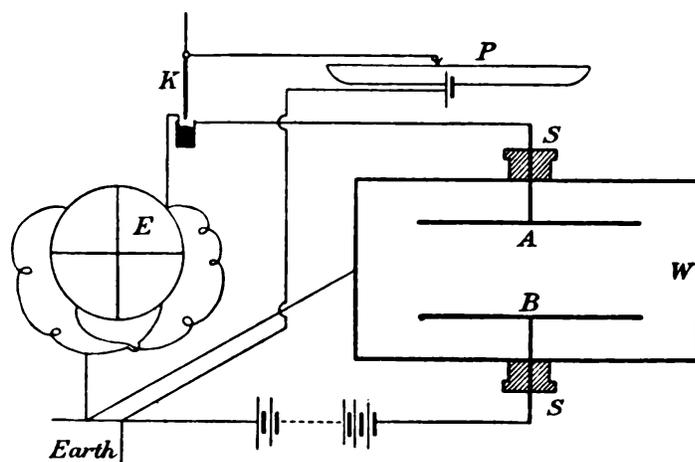
Fig. 6

8. **The ionization chamber.** The actual form of the vessel used for containing, and applying a field to, the gas varies very much with the nature of the effect to be observed. A suitable form for investigating the variation of current with potential, and for many other experiments in which the field needs to be definite, is shewn in Fig. 6.

The gas under investigation is contained in a metal box which is connected to earth, thus serving to shield the electrodes A and B from any stray electrostatic field. For a similar reason

the wire leading from the insulated electrode A to the electro-meter should also be surrounded by an earthed metal tube (not shewn in the diagram). The electrodes are placed parallel to each other a few centimetres apart; A is connected to one pair of quadrants of an electrometer, or to the leaf of a tilted electroscope, and B is raised to any required potential by means of a high tension battery. The system A can be placed at zero potential by means of a key K, which can be earth-connected. When the key K is raised the system A is completely insulated. If K is connected to a potentiometer, instead of directly to earth, the system A with its attached quadrants can be raised to a suitable known potential, and thus the electrometer can be calibrated.

The ionizing agent may be enclosed in the box, but it is generally more convenient to have it outside, in which case a window W of some substance transparent to the ionizing rays, and generally consisting of a very thin sheet of aluminium foil, must be made in the side of the box. The electrodes are insulated from the box by insulating stoppers S, S. The insulation of A is very important, and should be of amber, sulphur, or quartz. The box and its electrodes forms what is known as an *ionization chamber*.

Suppose B is now raised to some constant potential, say, 200 volts positive, while A is earthed by the key K, and the gas exposed to the action of the ionizing agent. The ions in the gas begin to move under the action of the field between the plates, the positive towards A, the negative towards B. As long as the wire K remains in the mercury cup, the potential of A remains zero. As soon as it is withdrawn A begins to charge up positively, and the needle of the electrometer begins to move. Let t be the time taken for the needle to reach the deflection corresponding to a potential V. Then if C is the capacity of A and its connected quadrants, etc., the average current through the gas is given by

$$i = C \cdot \frac{V}{t}.$$

The actual potential corresponding to a given deflection can easily be found by lowering the key K again into the mercury

cup, and sliding the end of the wire connected to K along the potentiometer wire until the deflection reaches the given value. The corresponding potential can then be read off on the potentiometer. For very accurate work, particularly with electroscopes, it is generally desirable to repeat this calibration after every reading.

9. **Variation of the current with the potential across the gas.** Suppose now the potential of B is gradually increased from some small initial value. For simplicity we will suppose that the maximum voltage acquired by A in charging up is
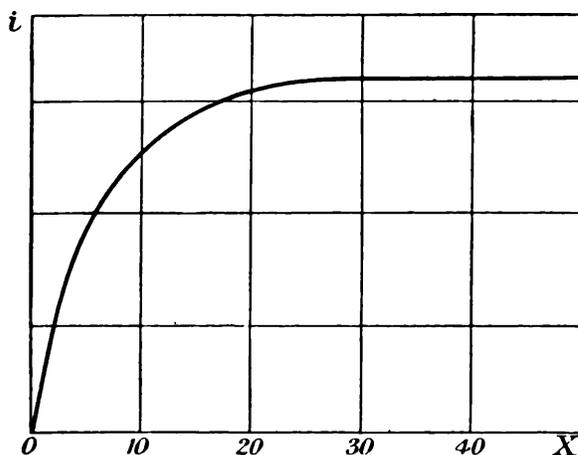
Fig. 7

not allowed to rise sufficiently to affect materially the potential difference between the plates. We can then study the magnitude of the current through the ionized gas for different potential differences between the plates. In the case of a metallic conductor or of an electrolyte with non-polarizable electrodes, the relation is expressed by Ohm's law, that is, the current is simply proportional to the potential difference. The relation for a gas is, however, more complex, and is represented by a curve such as that of Fig. 7 which is plotted from an actual set of readings.

For very small voltages, say, less than one volt, the current is approximately proportional to the applied potential difference; that is at this stage the gas obeys Ohm's law, though not with

the same degree of accuracy as a metallic conductor. As, however, the potential of B is raised, a stage is reached when the current falls appreciably below the value which would be given by Ohm's law.

If the potential is increased still further a point is reached at which further increase in the potential of B produces no further increase in the current through the gas. After this point the current is independent of the voltage. This maximum current is called the *saturation current* through the gas, and the potential necessary to produce this current is known as the *saturation voltage*. The actual value of the saturation voltage depends upon the distance apart of the electrodes, the pressure, and the intensity of the ionization in the gas. Except in cases of very intense ionization, a field of from 20 to 30 volts per cm. between the electrodes is sufficient to produce the saturation current.

10. Variation of the saturation current with the distance between the electrodes, and the pressure of the gas. If one of the electrodes is made movable the variation of the saturation current with the distance apart of the electrodes can be studied. In the case of a metallic conductor the current for a given potential difference is inversely proportional to the length of the conductor, and a similar result holds for electrolytes. For gases however, if we arrange that the effect of the ionizing agent is the same in all parts of the gas, the saturation current through the gas is directly proportional to the distance apart of the electrodes. It can also be shewn, by using electrodes of different sizes, to be directly proportional to the area of the electrodes. If the pressure of the gas is varied it is found that the saturation current is directly proportional to the pressure of the gas. In other words the saturation current through a gas is directly proportional to the mass of gas between the electrodes.

The effects when the current is not saturated are in general very complex, and need not concern us here.

11. Theory of conduction through gases. Let us assume that the ionizing agent is producing ions uniformly throughout the gas and at a constant rate, so that q pairs of ions are formed

per c.c. per second in the gas. These ions are charged positively and negatively, and since the gas as a whole is uncharged, the number of positive and negative systems must be equal, supposing that each carries a charge of the same magnitude e.

In general ions may be lost by the gas in three ways. In the first place since the ions are oppositely charged they attract each other according to the ordinary laws of electrostatics. On collision their charges may neutralise each other, and the ions return to their ordinary uncharged state. The chances of a given positively charged ion meeting a negative ion in a given time is obviously proportional to the number, n_2, of negative ions present per c.c., while the number of positive ions finding partners in a given time is proportional to the number, n_1, of positive ions actually present per c.c. of the gas. The rate at which combination goes on is thus proportional to $n_1 n_2$. It can, therefore, be written $a n_1 n_2$ where a is a constant under given conditions and is known as the *coefficient of recombination*. If, as is usually the case, the numbers of positive and negative ions are equal, this reduces to $a n^2$.

Ions are also withdrawn by the action of the electric field, and by diffusion to the electrodes or to the walls of the chamber. In general the effect of diffusion is small and may be neglected. In special circumstances it may become appreciable, and in these cases it can be measured.

Let us assume for a moment that there is no electric field across the gas and that the diffusion is negligible. Then the rate of increase in the number of ions per unit volume of the gas is equal to the number formed per second by the action of the ionizing agent less the number lost by recombination. Hence

$$\frac{dn}{dt} = q - a n^2 .$$

The ionization reaches a steady state when dn/dt is equal to zero or

$$q = a n^2. \qquad \ldots \ldots \ldots \quad (2)$$

If the ionizing agent is then withdrawn q becomes zero, and the ionization in the gas decreases according to the equation

$$\frac{dn}{dt} = - a n^2 ,$$

or $$\frac{1}{n_0} - \frac{1}{n} = -\alpha t, \quad \cdots \cdots \cdots \quad (3)$$

where n_0 is the value of the ionization at the moment when the agent was removed, and t the time which has elapsed.

12. Motion of the ions under a uniform electric field.

If X is the strength of the electric field across the gas the force acting on any ion is equal to Xe. If the ion were perfectly free to move this would produce a constant acceleration of Xe/m where m is the mass of the ion. The ion is, however, moving through other uncharged gas molecules; its path therefore is made up of a series of short runs, each terminating in a collision in which all the accumulated energy of the ion is lost. Under these circumstances it is easy to shew that the ion will move not with a uniform acceleration but with a constant velocity which is proportional to the field applied.

For let λ be the mean free path of the ion in the gas, and τ the time taken by the ion to describe its mean free path under the action of the field. We may suppose that the whole of the velocity added by the field is removed at each collision and that the ion thus starts its course again with zero velocity. Between two collisions the ion moves freely under the action of the field. If X is the intensity of the field and e the charge on the ion, the mechanical force is Xe and the velocity v' of the ion on reaching the end of its path is therefore given by $Xe\tau = mv'$,

or $$v' = \frac{Xe\tau}{m}.$$

The average velocity with which the ion describes its path is thus $\frac{1}{2}v'$, and if we assume that the time occupied by a collision is small compared with τ, this is also the mean velocity of the ion through the gas. The velocity of the ion is therefore given by

$$\frac{1}{2}\frac{Xe\tau}{m}, \quad \cdots \cdots \cdots \quad (4)$$

and is thus directly proportional to the applied field X, since e, m and τ are constants under given conditions.

Thus if u and v are the actual velocities of the positive and negative ions respectively in a field of strength X, we have

$$u = k_1 X, \ v = k_2 X,$$

where k_1 and k_2 will be constants for a given gas under given conditions of temperature and pressure. They are known as the *mobilities of the ions*.

13. **Theoretical relation between current and potential.** Let us now consider the current through the gas due to an applied potential difference V between the electrodes. Considering any plane in the gas normal to the direction of the field, then in one second all the positive ions which are situated at a distance of less than u cm. from it will be driven across the plane, while similarly all the negative ions distant less than v cm. from the plane will be driven across it in the opposite direction. The total transference of electricity across the plane in unit time will be the sum of the charges carried by the two sets of ions. If the magnitude of the charge e carried by an ion is the same for all ions the total transference is thus $ne \, (u + v)$ units per sq. cm. per sec. or if A is the area of the plane the total current across it will be

$$i = Ane \, (u + v)$$
$$= Ane \, (k_1 + k_2) \, X. \quad . \quad . \quad . \quad . \quad (5)$$

Now the passage of a current implies the withdrawal of a certain number of ions from the gas to the electrodes. The greater the current, the faster the ions will be removed, and hence the fewer will be the number of carriers left in the gas. Hence it is obvious that n, the number of ions present in unit volume of the gas, is a function of the current i. The problem is thus far from simple. We may however distinguish two limiting cases.

(1) *The current is so small that the number of ions withdrawn is negligible* compared with the number present per c.c. In this case the loss of ions is due solely to recombination and n is a constant, its value being given by (2).

If the electrodes are arranged so that the field is uniform, as for example in the case of two parallel plates, the field is equal

2-2

to V/d, where V is the potential difference between the electrodes and d their distance apart. In this case equation (5) becomes

$$i = Ane \, (k_1 + k_2) \, X = Ane \, (k_1 + k_2) \, \frac{V}{d}, \quad . \quad . \quad (6)$$

where A is the area of either electrode. This equation is of the same form as that for conduction through an electrolyte, if n is a constant. Under these circumstances the current through the gas obeys Ohm's law, and this case corresponds to the first straight portion of our experimental curve.

(2) *The field is so large that the ions are conveyed to the electrodes without appreciable recombination.*

If the field is large the velocities of the ions become so great that the number recombining in the small time taken to reach the electrodes becomes negligible. In this case it is obvious that all the ions formed in the gas by the ionizing agent will be conveyed to one or other of the electrodes. If B is the volume of the gas between the electrodes the number of ions formed per second is Bq and the total charge conveyed to either electrode in one second is therefore Bqe. This is the maximum current through the gas, and, provided that the voltage is sufficient to produce saturation, is obviously independent of the difference of potential between the plates. This case therefore corresponds to the saturation current through the gas. It will be seen that the saturation current should be directly proportional to the volume of the gas, a result which we have already found experimentally.

Since the time taken for the ions to reach the electrodes is proportional to the distance which they have to travel, that is, to the distance apart of the electrodes, while the field for a given potential difference is inversely proportional to the distance between the electrodes, it follows that the potential necessary to produce the saturation current through the gas is directly proportional to the square of the distance apart of the electrodes. It has also been shewn to be proportional to the square root of the intensity of ionization.

Since the saturation current is found to be proportional to the pressure, it follows that q, the rate of ionization for a given

strength of the ionizing radiation, is directly proportional to the pressure; that is to say, the number of ions formed is proportional to the number of molecules present.

(3) *The general case* has been considered by Sir J. J. Thomson, who found that on certain assumptions the current through the gas could be represented by an expression of the form

$$V = Ai + Bi^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where A and B are complicated constants and V is the P.D. across the gas. This expression is found to express the intermediate portion of the experimental curve (Fig. 7) reasonably well. This part of the curve is of no practical importance except in the case of the currents through flames where the ionization is so intense that the maximum fields which we can apply are insufficient to produce saturation.

CHAPTER III

THE PROPERTIES OF THE GASEOUS IONS

14. Measurement of ionic mobilities. The mobility of an ion is defined as its velocity in cm. per sec. under the action of an electric field of one volt per cm. Ionic mobilities may be measured in various ways, the most direct of which is one due to Rutherford.

Rutherford's method (1). Two large metal plates were placed parallel to each other and 16 cm. apart on insulating blocks.
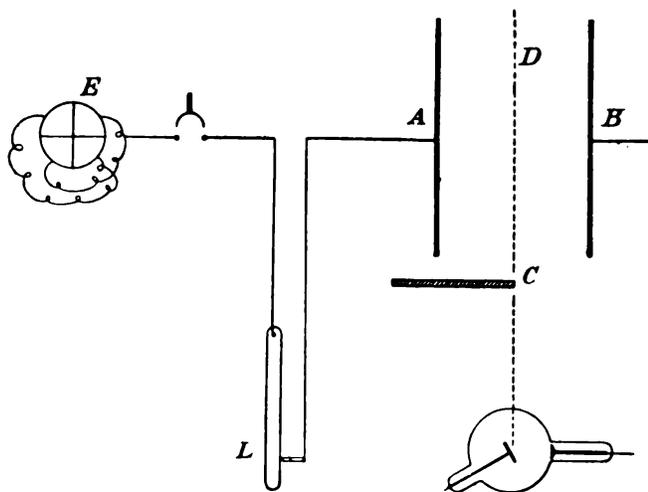
Fig. 8

One of these, B, was connected to a battery so that any suitable field could be applied across the gas, the other, A, was connected through an insulated lever to an electrometer E.

A heavy pendulum, not shewn in the diagram (Fig. 8), was arranged so that at one point of its swing it made the circuit of the primary of an induction coil the secondary of which was connected to the X-ray tube used for ionizing the gas. Rays

were therefore generated and the gas became ionized. After
a given interval (which could be calculated from the time of
swing of the pendulum and the distance apart of the switches)
the pendulum swung against the lever L and so disconnected
the plate A from the electrometer.

Owing to the screen C only the portion of the gas to the right
of the plane CD is ionized. Hence to reach A the ions must
travel through a distance equal at least to that between A and
the plane CD. Hence unless the time taken by the ions to
travel this distance is less than the time which elapses between
the switching on of the rays, and the breaking of the electro-
meter circuit at L, the electrometer will shew no charge. If
the time is gradually increased a point is reached when the
electrometer begins to shew a deflection, that is when the ions
from CD are just able to reach the plate A before the connection
at L is severed. This critical time is evidently the time taken
for the ions to travel under the action of the field from CD to
A. In Rutherford's experiment the critical time was 0·36 sec.,
when the potential of the plate B was 220 volts and the distance
to be travelled was 8 cm. The velocity of the ion was therefore
8/0·36 cm. per sec., with a potential gradient of 220/16 volts
per cm. The mobility of the ions was therefore $\dfrac{8}{0·36} \div \dfrac{220}{16}$
or about 1·6 cm. per sec. per volt per cm.

The method just described, though admirably direct, is not
susceptible of great accuracy. A more promising procedure, also
first used by Rutherford, is to employ an alternating field. Let
AB, CD, be a pair of parallel plates, the plate AB being connected
to an electrometer, and CD to a source of alternating potential.
We will suppose that the ionization is confined to a very
thin layer of the gas at the surface CD, and that the ions
are all of the same sign. This can be effected in practice by
making the plate CD of some metal such as zinc and illuminating
it with ultraviolet light (Chap. IX).

Since the potential applied to the plate CD is alternating, the
ions will, during one half of the complete cycle, be acted on by
an electric field urging them towards the plate AB. If the dis-
tance they can travel during this half cycle is greater than the

distance d between the plates some of them will reach the electrode AB and the electrometer will shew a charge which is added to at each alternate half cycle. If, however, the ions fail to reach AB before the field reverses they will be dragged back to CD by the reverse field which exists during the following half cycle, and thus the electrometer will receive no charge.

If the applied potential is represented by $a \sin pt$, the field is $\frac{a}{d} \sin pt$ and the velocity of the ions $= \frac{dx}{dt} = \frac{ka}{d} \sin pt$ where k is the mobility, and x is the distance of the ion from the plane CD. Since $x = 0$ when $t = 0$, the solution of this equation is

$$x = \frac{ka}{pd}(1 - \cos pt).$$
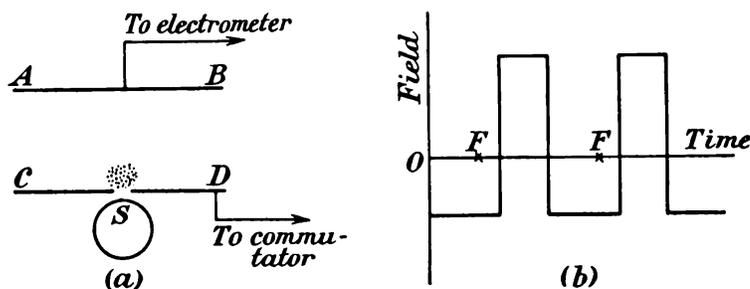
Fig. 9

Thus the greatest distance than an ion can travel from CD is $2ka/pd$. If the distance between the plates is gradually reduced until the electrometer begins to collect a charge we thus have for this critical distance d_0

$$d_0 = \frac{2ka}{pd_0} \quad \text{or} \quad k = \frac{pd_0^2}{2a}.$$

This method, though accurate, is somewhat limited in its application. An elegant and accurate modification of the method has been devised by Tyndall and Grindley[2]. Their alternating field was of the type shown in Fig. 9 (*b*), that is to say the ions under experiment are driven towards the collecting electrode by a field which is constant in magnitude while it lasts, but which, after acting for a suitable short interval is instantaneously reversed. The reverse field is somewhat less intense than the direct field, but acts for a sufficiently long time to ensure that all the ions which do not reach the collecting electrode are cleared

out from the space between the plates. An alternating field of this type can be produced conveniently by a rotating commutator which connects the plate CD of the apparatus first to the negative, and then to the positive pole of a high tension battery which is earthed at a point somewhat nearer one end than the other.

The ionization is produced by a speck of polonium S which is mounted on the shaft driving the commutator. Once in each revolution the polonium is brought directly under a small hole in the plate CD, and a flash of α particles from the polonium, passing through the hole, produces intense ionization in the gas which, owing to the very small penetrating power of these particles is confined to the immediate neighbourhood of the hole. This flash is timed to occur at a point F in the cycle, that is just before the reverse field gives place to the direct field. Since the polonium is carried on the commutator shaft it is evident that the flash will occur at the same point in each cycle.

Let T be the time of one complete revolution of the shaft. The interval between the ionizing flash and the reversal of the field, and the time for which the direct field is applied are both proportional to T, and may thus be represented by pT and qT respectively. Let d be the distance between the plates, and h the small depth of the ionized layer.

The ionized layer contains ions of both signs. If we wish to measure the mobility of the negative ions, say, the direct field is selected so as to drive the negative ions to the plate AB. The reverse will thus attract them to CD, and if the interval between the flash and the reversal of the field is sufficiently long, that is to say if the shaft is revolving slowly, all the negative ions will be absorbed by the plate CD, before the field changes, and thus no negative ions will remain in the gas to be driven to the plate AB. Thus the electrometer will collect no negative charge (it would actually collect a positive charge if the interval was so long that the positive ions could pass from the ionized layer to A). If X_2 is the reverse field the time taken by the ions to travel a distance h is h/kX_2. If pT is greater than this no negative charge can reach the electrometer. For more rapid rotations the number of negative ions left in the gas will increase as the interval during which they are attracted to CD becomes shorter.

On the other hand, the minimum time necessary for a negative ion to pass from CD to AB is d/kX_1, where X_1 is the field driving the ions to A. If qT is less than this the negative ions will be unable to reach A before the field is again reversed, and the electrometer will again shew no charge. Since the negative charge collected has been steadily increasing with increasing speed of the shaft up to this point, it is clear that the maximum charge will be collected when the ions left in the gas can just pass from CD to AB between one reversal and the next; that is when $qT = d/kX_1$. Thus a determination of the time of revolution of the shaft at which the maximum charge is collected will enable us to determine the mobility of the ions.
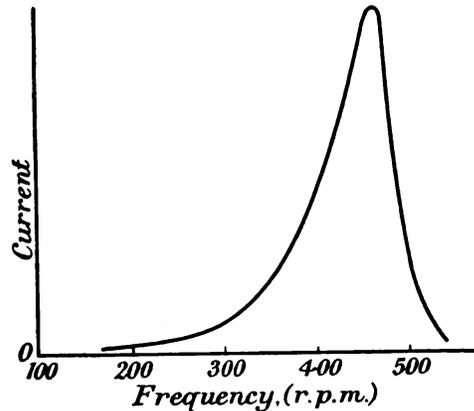
Fig. 10

An experimental curve shewing how the charge collected varies with the speed of the shaft $(1/T)$ is shewn in Fig. 10. It will be seen that it corresponds closely with the theoretical predictions given above. That the curves do not drop immediately to zero after passing the maximum is due mainly to the fact that the ions occupy a small but finite volume above CD, and hence have not all precisely the same distance to travel in order to reach AB. Positive ions can be measured in exactly the same way, merely by reversing the signs of the direct and inverse fields.

The mobility of an ion depends on the nature of the gas, and on the sign of the charge. In general the negative ion has a greater mobility than the positive. The mobilities of both kinds of ions are reduced by the presence of water vapour in the gas. A few representative values are given in Table I. They refer to

gases at normal temperature and pressure, and at the ordinary degree of purity and dryness. As we shall see later some of the values are very considerably altered when the measurements are made in gases of exceptional purity.

TABLE I

Ionic Mobilities in cm./sec. per volt/cm.

SUBSTANCE	$k_1(+)$	$k_2(-)$
Hydrogen	5·9	8·6
Nitrogen	1·27	1·84
Oxygen	1·31	1·80
Argon	1·37	1·70
Carbon monoxide	1·10	1·14
Carbon dioxide	0·84	0·98
Sulphur dioxide	0·41	0·41
Methyl iodide	0·21	0·22

15. Approximate calculation of the mobility of an ion. We have seen, (4), p. 18, that assuming that the ion retains none of the velocity produced in it by the field after collision with another atom, that its velocity through the gas is given by $v = \dfrac{1}{2}\dfrac{Xe}{m}\tau$ where τ is the time which elapses between two collisions. Now since the ion forms part of the gas it will participate in the thermal agitations of the gas molecules, and the kinetic theory shews that the kinetic energy of the ions for this motion must be equal to that of the molecules of the gas in which it is formed. This velocity will, therefore, vary as the square root of the mass of the ion. At ordinary temperatures these thermal velocities are very large. In the case of air for example the mean molecular speed at atmospheric pressure and 0° C. is 48,500 cm. per second. Since these velocities are distributed equally in all directions the number of ions carried by the thermal agitations across any plane in the gas in one direction will be equal to the number carried across it in the opposite direction, and hence the total transference of electric charge across the plane will be zero. Thus the thermal agitation causes no transference of electricity, and hence no current in the gas. We may, therefore, neglect it

in considering the transference of electricity through the gas. On the other hand it will be the controlling factor in determining the number of collisions made by the ion. If λ is the mean free path of the ion in the gas, and V_1 the velocity of the ion, then τ the time occupied in describing the mean free path will be equal to λ/V_1. But since the velocity of the thermal agitation is very large compared with the velocity added by the field (which in the case of a field as great as 100 volts per cm. would only amount to about 160 cm. per sec.), the value of V_1 will be practically equal to V the velocity of the thermal agitation. Hence we have, on substituting for τ in (4),

$$v = \frac{1}{2}\frac{e}{m}\frac{\lambda}{V}X \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or the mobility of the ion is equal to $\frac{1}{2}\frac{e}{m}\frac{\lambda}{V}$.

This formula should enable us to calculate the mobility of an ion if the size of the ions is known, or conversely to deduce the size of the ion from its mobility. If we assume that the ion formed in, say, oxygen is simply a charged molecule of the gas, then V is the ordinary velocity of the oxygen molecule, or 461 metres per second: the value of e/m for a hydrogen atom, as we shall see later (§ 20), is 10^4 e.m.u. per gm., and for the oxygen molecule therefore, assuming that all ions carry the same charge, it is $\frac{1}{32} \times 10^4$. The mean free path λ, of an uncharged molecule of oxygen at normal temperature and pressure is 10^{-5} cm.. Substituting these values we have the mobility in oxygen equal to $3\cdot2 \times 10^{-8}$ cm. per sec. per absolute e.m.u. of field or $3\cdot2$ cm. per sec. per volt per cm. since a volt is 10^8 absolute e.m.u. of potential. This is rather more than twice the measured mobility of the positive ion in oxygen.

16. Effect of pressure on the mobility of the ions. The mobility of the ion is represented by $\frac{1}{2}\frac{e}{m}\frac{\lambda}{V}$. But the mean free path λ is, by the kinetic theory of gases, inversely proportional to the pressure p of the gas. Hence if the nature of the ion does not change the mobility k of the ion should be inversely proportional to the pressure of the gas, or the product pk should be constant.

The experimental results obtained are represented by the curves in Fig. 11, where the mobility is plotted against the reciprocal of the corresponding pressure. The lower curve, which is straight, refers to positive ions, and the upper one to the negative. It will be seen that the product pk_1 for the positive ions remains practically independent of the pressure down to the lowest pressures used. With the negative ions however at pressures less than about one-tenth of an atmosphere the product pk_2 increases rapidly as the pressure is reduced, thus indicating that the mobility of the negative ion is increasing more rapidly than would be due merely to the alteration of the
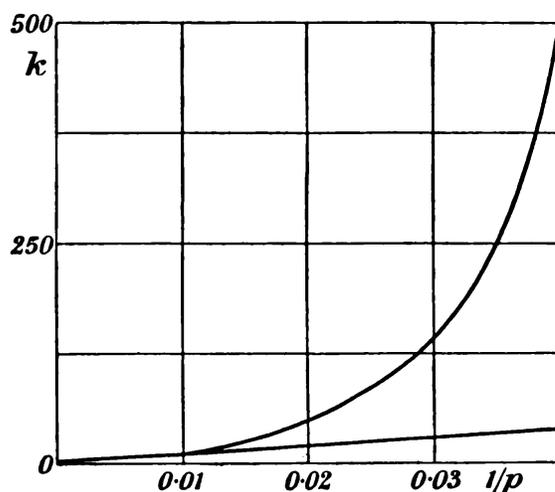
Fig. 11

free path with pressure. In other words the negative ion is becoming smaller as the pressure is reduced. If the ion at atmospheric pressure consists of a single molecule it is clear that at low pressures the negative carriers must be smaller than the molecule.

We have already seen (§ 1) that the atoms of all substances contain negatively charged particles, or electrons as they are usually called, of a mass equal to about 1/1839 of that of a hydrogen atom, and that under certain circumstances these electrons may be ejected from the atom and appear in a free state. We must therefore regard the mechanism of gaseous ionization in the following way. The action of the ionizing agent brings about the expulsion of an electron from the molecule

of the gas, leaving the latter with an excess of positive electri-
fication. This positively charged molecule forms the positive
ion. The negative electron is now, for a moment, in the free
state, but being strongly charged it readily attaches itself to
one of the neutral molecules by which it is surrounded, thus
forming a negative ion of the same size as the positive.

It may be noted that whereas the positive ion is formed
directly from a molecule, the negative carrier begins life in
the form of an electron. Since the electron is very small its
velocity under the action of an electric field will be very much
larger in the free state than when attached to a molecule. Thus
if the negative carriers pass any appreciable fraction of their
time in the free state the velocity with which negative electricity
passes across the gas will be materially increased, and thus
the mobility of the negative ions which measures the average
rate at which they are moving will be considerably increased.
In many gases, such as air for example, the effect is quite
appreciable even at ordinary pressures as shewn by the fact
that the measured mobility of the negative ion is greater than
that of the positive. As the pressure is reduced the time spent
by the charge in the free state is considerably increased
and the mobility becomes rapidly greater. Increase of
temperature causes a similar effect on the mobility of the
negative ion.

More recently Loeb[3] has found extremely high mobilities for
the negative ion, even at atmospheric pressure, for electro-
positive gases such as nitrogen, hydrogen, and helium when the
gases are purified with the utmost care. Thus mobilities up to
30,500 cm./sec. per volt/cm. have been recorded in very carefully
purified nitrogen, 22,000 in helium, and 7800 in hydrogen. In
such cases the negative ion must spend most of its life in the
electronic state, and it seems very probable that molecules of
these gases are incapable of attaching an electron to their
structure. These abnormal values at once drop to those given
in Table I if the gas is allowed to be contaminated by a minute
trace of oxygen, chlorine, or other more electronegative gas. Thus
the carriers of negative electricity in ordinary nitrogen whose
mobility is recorded in Table I are almost certainly not

molecules of nitrogen itself, but of some impurity, probably oxygen.

Even for electronegative molecules, however, the attachment of an electron is not instantaneous. Loeb has calculated that in chlorine, or oxygen, an electron will on an average make some 3000 collisions before becoming permanently attached to a molecule. It is this difficulty of attachment that gives to the negative ion its apparent greater mobility.

17. The nature of gaseous ions. We have seen that the measured mobility of an ion is appreciably smaller than that calculated on the approximate theory given in § 15. To account for this difference we may remember, in the first place, that since the ion bears a charge it will be attracted by neighbouring uncharged molecules, and will thus make collisions which an uncharged molecule would escape. Its mean free path will thus be less than that of an uncharged molecule, and this will result in a decrease in mobility. Unfortunately it does not seem possible to estimate the magnitude of this effect with any exactness.

A second possibility, which is clearly indicated by Loeb's experiments on nitrogen, is that the ion whose mobility is measured may be a molecule, not of the gas itself, but of some impurity of higher molecular weight. The number of ions present in a gas, even when the ionization is intense, is a very minute fraction of the number of molecules, of the order perhaps of one ion to 10^{10} uncharged molecules. The amount of impurity necessary to carry the charges would thus be quite imperceptible to any ordinary test. A further possibility is that the actual ion may be surrounded by a loose cluster of uncharged molecules which are attracted to it by the charge which it carries. These possibilities are not mutually exclusive.

Some information on the problem may be gained from experiments in which the mobilities of ions formed in one gas are measured while passing through gas of a different kind. The mobility of an ion of mass m moving through a gas consisting of molecules of mass M should be proportional to its coefficient of diffusion in the second gas, that is proportional to $\left(\dfrac{1}{m} + \dfrac{1}{M}\right)^{\frac{1}{2}}$.

Tyndall[4] has recently tested this point by introducing positive ions of the various alkali metals into exceptionally pure nitrogen, and exceptionally pure helium. The mobilities of the various metallic ions measured in this way are found to be in exact agreement with the theoretical relation if the ions are assumed to be single atoms of the metals concerned. On the other hand if a minute trace of hydrogen is present in the nitrogen and sodium ions are introduced into the gas, not only do we get a mobility corresponding to that of sodium as measured in the pure gas, but also smaller mobilities corresponding to the value we should expect from a sodium atom loaded with one or more molecules of ammonia. Clustering is, therefore, a real possibility, and no doubt the reduced mobilities of ions in moist gases is due to a clustering of molecules of water vapour round the actual ion.

Owing to the form of the relation we have just been considering an increase in the mass of an ion does not produce very much change in its mobility. Thus the ratio of the mobility of an ion of infinite mass to that of an ion consisting of a single molecule of the gas through which it is moving would be only $1/\sqrt{2}$. It is probably significant that Erikson has found that the mobilities of ions measured within a fraction of a second of their production have a mobility which is almost exactly $\sqrt{2}$, the value obtained if they are allowed to age by remaining in the gas for a few seconds before their mobility is measured. The interval seems to be used either in handing over the charge to some molecule of high molecular weight, or in building up a cluster of molecules round the original ion.

We shall probably not be far wrong if we suppose that in the case of an ordinary gas the ion is sometimes a molecule of the gas, sometimes a cluster of varying numbers of molecules, and that sometimes its actual nature changes as the charge is transferred to a molecule of some heavy impurity. The actual measured mobility is only an average taken over all these changes. It is only when very special precautions are taken, as in Tyndall's experiments, that its nature remains constant and definite.

18.   Measurement of the coefficient of recombination. The coefficient of recombination of the ions can be measured directly by a method due to Rutherford. A steady stream of gas is passed down a long tube (Fig. 12) at the entrance to which is placed a layer of uranium oxide. This supplies a constant source of ionizing rays so that the gas is all ionized to the same extent. At various points along the tube are placed electrodes which can be connected to an electrometer. These electrodes may conveniently take the form of thin rods of equal length parallel to the axis of the tube, while the tube itself, raised to a sufficiently high potential to produce the saturation current through the gas, forms the other electrode.
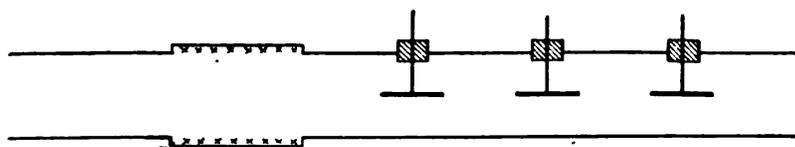
Fig. 12

The saturation current is measured successively at each of the electrodes. Since the electrodes are all equal and similar the saturation currents will obviously be proportional to the number of ions present in the gas per unit volume, at the given electrode. If the distance apart of the electrodes is known, and the rate of flow of the gas along the tube, the time taken for the gas to flow from one electrode to the next can be calculated, and thus the number of ions left in the gas after various intervals of time is obtained. In this way Rutherford was able to verify experimentally the equation (3) for the rate of decay of ionization in the gas. In one of his experiments, for example, he found that the ionization amounted to as much as 10 per cent. of its maximum value as long as four seconds after removal from the ionizing rays, while in another experiment where the initial ionization was less intense the gas even after 16 seconds retained 10 per cent. of its initial conductivity.

This method though simple, and direct, is not capable of any great accuracy, and has been replaced by one due to

Langevin(5), which however requires a knowledge of the mobilities of the ions under the conditions of the experiment. The gas to be experimented upon is contained between two parallel plates, A and B (Fig. 13), and a layer CD of it parallel to the plates is ionized by a single powerful flash of X-rays. An electric field is applied between the plates by connecting one of them to a suitable number of cells, the other being connected to an electrometer in the usual way.
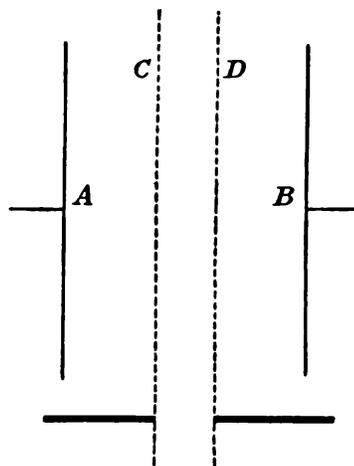
The ions begin to move under the field towards the opposite plates.

Fig. 13

All recombination must occur within the ionized layer. As soon as the ion leaves this layer it is surrounded only by ions of its own sign, and therefore cannot recombine. It is obvious that the faster we can pull the ions out of the layer the smaller the recombination will be, and the larger the charge we shall collect on the insulated plate, A.

Suppose that after an interval t there are in the ionized layer n positive and n negative ions per unit volume. The positive ions are moving with a velocity $k_1 X$ and the negative with a velocity $k_2 X$ in the opposite direction. The walls of the slab are therefore approaching each other with a velocity $(k_1 + k_2)X$. Thus in a small time dt the thickness of the layer is reduced by $(k_1 + k_2) X dt$ and the number of ions of each kind separated is

$$n (k_1 + k_2) X dt.$$

Since the ions so separated are no longer liable to be lost by recombination, they will eventually reach the corresponding electrode giving to it a charge

$$dQ = en (k_1 + k_2) X dt.$$

But by equation (3) $n = \dfrac{n_0}{1 + n_0 \alpha t}$,

where n_0 is the number of ions of each kind originally present in unit volume;

$$\therefore \quad dQ = \frac{(k_1 + k_2) \, n_0 e \, X dt}{1 + n_0 \alpha t} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

This process continues until the walls of the slab meet. If the thickness of the slab is d this obviously occurs when

$$t_1 = \frac{d}{(k_1 + k_2)\,X} \quad\quad\quad (14)$$

After this no recombination occurs. The total charge Q is therefore obtained by integrating between the limits $t = 0$ and $t = t_1$.

Thus the total charge given to the plate

$$Q = (k_1 + k_2)\,Xe \int_0^{t_1} \frac{n_0}{1 + \alpha n_0 t}\,dt$$

$$= \frac{(k_1 + k_2)\,Xe}{\alpha}\Big[\log(1 + n_0 \alpha t)\Big]_{t=0}^{t=t_1}$$

$$= \frac{(k_1 + k_2)\,Xe}{\alpha}\log\Big(1 + \frac{n_0 d\alpha}{(k_1 + k_2)\,X}\Big). \quad (15)$$

But $n_0 d$ is the total number of ions originally present and $n_0 de$ is thus the maximum charge Q_0 obtainable when the saturation voltage is applied between the plates. This can easily be determined.

Thus
$$Q = (k_1 + k_2)\,\frac{Xe}{\alpha}\log\Big(1 + \frac{Q_0 \alpha}{(k_1 + k_2)\,Xe}\Big)$$

$$= r\log\Big(1 + \frac{Q_0}{r}\Big), \quad\quad\quad (16)$$

where
$$r = \frac{(k_1 + k_2)\,Xe}{\alpha}.$$

Hence α can be calculated, if k_1, k_2 and e are all known. This method gives very accurate results. The determination of e, the charge carried by an ion, is described in the next chapter.

The values found for α vary very little in different gases. Air, oxygen, and carbon dioxide all give values of α of about 1.6×10^{-6} at atmospheric pressure, and temperature. The value for hydrogen is 1.4×10^{-6}. The coefficient decreases as the pressure is reduced, and has only one-quarter of its normal value at a pressure of $\frac{1}{3}$ atmosphere.

Assuming that every collision between a positive and a negative ion produces recombination, the number of collisions per second between n positive and n negative ions of oxygen is $1.6 \times 10^{-6}\,n^2$.

3-2

The number of collisions taking place per second in $2n$ uncharged molecules of oxygen is known, from the kinetic theory of gases, to be $4 \times 10^{-10} n^2$. The number of collisions producing recombinations between the ions is thus about 4000 times the total number of collisions which would occur in the same time between uncharged molecules of the gas. This must be due to the strong electrical attraction between the oppositely charged ions, which draws them together when otherwise they would never have met.

19. The diffusion of ions. If the ions are not uniformly distributed throughout the gas they will tend to become so by the process of diffusion, just as a mixture of two gases becomes uniform. In fact, since we can identify the ions by their charges, we can regard them as a special kind of gas mixed with the main mass of the gas which is uncharged, and the ordinary laws of diffusion can be applied to them. If the gas is contained in a metal box the ions which come in contact with the walls will give up their charges, and cease to be ions. The concentration of the ions will thus be zero at the walls and increase as we pass out into the main volume of the gas. We shall thus get a pressure gradient set up for the ions, and there will be a steady diffusion drift of the ions towards the walls. Ions can thus be lost by diffusion. In an ordinary ionization chamber, however, the loss by diffusion is quite negligible compared with that due to recombination.

The problem is mathematically equivalent to that of the diffusion of water vapour to a surface of strong sulphuric acid, and the treatment follows similar lines. The coefficient of diffusion of the ions in different gases was measured by Townsend, by drawing a measured stream of ionized gas through a bundle of narrow tubes and measuring the fraction of the total number originally present in the gas, which survived the process. The actual calculations required are lengthy and tedious, and need not concern us here. The coefficient of diffusion of the positive ions in air was 0·028, and that of the negative 0·043, as measured at atmospheric pressure. These coefficients are small compared with those for uncharged gases. The coefficient of diffusion of air through carbon dioxide, for example, is 0·134. Since diffusion

is mainly determined by the mean free path of the molecules this would indicate that the mean free path of the ions is considerably smaller than that of the uncharged molecule, a conclusion we have already drawn from the measured mobilities of the ions.

20. Determination of the total charge on one gram-molecule of ions. The interest of these diffusion measurements is mainly theoretical. Let n be the number of ions per c.c. at a point in the gas. The number per second crossing unit area of a plane at right angles to a given direction x in the gas is thus, by definition, $D.dn/dx$, where D is the coefficient of diffusion. We can thus regard the ions as drifting uniformly in the direction of x with a velocity $\frac{1}{n} . D \frac{dn}{dx}$. Regarding the ions as a separate kind of gas they will have a partial pressure p which is at any point proportional to n, and we may write their velocity in the form $\frac{1}{p} D . \frac{dp}{dx}$. But dp/dx is the force acting on unit volume of the ions owing to the pressure gradient. Assuming that the velocity is proportional to the force we see that the velocity of the ions under unit force is D/p.

Now let us suppose that an electric field of intensity X acts on the ions. The force on each ion is Xe, and the total force on all the ions in 1 c.c. of the gas is therefore nXe. Assuming that the resultant velocity u is proportional to the applied force per unit volume we have thus

$$u = \frac{D}{p} . Xen.$$

But $u = kX$, where k is the mobility of the ion. Thus

$$k = \frac{n}{p} . De.$$

But n/p is a constant, which is practically the same for all gases under the same conditions of pressure and temperature, and may be written n_0/π, where n_0 is the number of gas molecules in 1 c.c. of gas at the temperature of the experiment, and at standard atmospheric pressure π. Thus, finally,

$$\frac{k}{D} = \frac{n_0 e}{\pi}.$$

n_0e is the total charge on 1 c.c. of ions at normal atmospheric pressure, that is it is the total charge which would exist in one c.c. of gas if all the molecules were ionized. Taking the mobility of the positive ions in hydrogen as 5·3 cm./sec. per volt/cm., atmospheric pressure as 10^6 dynes per sq. cm. and the coefficient of diffusion of the ions in hydrogen at 0° C. and atmospheric pressure as 0·12 we have, converting the volts into absolute e.m.u.,

$$n_0e = \frac{5{\cdot}3 \times 10^{-8}}{0{\cdot}12} \times 10^6 \text{ e.m.u.} = 0{\cdot}44 \text{ e.m.u.}$$

This is the total charge in 1 c.c. of charged ions at normal temperature and pressure. If N is the number of molecules in a gram-molecule, an important constant which is known as Avogadro's number, then, since the volume of a gram-molecule of any substance when in the gaseous state is $2{\cdot}22 \times 10^4$ c.c. at normal temperature and pressure, the total charge on all the molecules in a gram-molecule, if they were all ionized, would be $0{\cdot}44 \times 2{\cdot}22 \times 10^4$, that is 9768 e.m.u. Townsend's mean value, for all his observations on different gases, was $9{\cdot}8 \times 10^3$ e.m.u.

It is instructive to compare this estimate for gaseous ions with that obtained from electrolysis experiments. The passage of 1 e.m.u. of electricity through acidulated water liberates $1{\cdot}04 \times 10^{-4}$ gm. of hydrogen, or in other words 1 gm. of hydrogen ions carries a charge of $1/1{\cdot}04 \times 10^{-4}$, or 9649 e.m.u. of charge. If we regard the hydrogen ions as the molecules of a gas of molecular weight unity, then 1 gm. constitutes a gram-molecule of the hydrogen ions. Thus, if E is the charge on a monovalent electrolytic ion, and N is Avogadro's number, the charge carried by 1 gram-molecule of electrolytic ions is given by $NE = 9649$ e.m.u. This, however, is within the limits of experimental error identical with Townsend's value for the gaseous ions. Hence, since N is a constant for all gases, the charge on a gaseous ion is identical with that on a monovalent ion in solution. This was by far the earliest and is still in many ways the most direct proof of this very important fact.

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CHAPTER IV

THE CHARGE ON AN ION

21. Condensation of water drops on ions. By applying a saturation voltage across a gas we can, as we have seen, sweep all the ions in the gas to one or other of the electrodes. The charge given to either electrode is then equal to the sum of the charges on all the ions of one sign present in the gas, that is, to ne where n is the total number of ions of either sign, and e the charge carried by each. To determine e it is necessary to find some method of counting the number of ions present in the gas.

A method of doing this was afforded by the discovery of C. T. R. Wilson that charged ions can serve as nuclei for the condensation of water vapour. It had long been known from the researches of Aitken that the water drops which form when a space becomes supersaturated with water vapour always collect about dust particles or similar nuclei present in the gas. If all nuclei are removed (either by filtration through cotton wool or better still by repeatedly forming clouds in the same closed space and allowing the drops so formed to settle, thus carrying the nuclei with them), a very considerable degree of supersaturation may exist in the gas without the separation of any drops. If, however, the pressure of the aqueous vapour in the gas exceeds about eight times its saturation pressure for the temperature of the experiment a fine drizzle sets in even in the absence of all nuclei.

Wilson shewed that if the gas was ionized deposition could take place in the absence of other nuclei, the ions themselves serving as nuclei about which the drops could form. It was found that deposition would take place on negative ions when the pressure of the aqueous vapour was four times the saturation value, and on the positive ions when it reached about six times that amount.

These effects are due to surface tension. It can be shewn that the vapour pressure over a convex surface of liquid is greater than that over a plane surface by $\dfrac{\sigma}{\rho - \sigma} \dfrac{2T}{r}$ where σ is the density of the vapour, ρ that of the liquid, T the surface tension, and r the radius of curvature of the surface. If r becomes indefinitely small as would be the case for a drop starting from zero dimensions this excess of pressure would be infinite, and the drop would immediately evaporate. The nuclei, by providing surfaces of finite radius of curvature on which to condense, enable the drops to commence at a finite size, and hence to grow to visible dimensions even with a comparatively small degree of supersaturation. The drizzle which sets in when the supersaturation is eight-fold is probably due to deposition round molecules of vapour or gas.

The effect of giving a charge to the drop can most easily be discussed from the considerations of potential energy. The potential energy of a drop due to its surface tension is equal to its area multiplied by the surface tension, that is to $4\pi r^2 T$, and becomes smaller as the radius is decreased. Hence surface tension will tend to reduce the size of the drop, that is, to assist evaporation, since any system tends to reduce its potential energy to a minimum. On the other hand the potential energy of a drop due to a charge e upon it is $\dfrac{1}{2}\dfrac{e^2}{r}$. This increases as r becomes smaller, and hence the effect of the charge is to tend to increase the size of the drop. The electric charge therefore acts in the opposite sense to the surface tension, and may be regarded as producing a diminution in it. Thus a charged drop will grow under conditions under which an uncharged drop of the same radius would evaporate. It is obvious, therefore, that a drop will be formed around a charged molecule, or ion, with a smaller degree of supersaturation than that required when the molecule is uncharged.

22. C. T. R. Wilson's cloud experiments. The method adopted for producing supersaturation in the air is based on the cooling of a gas by adiabatic expansion. The apparatus used

is shewn in Fig. 14. The gas in the expansion chamber is shut in by a movable piston P, which is made as light as possible so as to move with ease and rapidity. The joint is made air-tight with water W, which also serves to keep the space saturated with moisture. The air space inside the hollow piston communicates by means of a wide tube T with the barrel B, and the piston can be raised to any required position in the outer glass cylinder D by forcing a little air in through the tap
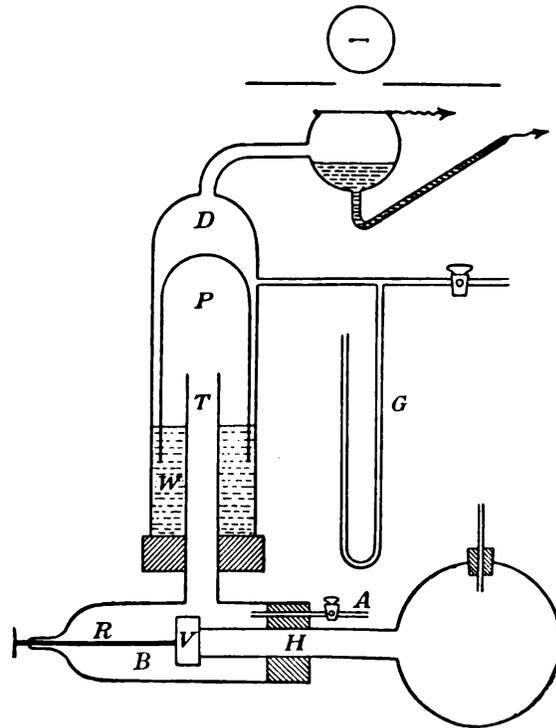
Fig. 14

A. Thus by suitably adjusting the initial position of the piston an expansion of any desired amount can be made.

The expansion is made as follows. A wide tube H connects B with a large vessel of several litres capacity which is kept at a low pressure by the continuous action of a water pump. H is normally closed by a valve V, but by smartly pulling back the rod R the valve is opened allowing the space beneath the piston to be exhausted very quickly through the tubes T and H. The pressure below P being thus reduced, it falls with

great rapidity, producing a nearly instantaneous expansion of the gas in the expansion chamber.

The actual expansion can easily be deduced by reading the pressure gauge G before and after the experiment. Let π be the atmospheric pressure and p_1 the difference of pressure in the two arms of the gauge before expansion. Then P_1 the initial pressure of the gas in the chamber is $(\pi - p_1 - \sigma)$ where σ is the saturation pressure of aqueous vapour at the temperature of the experiment. The final pressure of the gas after the apparatus has again attained the temperature of the laboratory is $(\pi - p_2 - \sigma)$ where p_2 is the new reading of the gauge. Hence by Boyle's law

$$\frac{v_2}{v_1} = \frac{\pi - p_1 - \sigma}{\pi - p_2 - \sigma},$$

which gives the expansion.

Since the expansion of the gas is adiabatic, $\theta v^{\gamma-1}$ is a constant

and

$$v_1{}^{\gamma-1}\theta_1 = v_2{}^{\gamma-1}\theta_2,$$

$$\log_e \frac{\theta_1}{\theta_2} = (\gamma - 1) \log_e \frac{v_2}{v_1} \quad . \quad . \quad . \quad . \quad (17)$$

which gives θ_2 since γ is known. The values of the saturation pressure of aqueous vapour at the temperatures θ_1 and θ_2 can be ascertained from tables and hence the degree of super-saturation produced in the space by the expansion can be obtained.

Working with this apparatus Wilson[1] found that, after freeing the chamber from dust nuclei no cloud was formed for values of v_2/v_1 less than 1·375, which was the expansion necessary to produce eight-fold supersaturation. If, however, the gas was previously ionized by passing X-rays into it through an aluminium window, a dense cloud appeared when the expansion exceeded 1·26, shewing that fresh nuclei are formed in the gas by the action of the rays. If these nuclei are gaseous ions they should be removable by the action of an electric field. This was found to be the case.

Later experiments shewed that for an expansion of 1·26 condensation took place only on the negative ions in the gas. If positive ions alone are present a considerably greater expansion,

1·30, corresponding to a six fold degree of supersaturation, is necessary to produce any condensation in the gas. The negative ions are thus more efficient in condensing drops of water than the positive.

23. C. T. R. Wilson's improved cloud apparatus(2). In the original form of cloud chamber the gas expanded through a side tube, thus setting up eddy currents in the chamber and producing a thorough mixing of the gas. A simple but great improvement in the apparatus consists in making the whole . floor of the apparatus act as the piston producing the expansion
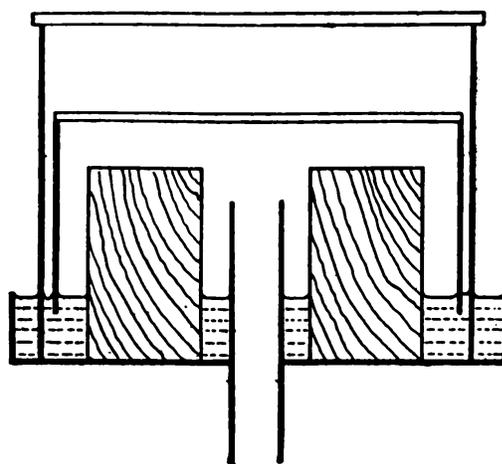
Fig. 15

(Fig. 15). The gas, after expansion, is perfectly at rest. If now one or two ionizing particles are fired through the chamber immediately after expansion, ions are formed along the actual track of the particles, and since the gas is already supersaturated, deposition takes place with these ions still in situ. The actual track of the particle is thus made visible as a string of shining beads of water, when the chamber is suitably illuminated from the side. Permanent records can be made by focussing a camera on the chamber through the upper face, which is made of plate glass. In practice the camera shutter is opened before the expansion is made, and the tracks are illuminated by an intense electric spark, which is timed to take place immediately after the passage of the ionizing particle.
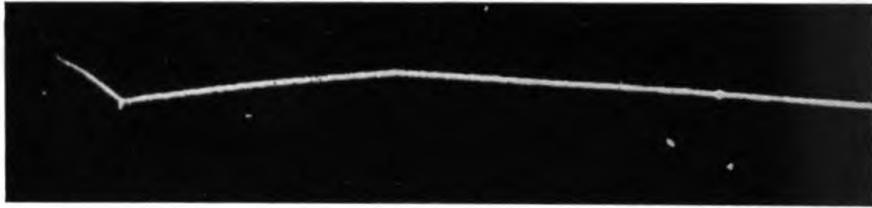
FIG. 16. TRACK OF AN α-PARTICLE.

C. T. R. Wilson.

FIG. 17. TRACK OF A β-PARTICLE.

C. T. R. Wilson.

C. T. R. Wilson.

FIG. 18. X-RAYS.

C. T. R. Wilson.

FIG. 18α.
TRANSFORMATION OF AN
X-RAY.

C. T. R. Wilson.
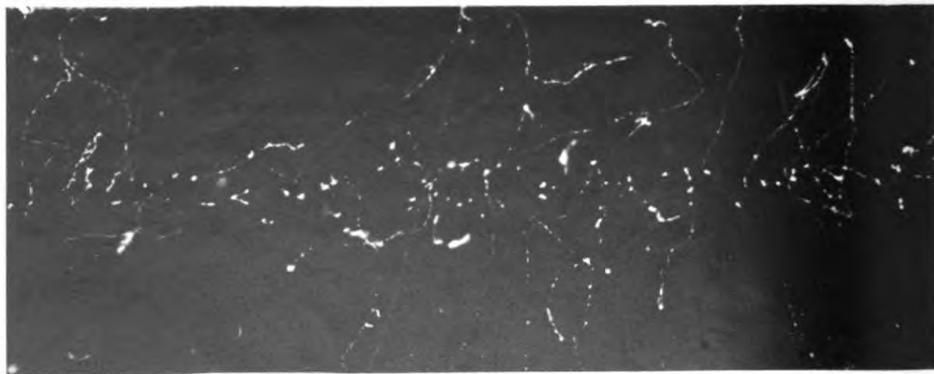
FIG. 59. X-RAYS SHOWING SHORT TRACKS OF RECOIL ELECTRONS.

The photographs shewn in Plate I were taken by C. T. R. Wilson in this way. Shimizu, Blackett, and others have, by various ingenious devices, succeeded in making the whole cycle of operations completely automatic, so that a long series of successive expansions can be made with a minimum of delay, the tracks obtained being photographed by a cinematic camera. We shall see later that many important researches have been made possible by this device. Fig. 16 (Plate I) shews a photograph of the track made by an α-particle from radium. The ionization caused by the α-particle is so intense that the drops coalesce into a single continuous streak. Fig. 17 in the same plate shews the track left by a single β-particle. Here the ions formed per cm. are far less numerous than in the case of the α-particle and the individual ions can be clearly seen. Fig. 18 is a photograph of the track left by a beam of X-rays passing from left to right. We shall refer to this later.

24. Application of the condensation experiments to the determination of e. *Thomson's method* (4). Suppose a cloud is formed in a cloud chamber of the form in Fig. 14, the expansion being arranged so that the drops condense only on the negative ions in the gas. These ions may be produced by any convenient ionizing agent. Let W_1 be the weight of water vapour required to saturate the space inside the chamber completely at the initial temperature, and W_2 that required to saturate it at the lowest temperature reached during expansion. Then the weight of water deposited is given by $M = W_1 - W_2$, and is known since W_1 and W_2 can be calculated from the volume of the chamber and the densities of the saturated vapour at the two temperatures. It may be assumed that, providing that drops are formed, the whole of the vapour over and above that required to saturate the space will be deposited.

The small drops making up the cloud will fall under the action of gravity with a uniform limiting velocity given by Stokes' law. Thus if r is the radius of the drop, η the viscosity and σ the density of air, ρ the density of water, and g the acceleration due to gravity, the drops will fall with a uniform velocity given by

$$v = \frac{2}{9} \frac{gr^2}{\eta} (\rho - \sigma). \quad . \quad . \quad . \quad . \quad (18)$$

This velocity can be measured by observing the rate at which the surface of the cloud settles down by means of a cathetometer or reading microscope. Since all the constants are known the observed value of v will enable us to calculate the radius r of a single drop. It is found that the drops are all the same size, as can be seen from the fact that the cloud settles down as a whole without separating into layers. The mass of each drop is therefore $\frac{4}{3}\pi r^3 \rho$ and if n is the total number of drops in the cloud

$$\frac{4}{3}\pi r^3 \rho n = M \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

which gives us n since M the mass of the cloud is known.

If the water surface is connected to an electrometer the quantity Q of electricity brought down by the cloud can be measured. The charge on a single ion is then equal to $\dfrac{Q}{n}$.

Balancing method of determining e. The previous method was first carried out by Sir J. J. Thomson. An interesting modification is due to H. A. Wilson [5]. In this the clouds were formed and the radius of the drops determined by the application of Stokes' law as in the previous experiment. An electric field, X, was then applied across the chamber so as to attract the drops towards an upper plate which was positively charged, the lower surface being earthed. The electric force Xe acting on the drops was thus in the opposite direction to that of gravity, and by suitably adjusting the strength of the field the two forces could be made to neutralize each other exactly so that the cloud remained stationary in the chamber, suspended in air "like Mahomet's coffin." When this state is reached we have

$$Xe = mg \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where X is the electric field and m the mass of the drop. But m can be calculated, as before, from the velocity of the free fall under gravity and hence e can be obtained. Assuming that each drop forms round a single ion this is the charge on the ion.

Both these experiments are subject to a serious error. The gas after expansion begins to warm up again by conduction and radiation from the room, and consequently the space

around the drops soon ceases to be saturated. Hence the drops begin to evaporate and their mass m is constantly decreasing during the course of the experiment. This defect has been overcome by a method due to Millikan.

25. Millikan's experimental determination of e. The question has been investigated very fully by Millikan [6] using a method similar to that of Wilson but free from the uncertainties caused by evaporation. Instead of condensing drops of liquid on the ions Millikan forms his drops mechanically by some form of sprayer in an atmosphere saturated with the liquid, and leaves them to acquire charges from the surrounding ionized air by collision with the ions. His apparatus is shewn very diagrammatically in Fig. 19.
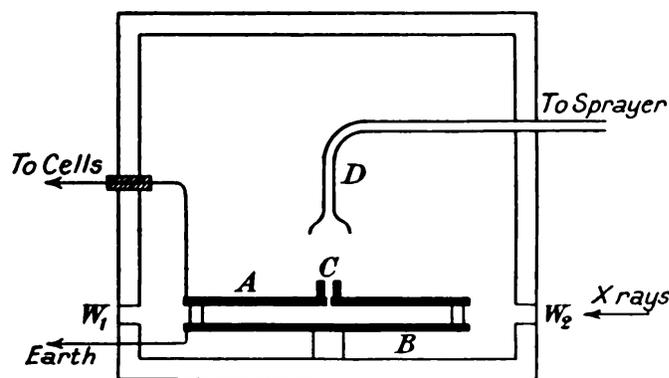
Fig. 19

It consists essentially of a pair of optically flat brass plates, A and B, each 22 cm. in diameter held perfectly parallel to each other by glass distance pieces optically worked to exactly the same thickness, 14·9174 mm. The lower plate B is earthed, while the upper plate A can be charged to a suitable positive or negative potential, usually of the order of 6000 volts from a large high tension battery. A constant and very accurately measurable field can thus be applied across the central part of the space between the plates. The whole apparatus is enclosed in a large metal box, which itself is immersed in a thermostat to avoid errors which might arise from convection currents in the apparatus. Drops, usually of oil, but sometimes of mercury,

were sprayed into the space above A through the tube D, and some of them fell through a small hole C into the space between the plates. The drops were illuminated by a beam of light introduced through a suitable window, W_1, and were viewed, in a direction nearly perpendicular to the light, by a microscope with a micrometer eye-piece. If required the air in the space between the plates could be ionized by X-rays, introduced through another window, W_2.

The drops were sometimes found to be charged by friction in passing through the sprayer. If not, they become charged by collision with the ions in the space AB. Since the diameter of the drop is large compared with that of an ion, the potential of the drop rises slowly, and it may accumulate a considerable number of charges of the same sign before its potential becomes sufficiently large to prevent other like charges from reaching it. On the other hand if an ion of opposite sign strikes it, part of the charge will be neutralized, and the total charge on the drop decreased. Since a drop has no tendency to evaporate the same drop may be kept under observation several hours, being kept in the field of view of the microscope by adjusting the electrical field to balance the gravitational forces, as in H. A. Wilson's experiments.

Suppose now that the plates are connected together so that the field is zero.

The drop will begin to fall under the force of gravity upon it, that is, mg, where m is the effective mass of the drop. As it is falling through a viscous fluid it will, by Stoke's law, move with a uniform terminal velocity v_1 which is directly proportional to the force acting upon it. Thus $mg = kv_1$ where k is some constant which depends on the viscosity of the air and the dimensions of the drop, but will remain unaltered as long as we confine our attention to the same drop. If the plate A is now raised to a sufficiently high potential of opposite sign to the charge on the drop the electrical attraction will be greater than the gravitational force and the drop will move upwards with a velocity v_2 given by $XE - mg = kv_2$, where X is the field and E the charge on the drop. The velocities v_1, v_2 are measured by timing the transit of the drop between two fixed hair lines at a known distance apart

in the micrometer eyepiece. Combining our two equations we have

$$E = \frac{k}{X}\,(v_1 + v_2).$$

The same drop can be observed for many hours during which its total charge will undergo many changes owing to collision with either positive or negative ions. A large number of different values for E (in terms of the constant k) can thus be obtained with the same drop. As a result of many experiments Millikan found that when the drop changed its charge it did so always by exactly the same amount, and further that the total charge on the drop was always an exact integral multiple of this amount. This was the case whether the whole charge was due to ionic collisions, or whether it was derived from friction in the sprayer. Thus all the charges measured by Millikan could be represented by the relation $E = ne$, where E was a constant, and n an integer which generally lay between 3 and 20.

It would be impossible to imagine a more direct proof of the fact that electricity, like matter, is not indefinitely indivisible. It consists of units, or "atoms" which cannot be further sub-divided, and all these atoms have exactly the same charge. This is the charge carried by a gaseous ion. A negative ion, however, is merely an atom which has gained an electron. The electron is thus the atom of electricity, and we shall refer to this natural unit of electricity as the *electronic charge*, and denote it by e. The fact that the frictional charges on the drops were also found to be integral multiples of e, shews that ordinary frictional charges are also made up of electrons.

The proof of the atomicity of electricity requires no further measurements than those of the two velocities of the drop, and involves no assumptions except that the velocity of the drop is proportional to the force acting upon it. To find the value of e in absolute units it is necessary to determine the value of k. According to Stokes' law $k = 6\pi\eta a$, where a is the radius of the drop, and η the viscosity of air. Since the mass m of the drop is equal to $\frac{4}{3}\pi\rho a^3$ or allowing for the buoyancy of the air, to $\frac{4}{3}\pi\,(\rho - \sigma)\,a^3$ where σ is the density of the air and $mg = kv_1$, k can be calculated when the density ρ of the drop and the viscosity of air are known.

C I   4

On evaluating his results, however, Millikan found that the value obtained for e varied with the size of the drop used, becoming progressively larger as the drop became smaller. When the radius of a drop becomes comparable with the average distance between the molecules of the air it is no longer possible to regard the air as a continuous homogeneous medium as required in Stokes' law. To put the matter somewhat crudely the small drop finds occasional gaps between the air molecules through which it can move freely under the action of the forces upon it, and it thus acquires a rather larger average velocity than it would if the medium were really homogeneous. It can be shewn that the constant k in these circumstances is of the form $6\pi\eta a\left(1+\dfrac{A\lambda}{a}\right)^{-1}$ where λ is the mean free path of a molecule in the gas, and A is a numerical constant. The value of A can be deduced from the measurements of e made with drops of very different radii. Millikan found that on using this corrected form of Stokes' law, all his experimental data were completely consistent, and the value of e was exactly the same for drops of all sizes.

Corrections were also made for the effect of the finite size of his apparatus on the motion of the drops, and new determinations were made of the viscosity of air, the accepted value having been found to be in error by about 2 per cent. As a final result Millikan found that the electronic charge had the value $4\cdot774\times10^{-10}$ e.s.u. with a probable error of about $0\cdot1$ per cent.

Millikan repeated his experiments using different gases, and different sources of ionization, but with exactly the same result. One point of interest may be mentioned. Whereas in nearly all the experiments the charge carried by a gaseous ion was found to be the single electronic charge e, when the experiments were done in helium gas, with α-particles as the source of ionization, about 16 per cent. of the ionic encounters added not a single charge e, but a double charge $2e$ to the drop.

Thus about 16 per cent. of the helium ions must be doubly charged. We must suppose that in this case about $\frac{1}{6}$th of the encounters between the α-particles and the helium atom result in the ejection of two electrons from the atom. Apparently in

all other cases ionization is produced by the ejection of a single electron only.

26. **Perrin's determination of e from the Brownian movement.** We have already seen (§ 20) that the total charge on a gram-molecule of charged ions is given by $N.e = 9649$ e.m.u. where e is the charge on a single ion and N is Avogadro's number. Thus if we can determine N, we have an independent method of determining e. An interesting method of determining N is afforded by Perrin's[9] experiments on the Brownian movement.

Suppose a small particle, not too small to be visible with an ultra-microscope yet not too large in comparison with the size of the molecules to be affected by collision with them, is suspended in water. This particle will, by the kinetic theory, be bombarded on all sides by the molecules of the water moving under their velocities of thermal agitation. On an average the number striking the particle will be the same in all directions and the average momentum communicated to the particle in any direction will be zero. Since, however, the collisions are governed by the law of probability there will, if the interval of time considered be sufficiently small, be an excess of momentum in one direction or the other, and if the mass of the particle is not too large compared with the masses of the colliding molecules it will be given an irregular kind of motion which may be observed under a microscope. This motion has been known for many years as the Brownian movement and is always to be observed in suspensions of fine particles in a liquid.

The particles in Brownian movement are thus sharing the thermal agitations of the molecules of the surrounding liquid in exactly the same way that the molecules of a heavy vapour share the motion of the molecules of a light gas in which they may be placed. In other words, from the point of view of the kinetic theory the particles in a suspension behave like the molecules of a dilute gas of very high molecular weight, each particle functioning as a single molecule. We can, therefore, apply the gas laws to them, and from observations on these

4-2

visible particles determine the various unknown constants in the gas equations.

Distribution of the particles in a suspension in a vertical direction when in equilibrium under gravity. The most direct method of applying this result is to determine the way in which the particles of a suspension distribute themselves under the action of gravity. The case is similar to that of a gas under gravity.

Consider two horizontal planes separated by a distance dh in a vertical column of gas of unit cross section. If p and $p + dp$ are the pressures at the two planes, the difference dp is equal to the weight of the gas enclosed between the two planes, since the cross section is unity. Hence if ρ is the density of the gas

$$dp = mg = \rho g \cdot dh$$

$$= \frac{M}{V} g \cdot dh$$

where M is the molecular weight of the gas in grams and V is the volume of one gram-molecule. But $V = RT/p$ where T is the absolute temperature and R is the gas constant. Thus

$$dp = \frac{Mgp}{RT} dh,$$

$$\therefore \quad \log_e \frac{p_0}{p} = \frac{Mg}{RT} H \ . \quad . \quad . \quad . \quad . \quad (21)$$

where H is the vertical distance between the two points in the vertical column where the pressures are p_0 and p.

But the pressure is directly proportional to the number of molecules per c.c. in the gas. Hence we may write (21) in the form

$$\log_e \frac{n_0}{n} = \frac{MgH}{RT} \quad . \quad . \quad . \quad . \quad (22)$$

which gives the distribution of the molecules in a vertical column of the gas.

We can now apply this result to the case of the suspension. In this case if m is the mass of a single particle the "molecular weight in grams" will be equal to mN where N is the number of molecules in one gram-molecule of a gas, which by hypothesis is the same for all gases. The apparent mass of a particle

suspended in a liquid is, however, less than its true mass m by the weight of the liquid it displaces; that is, it will be equal to

$$m\left(\frac{D-d}{D}\right),$$

where D is the density of the particle and d that of the liquid. Hence substituting in equation (22), we have

$$\log_e \frac{n_0}{n} = \frac{Nm}{RT}\left(1 - \frac{d}{D}\right)gH. \quad . \quad . \quad . \quad (23)$$

If the mass of the particles and their density are known a determination of the ratio of n_0/n for different depths will enable us to calculate N, the constant of Avogadro.

A suitable emulsion was found in gamboge, the particles being obtained of uniform size by centrifugal fractionation. The density could be determined by finding some solution in which the particles would remain suspended without falling, while the volume could be determined either by direct measurement of the radius of the particle or by calculating the latter from its rate of fall under gravity by Stokes' law.

To find the vertical distribution of the particles when in equilibrium a small drop of the emulsion was placed in a hollow cut out in a microscope slide (Fig. 20) and covered with a thin cover slip to prevent evaporation. A high power microscope was then focused on some definite layer of the emulsion and the field of view
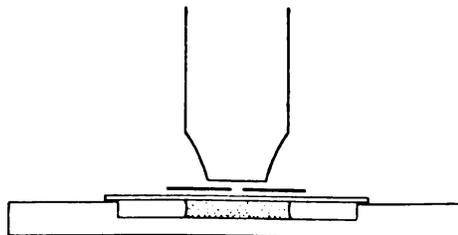
Fig. 20

limited by a stop so that not more than five or six grains were in the field of view at the same instant. Owing to the Brownian movement the particles are constantly appearing and disappearing but if not more than five or six are visible at the same time a practised eye can immediately grasp the number present at any given moment. Readings were made at equal short intervals of time, and the average number present in view is taken as proportional to n for that layer. Thus for some

particular layer A in one set of experiments the numbers visible at ten successive moments were

$$2, 2, 0, 3, 2, 2, 5, 3, 1, 2,$$

giving an average of 2·2. At some higher level B the first ten readings were

$$2, 1, 0, 0, 1, 1, 3, 1, 0, 0,$$

giving an average of 0·9. The ratio n_1/n_2 for these two layers was therefore 2·2/0·9. In this way the average number of particles occurring at different depths in the liquid was determined and was found to agree very closely with the theoretical distribution, as calculated above. Substituting the experimental values in equation (23) N was found to be $68·2 \times 10^{22}$. A second method based on the distribution after a definite interval of time in a horizontal plane of a number of particles introduced at a given point in the liquid gave a mean value of $N = 68·8 \times 10^{22}$. Substituting these results in the equation $NE = 9649$ we find that the value of E the charge on a monovalent ion in electrolysis is equal to $1·40 \times 10^{-20}$ e.m.u. or $4·2 \times 10^{-10}$ e.s.u.

27. Summary of results. Perrin's experiments are important as providing an entirely independent method of determining Avogadro's number, and thus, indirectly, of the electronic charge. The method is clearly not capable of a very high order of accuracy, although the discrepancy between the values obtained by Perrin and Millikan is larger than would have been expected. This gave rise to a suggestion that Stokes's law might not be applicable to bodies as small as the oil drops used by Millikan. An alternative method of deducing Avogadro's number from experiments on the Brownian movements is to observe, not the density distribution of the particles at different levels as in Perrin's experiments, but the actual excursions of individual particles, or their rate of diffusion through the supporting medium. Very minute oil drops shew Brownian movement very markedly in air, and their displacements can very readily be observed and measured by a micrometer microscope. A theory of the effect has been worked out by Einstein which enables N

to be calculated from the observations. Experiments made on these lines by Fletcher[10] give a value for N of 60.3×10^{22}, and consequently a value for e of 4.79×10^{-10} e.s.u. in close agreement with that of Millikan. As, however, Fletcher used Stokes's law to determine the mass of his drops, his experiments hardly provide independent confirmation of Millikan's experiments.

On the other hand the value of e can be determined from entirely different considerations, such for example as the determination of the charge on an α particle (§ 98), the determination of the wave length of X radiation (§ 94), and from Planck's theory of radiation. Values deduced in these ways, some of which are collected in Table II, leave no doubt as to the substantial accuracy of Millikan's method.

TABLE II
The charge on an electron

OBSERVER	METHOD	e in e.s.u.
Begeman	Water drops (original method of Thomson)	4.67×10^{-10}
Millikan	Oil and mercury drops	4.774×10^{-10}
Matteuch	,, ,,	4.758×10^{-10}
Fletcher	Brownian movements	4.79×10^{-10}
Rutherford	Charge on a-particle	4.65×10^{-10}
Regener	,, ,,	4.79×10^{-10}
Wadlund	X-ray measurements	4.774×10^{-10}
Planck	Theory of radiation	4.69×10^{-10}

The most probable value for e appears to be

$$4.770 \times 10^{-10} \text{ e.s.u.} \quad \text{or} \quad 1.591 \times 10^{-20} \text{ e.m.u.}$$

Assuming this value for e the value of Avogadro's constant becomes 60.6×10^{22} molecules per gm. molecule. The Faraday constant is 9649 e.m.u. per gm. equivalent. The number of monovalent atoms per gm. of a substance of unit atomic weight would thus be $9649/1.591 \times 10^{-20}$, and the actual mass of an atom of unit atomic weight would thus be $1.591 \times 10^{-20} \div 9649$ or 1.649×10^{-24} gm. The masses of atoms of other elements can be obtained by multiplying this number by the chemical atomic weight (oxygen = 16). Thus the mass of a hydrogen atom is $1.0077 \times 1.649 \times 10^{-24}$ gm. or 1.661×10^{-24} gm.

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CHAPTER V

IONIZATION BY COLLISION. THE SPARK DISCHARGE

28. Ionization currents with large voltages. We have already seen (§ 9) that the current through an ionized gas increases with increasing electric field up to a certain maximum value known as the saturation current. There is then a considerable range of electric fields greater than this saturation value for which increasing the field produces no appreciable increase in the current. It is found, however, that if the field is increased above a certain value the current again begins to increase,
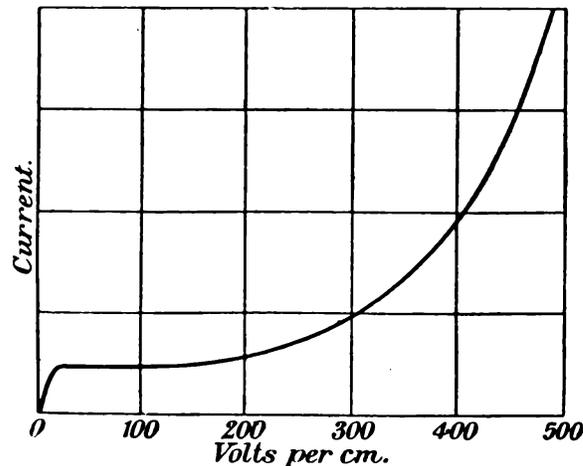
Fig. 21

at first slowly but soon with great rapidity (Fig. 21) until finally a spark passes between the electrodes, accompanied by a temporary but very considerable current. The field X required to produce an appreciable increase in the current above its saturation value depends on the distance apart of the electrodes, and on the nature and pressure of the gas. For air at ordinary pressures, and with distances of half a centimetre or more between the electrodes it is very large. It diminishes, however, as the pressure of the gas is reduced, and the phenomena are

most conveniently investigated in gases at the comparatively low pressures of from one to ten millimetres of mercury. With such pressures it is possible to produce a considerable increase in the current through the gas with potential differences of not more than 50 volts.

The effect is to be ascribed to collision between the ions generated in the gas and the molecules of the gas. We have already shewn (§ 15) that the velocity acquired by an ion of mass m and charge e moving under the action of a field of strength X between two successive collisions is

$$\frac{Xe}{m}\frac{\lambda}{V}$$

where λ is the length of the free path of the ion. Its velocity, on striking another molecule of the gas, is thus, for a given field, proportional to its free path.

The mechanism of ionization is a little obscure. Since however it involves the complete separation of a negative from a positive charge it is obvious that work must be done on the molecule so ionized, and the energy for this must be supplied by the source of ionization. In what follows we assume that this energy is supplied by the kinetic energy of the colliding particle. The kinetic energy of this particle must, therefore, reach a certain minimum value if fresh ions are to be produced by it in the gas by the process of collision.

The mean free path of a particle in a gas can be calculated from the kinetic theory of gases. The same theory, however, shews that in a considerable number of cases collision will not occur until the particle has described a free path considerably longer than the mean, while in others collision takes place before the mean free path has been described. Thus it can be shewn that in 14 per cent. of the total number of collisions, collision will not occur until the particle has described a path at least twice as great as the mean, while in 10 per cent. of the cases it takes place before one-tenth of the mean path has been completed. Thus assuming that the particle must describe a path λ before it has sufficient kinetic energy to produce fresh ions, ionization by collision will commence long before the mean

path of the ions has reached this critical value, and will not be even approximately complete until the conditions in the gas correspond to a mean free path considerably greater than the critical value.

Kinetic theory shews that, if λ is the mean free path of a molecule in a gas, a molecule will in a centimetre of its path make $\frac{1}{\lambda} \epsilon^{-x/\lambda}$ collisions for which its actual free path has been greater than x. The energy of an ion on collision, assuming it to be due entirely to the electrical field X acting upon it, is Xex, where e is the ionic charge. If we assume that ionization will occur if this energy exceeds some constant value T, the number α of fresh ions formed per cm. by the given ion will be equal to the number of encounters terminating free paths greater than the critical value x given by $Xex = T$, or $x = T/Xe$. Substituting this value of x in the equation, and remembering that the mean free path is inversely proportional to the pressure we have

$$\alpha = Cp\epsilon^{-\frac{CTp}{Xe}} \qquad \ldots \quad \ldots \quad \ldots \quad (24)$$

where C is a constant for the gas.

The value of α thus depends on the pressure and nature of the gas and on the field. For the negative ion in air at a pressure of 4·1 mm. in a field of 200 volts per cm. Townsend found a value for α of 0·50 per cm. In carbon dioxide at a pressure of 3·95 mm. and with a field of 972 volts per cm. the value was as high as 4330.

29. Expression for the current through the gas when ionization by collision occurs. Experiment shews that ionization by collision occurs in much lower fields for negative than for positive ions. Thus in circumstances where negative ions were found to be producing fresh ions by collision with a potential of 100 volts between the electrodes, the potential had to be raised to 350 volts before any appreciable increase in current was observed when the ions originally present were all positive. When the gas, as is usually the case, contains ions of both signs the initial rise in the saturation current is thus due entirely to the negative ions. Confining our attention for the moment to this case, let us consider the current between two parallel plates

separated by d cm. of gas. Let n_0 be the number of ions generated per cubic cm. of gas by the ionizing agent at a distance x from the positive electrode. Let a be the number of ions which a single negative ion produces by collision in 1 cm. of its path. a will depend on the field and on the mean free path, but will be constant under the conditions of any one experiment. Then assuming that the ions so formed will in turn produce fresh ions by their collision the number of ions generated by collision in a distance dx will be equal to $a\,n\,dx$, where n is the total number of negative ions present per unit volume at the point considered. Hence the rate at which negative ions are increasing as the positive electrode is approached is given by

$$\frac{dn}{dx} = an.$$

Thus the number reaching the positive electrode, which is equal to the sum of all the ions generated, is given by

$$\log n/n_0 = ax \text{ (on integrating)},$$

$$\therefore \quad n = n_0 \epsilon^{ax}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

In other words for every n_0 ions produced in a plane at a distance x cm. from the positive electrode a number $n_0 \epsilon^{ax}$ reach the positive electrode, assuming that there is no recombination.

If the ionization is confined to a single plane at a definite distance x from the positive electrode this expression will give the current across the gas. If, however, the gas is uniformly ionized throughout its volume, the number of ions formed per c.c. per sec. being n_0 as before, we may proceed as follows. Consider two planes distant x and $x + dx$ from the positive electrode, the number of ions formed in this layer will be $n_0 dx$ and the number reaching the positive electrode due to this layer $n_0 \epsilon^{ax} dx$. The total number reaching the positive electrode will thus be the integral of this from $x = 0$ to $x = d$,

$$\text{or} \qquad \int_0^d n_0 \epsilon^{ax}\, dx = n_0\, \frac{\epsilon^{ad} - 1}{a}, \quad . \quad . \quad . \quad . \quad (26)$$

where d is the distance between the two electrodes. If there were no ionization by collision the number reaching the electrode in the same time would be $n_0 d$ which is the number formed by

the ionizing agent in the same time. Hence, since the currents are proportional to the number of ions, the actual current i across the gas is given by

$$i = i_0 \frac{\epsilon^{ad} - 1}{ad}, \quad \cdots \cdots \quad (27)$$

where i_0 is the saturation current.

Similarly equation (25) can be written in the form

$$i = i_0 \epsilon^{ax}. \quad \cdots \cdots \quad (28)$$

The latter equation has been very carefully tested by Townsend, to whom it is due, by measuring the current between a pair of parallel plates for different potential differences between the plates, and for different distances between the plates. The ionization can be confined to a layer of gas at the surface of the negative electrode, by making the latter of some electropositive metal such as zinc, and illuminating it with ultra-violet light from a quartz mercury lamp. Light from such a source does not produce ionization in a gas, but liberates a copious supply of negative electrons from the plate, which form negative ions by attaching themselves to neutral gas molecules. If the plates are enclosed in an air-tight container experiments can be made on different gases at various pressures. The experimental values obtained for α under different conditions substantiated the theory given in the two preceding sections.

30. Effect on the current of ionization by positive ions. If the electric field across the gas increases beyond a certain limit the effect of the ionization produced by the positive ions becomes important. For simplicity we will limit our attention to the case where initial ionization is confined to the negative electrode, as in Townsend's experiments outlined above. The negative ions moving out from the negative electrode produce ions of both signs in the gas, and the positive ions so produced give rise in turn to ions of both signs by collision during their motion towards the negative electrode. Let β be the number of pairs of ions produced per cm. of its path by the positive ion.

Consider a pair of planes AB and CD parallel to the electrodes at a distance dx apart and x cm. from the negative electrode.

Let p be the number of pairs of ions generated by both positive and negative ions between the negative electrode and AB, and q the number of pairs of ions generated between CD and the positive electrode. The number of ions arriving at the positive electrode per second is thus $n = p + q + n_0$ where n_0 is the number generated per second at the negative electrode. The number dp of pairs of ions generated between x and $x + dx$ is

$$(n_0 + p)\, \alpha dx + q\beta dx \quad . \quad . \quad . \quad . \quad (29)$$

since all the negative ions generated per second cross the planes in one direction and all the positive ions in the space below the planes cross them in the opposite direction, assuming that there is no recombination. This is obviously true since the saturation voltage is exceeded before ionization by collision begins. Substituting for q we have

$$\frac{dp}{dx} = (n_0 + p)(\alpha - \beta) + n\beta. \quad . \quad . \quad . \quad (30)$$

The solution of this equation is of the form

$$n_0 + p = A\epsilon^{(\alpha-\beta)x} - \frac{n\beta}{\alpha - \beta} \quad . \quad . \quad . \quad (31)$$

and A can be found from the condition that $p = 0$ when $x = 0$. Thus substituting for A and solving for n we have

$$n = n_0 \frac{(\alpha - \beta)\epsilon^{(\alpha-\beta)d}}{\alpha - \beta\epsilon^{(\alpha-\beta)d}}, \quad . \quad . \quad . \quad (32)$$

where d is the distance between the electrodes.

This equation is due to Townsend and was carefully tested by him with the apparatus already described [2]. It was found that an expression of this form represented the experimental results with considerable accuracy over the whole range of distances and fields.

The values of β are generally small compared with those of α. For air the ratio of β/α is less than one per cent. and for carbon dioxide less than 1/1000. This disparity is due to the fact that the positive ions are molecules of the gas, while the negative as we have seen are at the pressures used in these experiments probably electrons.

31. The spark discharge. The equation (32) just developed suggests curious possibilities. It is evident that the current will become infinite for some distance d such that

$$\alpha = \beta \epsilon^{(\alpha-\beta)d} \qquad \ldots \ldots \ldots \quad (33)$$

This case corresponds to what is known as the spark discharge. A considerable amount of experimental research has been devoted to the spark discharge. If two electrodes are separated by a gas at any pressure and the difference of potential between them is gradually increased eventually a point is reached at which a bright spark accompanied by the well-known crackling noise will pass between them and the two conductors become completely discharged. If the difference of potential is continuously restored by connecting the two electrodes to an electrical machine a continuous torrent of sparks is obtained which may pass into the form of an arc. In this case the current may rise to many amperes.

The spark may also be made to pass by bringing the electrodes nearer together as in the case of the discharge of a Leyden jar by discharging tongs, or by reducing the pressure of the gas between the electrodes. This latter is, however, only effective down to a certain point. It is found that for any given distance apart of the electrodes there is a critical pressure at which the discharge passes most easily. Reducing the pressure below this critical value causes a very rapid rise in the potential necessary to produce a spark, so that the potential at very low pressures may easily exceed by many times that which would suffice to produce discharge at the same distance in air at atmospheric pressure.

The critical potential difference between the electrodes necessary to produce a spark is called the sparking potential. If we assume that the spark takes place between two parallel plate electrodes situated S cm. apart the value of the sparking potential is equal to XS where X is the field between the plates.

Thus if α and β are the two coefficients of ionization under the conditions of the experiment, sparks should pass between the electrodes when their distance apart is given by

$$\alpha = \beta \epsilon^{(\alpha-\beta)S} \qquad \ldots \ldots \ldots \quad (34)$$

and the sparking potential should be equal to XS where X is the field between the plates.

This equation was tested by Townsend. α and β were measured for some definite field X and the value of S calculated from equation (34). The plates were then set at this distance apart and the potential difference between them gradually increased until a spark passed. The minimum sparking potential as thus obtained was found to agree in every case with the product XS as previously determined, the divergence between the two values being less than one per cent. This agreement is strong proof of the substantial accuracy of the theory.

It will be seen that this theory requires the existence of a certain number of free ions in the gas between the electrodes if the spark is to pass. Under normal circumstances the air generally contains a few ions especially if the electrodes are illuminated by sunlight which contains a small proportion of ultra-violet light. If, however, the ions present are very few, as, for example, if the sparking experiments are made in the dark, a considerable time may elapse before the few ions originally present have increased sufficiently in number to give rise to a spark discharge, and under these circumstances the difference of potential may be increased considerably beyond the critical sparking potential without a spark passing. This phenomenon is well known and is called the retardation of the spark. Under certain circumstances this retardation may amount to several minutes. It is reduced to zero if the negative electrode is exposed to a weak source of ultra-violet light. Many early experiments were vitiated by the neglect of this precaution.

32. **Sparking potential for parallel plate electrodes.** The conditions are most easily interpreted when the electrodes take the form of a pair of parallel plates. Experiments of this kind have been made by Carr (4), using apparatus as shewn in Fig. 22. If the discharge is taken between two metallic plates in the usual way it is found that the spark always passes between rough points or small projections on the edges of the disks. To avoid this the electrodes E, E were completely embedded

in ebonite except for a portion near the centre which was
carefully planed and polished. The plates were separated by
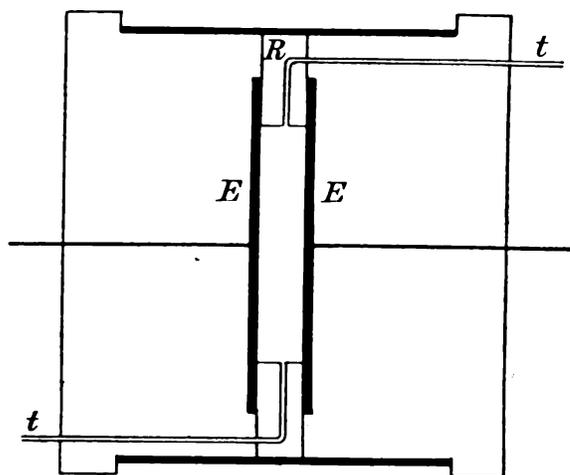
Fig. 22

ebonite rings *R* of varying thickness so that spark lengths of
different values could be used. The gas to be experimented
on could be introduced by fine tubes *t, t* running through the
ebonite, and the whole apparatus was made air-tight.
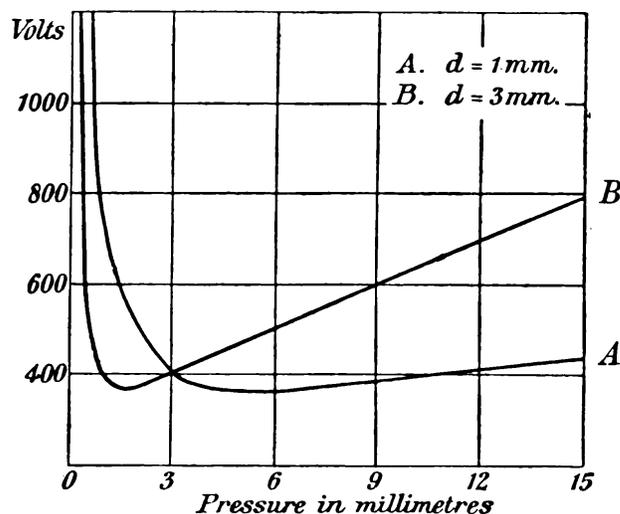
Fig. 23

The experiments shewed that for a given gas there was a
minimum potential difference depending only on the nature
of the gas below which a spark would not pass. For any given
distance between the plates it was always possible to find

some pressure at which the spark passed at this minimum potential. Either increasing or decreasing the pressure from this critical value increased the sparking potential. These results are shewn in Fig. 23 which represents some of Carr's observations on air at various pressures and for various distances between the electrodes. Similar results were obtained for other gases. Within the limits of experimental error the product of the sparking distance into the critical pressure is a constant for a given gas. For different gases this product is approximately proportional to the mean free path of the molecules of the gas.

33. Paschen's Law. As the result of a large number of experiments Paschen[5] came to the conclusion that for a given gas the sparking potential was a function only of the product of the sparking distance into the pressure of the gas, that is to say, of the mass of gas between unit area of the electrodes. This result applies also to the case of the discharge between two spheres if the distance between the spheres is appreciably less than the radius of curvature. It can easily be shewn that this result follows from the theory given above. Let V be the sparking potential. Then $V = SX$, and if M represents the product pS we have from (24),

$$\alpha = pf\left(\frac{X}{p}\right) = \frac{M}{S}\,f\left(\frac{V}{M}\right),$$

writing $f\left(\dfrac{X}{p}\right)$ for $C\epsilon^{-\frac{CTp}{eX}}$ and similarly

$$\beta = p\phi\left(\frac{X}{p}\right) = \frac{M}{S}\,\phi\left(\frac{V}{M}\right).$$

Hence, substituting in the equation,

$$\alpha = \beta\epsilon^{(\alpha-\beta)S}$$

we have $\qquad (\alpha - \beta)\,S = \log_\epsilon\left(\dfrac{\alpha}{\beta}\right).$

$$\therefore M\left[f\left(\frac{V}{M}\right) - \phi\left(\frac{V}{M}\right)\right] = \log\left[f\left(\frac{V}{M}\right)\Big/\phi\left(\frac{V}{M}\right)\right], \quad (35)$$

thus shewing that the sparking potential V depends only on M, that is, the product pS. Carr has shewn that this law is

true for all pressures both above and below the critical pressure. It is thus a result of great importance. It follows that if p and S are varied in such a way that the product pS remains constant the sparking potential will be unaltered. The sparking potential is not affected by temperature provided that the mass of gas between the electrodes remains constant.

34. Minimum energy required to produce ionization. The determination of the energy necessary to produce an ion in a given gas can be made more conveniently and more accurately if electrons are substituted for the ions of the gas itself as the bombarding particles. The simplest arrangement, due to Lenard, is shewn diagrammatically, in Fig. 24. Z represents a metal filament, which is heated to incandescence by the passage of an electric current, and serves as the source of electrons (§ 56). The electrons, which are emitted with very small initial velocities, are accelerated in an electric field applied between the

Fig. 24

filament Z and a wire gauze, or grid, G which is at a positive potential with respect to the filament. The distance between the filament and the grid is small compared with the mean free path of an electron in the gas at the low pressure at which the experiments are conducted, and the majority of the electrons pass through the grid without having made a collision in the gas, and thus with the full velocity v produced by a free fall through the potential difference $(V_G - V_Z)$ existing between the filament and the grid. They thus pass into the space above the grid with a definite kinetic energy $\frac{1}{2}mv^2 = (V_G - V_Z)e$ where m is the mass and e the charge on the electron.
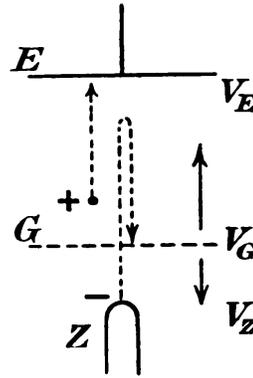
If this energy is sufficient to produce ionization by collision in the molecules of the gas, positive ions will be formed in the large space between G and the collecting plate E, which is connected to an electrometer, and will be directed to the plate by the field $(V_G - V_E)$ acting from the grid to the plate. The electrometer will thus charge up with positive electricity. The

5-2

potentials are so ordered that $(V_G - V_E)$ is greater than $(V_G - V_Z)$ so that any electrons which make no collisions in the gas will be unable to penetrate to the plate, and will be returned, together with any negative ions formed in the gas, to the grid. The electrodes are, of course, enclosed in a suitable glass vessel, so that the experiment can be carried out at a suitable low pressure, usually of the order of a millimetre of mercury.
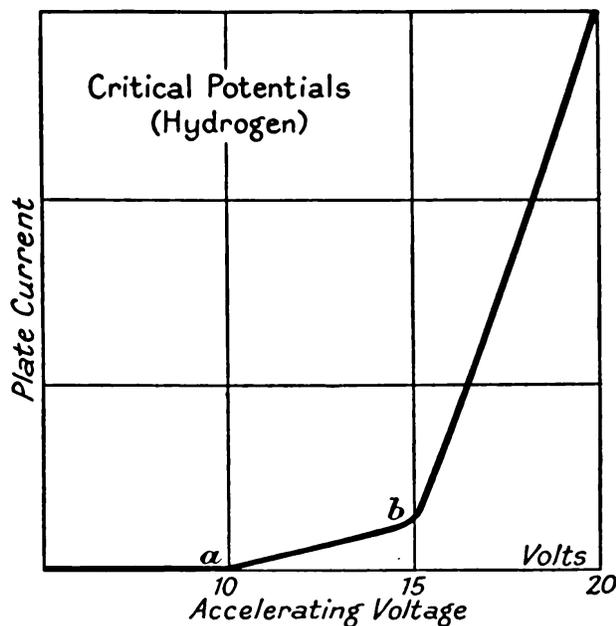
Fig. 25

It will be seen that if the filament is heated and $(V_G - V_Z)$ is gradually increased from zero no current should be registered by the electrometer until this potential difference reaches the value necessary to give the electrons the kinetic energy required to ionize the gas. This critical value is known as the ionization potential of the gas. The actual energy is obtained by multiplying this potential by the electronic charge. In Fig. 25, which represents a set of experiments carried out in this way in hydrogen, it will be seen that no current reaches the collecting plate until the accelerating potential on the electrons reaches 10 volts. A current then begins to flow which increases with increasing voltage. It was natural to identify this critical potential with the ionization potential of the gas, and this was the interpretation at first put upon it. Further work, however, threw doubt on this interpretation.

When the P.D. between G and Z is still further increased other critical points make themselves manifest on the current voltage curve. The curve, in fact, instead of rising continuously, shews a series of points (a, b, Fig. 25) at which the slope of the curve changes abruptly, shewing that new sources of current are coming into action. There is thus not one but a series of *critical potentials* for the gas (as many as fourteen have been recorded for mercury vapour) and it becomes necessary to interpret these.

35. Radiation and Ionization Potentials. A closer investigation of what is going on in the gas shews that the lower critical potentials are not ionization potentials; no ions are formed in the gas by electrons with the corresponding energies. The absence of ions in the gas can be demonstrated quite simply by substituting a fine wire for the solid plate collector E (Fig. 24). Since the field would be directed towards the wire, this would collect ions from the gas as efficiently as the plate. It is found, however, that the current collected by the wire at the lower critical potentials is vanishingly small, it is, in fact, proportional to the area of the collector, and is due to some action taking place at its surface, leading to the emission of negative electrons from it.

This emission of negative electricity, which simulates the collection of a positive charge, has been shewn to be due to ultra-violet light (Chapter ix) emitted by the gas in the tube under the bombardment of the negative electrons from the filament. The radiation can, in fact, be detected spectroscopically when the electron stream is sufficiently intense. The light emitted at the lowest potential is monochromatic and consists of a single line from the normal spectrum of the gas in the tube. Further lines appear at other perfectly definite higher critical potentials. The complete spectrum is only evoked when true ionization takes place in the gas.

Since the lower critical potentials correspond to the emission of radiation, they are called radiation or, less happily, "resonance" potentials. They are of great importance in the study of spectra, and we shall return to them later. For the present we

may say that the ionization potential measures the work which must be done to remove an electron completely from the atom; the radiation potential measures the energy necessary to transfer an electron from its normal position in the atom to some other possible position, where its energy is greater than normal. The fact that the critical potentials are quite few shews that the positions which the electron can occupy in the atomic structure are strictly limited; they can most easily be specified by the energy necessary to move the electron from its normal to its new position, that is to say by the corresponding critical potential.

The atom which has been thrown into one of these "excited" states, as we may call them, is unstable, as the excited electron tends to return to its normal position. In so doing the extra energy which the excited atom possesses is given out as we have seen in the form of monochromatic radiation.

36. Accurate determinations of critical potentials. The original Lenard method is not capable of much accuracy, as it is very difficult to fix with precision the position of a kink in a rapidly rising experimental curve. Other sources of inaccuracy are the Volta potential difference between the filament and the grid, and the finite velocity of emission of the electrons from the filament. A very accurate method, due to Franck and Hertz, is available when the gas has no electron affinity (§ 16). The grid G is removed from its position near the filament and placed just in front of the collecting plate E (Fig. 26 a), which is at a potential about half a volt lower than that of the grid. Negative electrons passing through the grid must therefore have sufficient energy to enable them to travel against an adverse P.D. of this amount if they are to be collected by the plate. An accelerating field is applied, as in the earlier form of apparatus, between the filament and the grid.

The electrons make numerous collisions in the space between Z and G, but if the molecules have no electron affinity the collisions are perfectly elastic, and cause no loss of energy in the electron, some of which consequently ultimately reach G with energy corresponding to V_A, the P.D. between the filament and the grid. If this is greater than half a volt, or if the electrons are

emitted from the filament with the corresponding energy, a small negative current will flow into E, and can be measured by an electrometer. This current steadily increases, as V_A is increased, until V_A reaches a critical potential for the gas. Since now the electrons have the energy necessary to throw the atom into an excited state, the collisions become inelastic, the electron handing over the whole of this energy to the atom with which it collides. The electron is thus left immediately in front of G with practically zero energy. It is thus unable to penetrate the adverse field between the plate and the grid, and the current begins to fall. The value of V_A for which the current is a maximum thus corresponds to the critical potential of the gas.
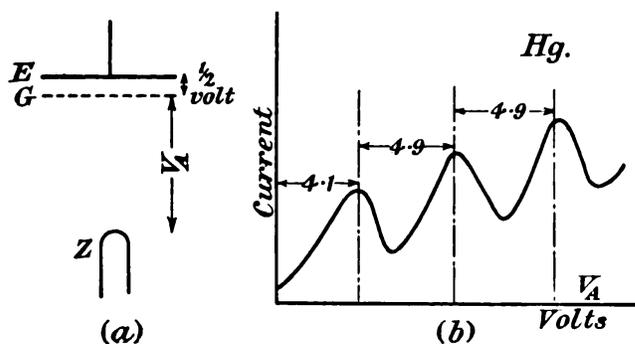
Fig. 26

As V_A is further increased the inelastic collisions occur nearer the filament, and ultimately at such a distance from the grid that the electrons in falling to the grid gain sufficient energy to reach E. The current then rises again.

If, however, V_A is increased to about twice the critical potential, the inelastic collisions occur half way between the filament and the grid, and the acceleration of the electrons in the remaining half of the field will be just sufficient to give them the necessary critical energy again just before reaching G, and the current will again fall. The graph relating the plate current with the potential V_A thus shews a series of peaks, as in Fig. 26b. It is clear that the distance between two peaks gives the critical potential. If the gas has a series of critical potentials each will produce its own set of peaks.

It will be noticed that the distance of the first peak from the origin is distinctly less than that between successive peaks.

This is due to the finite velocity of emission of the electrons, and to the Volta effect, and the difference between the two values (0·8 volt in the diagram) gives the magnitude of these effects for the given apparatus.

This method is not applicable to gases such as oxygen which have a strong electron affinity. The critical potentials for such gases are not known with great certainty.

A few values are given in Table III. Some gases give two ionization potentials. The higher value corresponds to the simultaneous ejection of two electrons from the atom.

TABLE III

Some Critical Potentials (in volts)

Atom or molecule	Ionization potential	Radiation potentials
H_2	15·9	10·8
He	24·6	20·5
N_2	16·7	8·1
O_2	12·8	7·9
Ne	21·5	16·6
Na	5·13	2·1
Hg	10·4	4·9, 5·76; 6·73, 7·73, 8·64, 8·86

The ionization potential measures, as we have seen, the potential difference through which an electron must fall to acquire sufficient energy to ionize the molecule. Since 1 volt is 1/300 e.s.u. and the electronic charge is $4·770 \times 10^{-10}$ e.s.u., the energy of an electron which has fallen through a P.D. of 1 volt is $4·770 \times 10^{-10}/300$ ergs or $\mathbf{1·591 \times 10^{-12}}$ ergs. This forms a very convenient unit of energy in atomic physics, and is now very largely used. Thus we should say that the energy required to ionize a molecule of hydrogen was 15·9 volts or, more precisely, 15·9 electron-volts. This nomenclature causes no confusion, when once its meaning has been clearly understood.

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CHAPTER VI

THE PHENOMENA OF THE DISCHARGE TUBE

37. Phenomena of the discharge in a gas at low pressure. If the discharge takes place between electrodes enclosed in a glass tube containing gas at low pressure, say, from a millimetre or so downwards, some very beautiful and interesting effects are observed. If the potential difference across the tube is not much more than the minimum necessary to maintain a current through the tube the luminosity is at first confined to the region of the two electrodes, the rest of the discharge being dark, as indicated in Fig. 27. As the
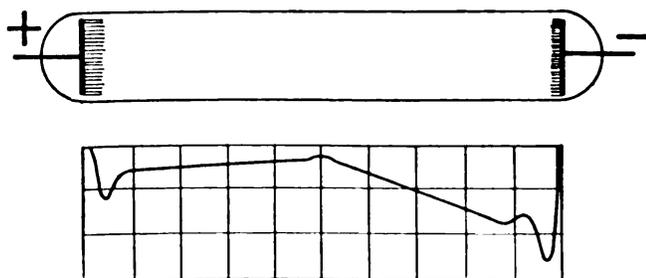
Fig. 27

pressure of the gas is reduced, say, to about one mm. or so of mercury, the two glows extend outward especially that at the positive electrode which now occupies the major portion of the tube. The potential necessary to maintain a current across the tube has now its minimum value.

As the pressure is still further reduced it is seen that the glow near the cathode consists of two parts separated by a dark space. The glow nearest the cathode, covering its surface with a velvety light, is called the *cathode glow*, the other which is much more extensive stretching at low pressures some considerable distance into the tube is known as the *negative glow*. The space between them which is comparatively non-

luminous is the *Crookes dark space*, while the similar region between the negative glow and the positive column is known as the *Faraday dark space*. At pressures of a millimetre or so of mercury the positive column presents a uniform luminosity, but as the pressure is reduced it generally breaks up into a series of bright and dark striae. The typical appearance of a
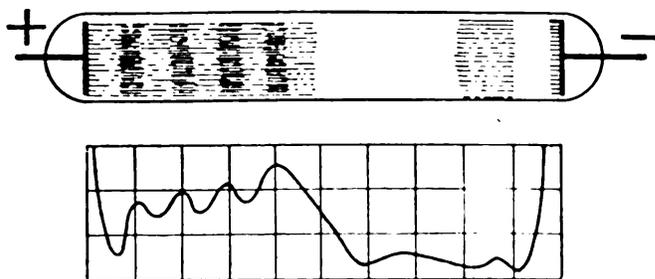
Fig. 28

discharge tube at this stage is represented in Fig. 28, which corresponds to a pressure of about half a mm. in the case of air.

The length of the tube occupied by the phenomena near the negative electrode depends principally upon the nature and pressure of the gas and is independent of the length of the discharge tube. The rest of the tube, however long, is filled by the positive column.
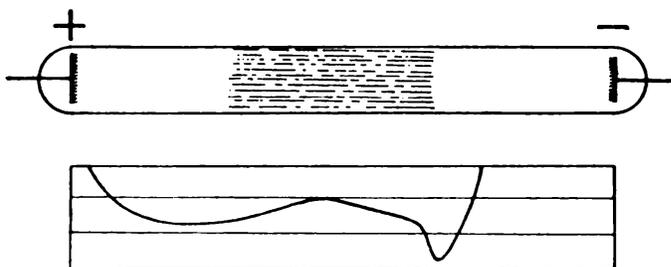
Fig. 29

As the pressure is reduced still further the negative glow and the Crookes dark space increase in length while the positive column contracts towards the anode and at very low pressures is represented only by a feeble glow on the surface of the anode (Fig. 29); at this stage there is no region of constant intensity in the tube. Finally if the exhaustion is pushed to extreme

limits as in a X-ray bulb, the Crookes dark space expands until it fills the whole of the discharge tube which is then entirely dark. At this stage the walls of the glass vessel fluoresce brightly, the fluorescence being bluish with soda glass, and greenish with German glass. The greenish fluorescence is probably due to traces of manganese.

38. Investigation of the intensity of the field in various parts of the discharge. The electric intensity in various parts of the discharge has been investigated by many observers. The most usual way is to insert in the tube a small subsidiary electrode consisting of a fine pointed platinum wire. If there are free ions in the tube and the potential of the wire is less than the potential of the space in its immediate neighbourhood there will be a field in the gas tending to drive ions of the appropriate sign up to the wire. For example if the wire has a smaller potential than the surrounding gas the field will drive up positive ions until the potential of the electrode becomes equal to that of the gas.

The accuracy of the method obviously depends on there being a plentiful supply of ions of both signs in the gas around the wire. If ions of one sign only are present the results may be very misleading. For example supposing only negative ions are present which is practically the case at points in close proximity to the anode, these negative ions will strike the surface of the wire and continue to do so until its negative potential is so high as to prevent by its electric repulsion any further ions from reaching it. As there are no positive ions to neutralize it, it will thus acquire a negative potential which may be considerably higher than that in any part of the original space before the introduction of the wire. Hence at points very near either electrode the results obtained by the exploring wire are apt to be misleading. In the main part of the discharge its results are no doubt sufficiently near the truth.

The method has been applied by means of the apparatus shewn in Fig. 30. The electrodes C and A were kept at a fixed distance apart by means of the glass rod d to which they were both attached. The glass tube containing the electrodes was

much longer than the distance between the electrodes which were connected to terminals passing through the ends of the tube by long wire spirals. A piece of soft iron R attached to one electrode enabled the electrodes to be moved about from one end of the tube to the other by means of a magnet. Two electrodes, e, f, were sealed into the tube, the line joining them being along the axis of the tube, and their distance apart about 1 mm. If the two electrodes are connected to opposite quadrants of an electrometer the deflection indicates the difference of potential between the two points: that is, since ef is constant, it is proportional to the field in the gas in the region of e, f. By sliding the electrodes along this region could be made to coincide with any part of the discharge, and in this way the field in any part of the discharge could be investigated.
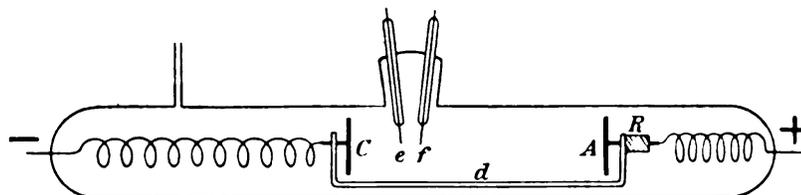
Fig. 30

An ingenious method which does not involve the uncertainties of the previous method is due to Sir J. J. Thomson (1). In this the fact that a beam of cathode rays is deflected by an electric field is made use of. It will be shewn later (§ 44) that the deflection of the rays is proportional to the field through which they pass. The main discharge passes between C and A (Fig. 31), the experimental devices for moving the discharge electrodes being the same as in the apparatus just described. The cathode rays are generated in a side tube T at right angles to the discharge, and pass across the main discharge through a fine hole in the metal ring G which serves as anode. The deflected beam passes down a long tube S falling on a screen at the end of the tube where the deflection of the beam is readily measured. This method has been applied to investigate the field very near the cathode.

The results obtained vary somewhat with the state of the discharge, and are shewn in Figs. 27–29 immediately below the

diagrams of the discharge to which they refer. It will be seen however that they present certain constant features.

Starting at the cathode there is a very strong field in the Crookes dark space which drops with considerable rapidity as we approach the negative boundary of the negative glow where indeed it reaches its minimum value for the tube. The field in general rises again slightly in the negative glow and falls again in the Faraday dark space rising gradually as the edge of the positive column is approached.

If the positive column is uniform or unstriated the field has a constant value until the neighbourhood of the anode is reached
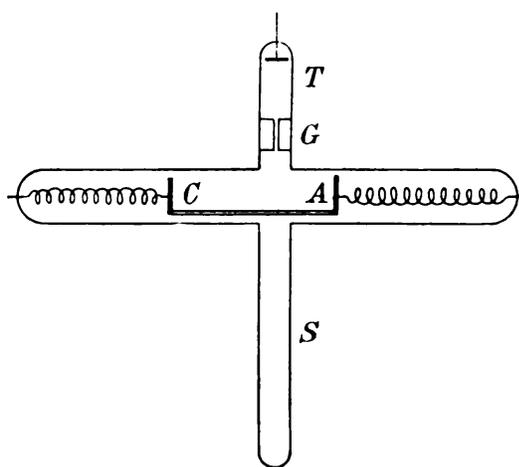
Fig. 31

when there is again a sharp increase in the field accompanied by rapid increase of potential up to the anode. This anode fall of potential is, however, always much less than that at the cathode.

If the column is striated the field shews variations superimposed upon the steady field, being a maximum where the striation reaches its maximum brightness. This is shewn in Fig. 28.

39. Number of ions in various parts of the discharge. The apparatus of Fig. 30 can be modified so as to give the relative number of ions in different parts of the discharge. If the two points e, f are replaced by two small plates, their planes being parallel to the discharge, the current between the plates when some small constant difference of potential is

maintained between them (say, for example, that of a Clark cell), will by (5), § 13, be roughly proportional to the sum of the ions of each kind present in the gas at the given point. In this way by moving the discharge so that various parts of it come between the plates the distribution of ions in the discharge can be found. The results obtained by H. A. Wilson [2] are shewn in Fig. 32. It will be noticed that the number of ions is very small near the anode and again in the Crookes dark space. It rises to a maximum in the negative glow, falls again in the Faraday dark space to rise again in the positive column. If the column is striated the ions are most numerous in the luminous parts and less numerous in the dark parts.

POSITIVE COLUMN   FARADAY DARK SPACE
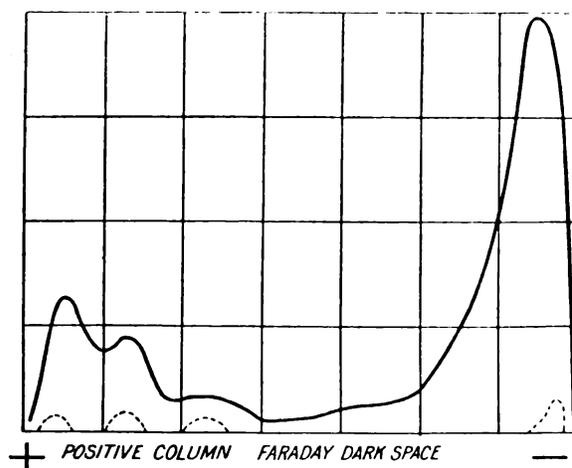
Fig. 32

Later, however, van der Pol [3] has investigated the matter again by a method not involving the use of subsidiary electrodes, with their attendant uncertainties. The discharge tube is placed between the plates of a small parallel plate condenser which forms part of an oscillating circuit, the current in which can be measured by a Duddell galvanometer. If the medium between the plates becomes slightly conducting the current in the circuit diminishes as the conductivity increases. By bringing different parts of the discharge tube successively between the condenser plates the relative conductivities of the different portions of the discharge can be estimated. It was found that if the positive column was unstriated the conductivity along it was constant and somewhat

higher than that in the dark space. If the column was striated the conductivity was found to be a minimum at the bright edge of the striation. This is exactly the reverse of Wilson's result. It is, however, what might be expected from Sir J. J. Thomson's observation that the field is a maximum at this point. A large field would tend to remove the ions from the space more rapidly than a small field, and the ionization and hence the conductivity should be smaller as found by van der Pol.

40. The cathode fall of potential. The potential difference between the cathode and the boundary of the negative glow is called the cathode fall of potential. Owing to the very large field in the Crookes dark space the cathode fall is usually a large fraction of the whole potential difference across the tube. For small currents the discharge passes only from a small area of the cathode covered by the cathode glow. The area of this glow increases with increasing current so that the current density at the cathode remains constant until the glow covers the whole surface of the electrode. The cathode fall of potential remains constant until this stage is reached. If the current is then still further increased the cathode fall increases with the current.

The cathode fall varies with the nature of the electrode and of the residual gas. It is small for the electropositive metals such as magnesium, sodium or potassium, but increases for the less electropositive metals such as platinum or silver. The effect is probably connected with the work which must be done to extract an electron from the metal (§ 59). The cathode fall is smaller for the inert gases, helium neon and argon, than for oxygen or hydrogen.

If the current through the tube is not too large, so that the whole of the cathode is not covered by the cathode glow, Aston has shewn that the cathode fall is directly proportional to the square of the length of the Crookes dark space.

The abrupt change of potential near the anode is much less than that at the cathode and varies little either with the pressure or nature of the gas or the nature of the electrodes. It lies between 18 and 24 volts.

41. Theory of the discharge. The phenomena of the discharge tube can be grasped most readily if we suppose that a steady discharge is already established in the tube, and consider the conditions requisite for its maintenance. Since luminosity in a gas results from the recombination of ions (§ 35) the negative glow must contain a plentiful supply of ions of both signs. Let us take the positive ions first. Some of these will be directed towards the cathode by the existing electric field and, since the intensity in the Crookes dark space is very high will strike the cathode with very high velocities, and with energy corresponding in some instances to a free fall through the full cathode fall of potential. The impact of these particles on the cathode is sufficient to liberate electrons from the surface of the cathode which, in turn, falling through the strong field in the dark space acquire more than sufficient energy to produce fresh ionization in the negative glow. Since the cathode fall of potential is many times greater than the ionization potential of a gas, they will, in fact, attain the necessary energy at quite a short distance from the cathode. The Crookes dark space thus represents the distance an electron travels before making a collision with a gas molecule, that is to say it is the mean free path of the electrons at the pressure existing in the tube.

The negative electrons owing to their small mass, and consequent high acceleration, are rapidly removed from the Crookes dark space leaving a positive space charge due to the much more slowly moving positive ions from the negative glow. This accumulation of free positive charges in proximity to the cathode, which is of course negatively charged, maintains the high value of the electric field which is characteristic of this part of the discharge.

The positive ion bombardment of the cathode can be verified by using a perforated cathode. A stream of positive particles then emerges from the hole into the space behind the cathode, where it is visible, if the gas pressure is not too low, by the luminosity it excites in the gas. The investigation of this positive stream is described in a later section (§ 49).

The negative glow is produced by the recombination of the ions produced by the electrons from the cathode. As, however,

the cathode is screened by the large positive space charge in the Crookes dark space, the field in the negative glow is very small. Thus when the initial energy of the electrons is spent they are no longer able to gain fresh energy from the field to produce ionization by collision. Ionization thus ceases, luminosity disappears, and we have the commencement of a new dark space, the Faraday dark space.

The residual field is, however, sufficient to direct the electrons across the Faraday dark space, and these electrons form a negative space charge which increases the field between the dark space and the anode. The field thus increases steadily through the dark space and finally attains a sufficiently high value to enable the negative ions again to ionize by collision. Hence luminosity is restored and we have the beginnings of the positive column. As the field in the positive column remains practically uniform, ionization by collision of the negative ions will occur along its whole length and we shall get a uniform column of light. If, however, there happens to be an accumulation of positive ions at any point, this may produce a local fall of field and the discharge will cease to be luminous at that point. Just as in the case of the Faraday dark space this loss of ionizing power will be attended with an accumulation of negative electricity which will restore the field to its normal value. Thus a series of striae may be set up in the positive column, as is often found to be the case. The non-luminous parts of the striae on this hypothesis are thus a repetition of the phenomena of the Faraday dark space.

The theory outlined above accounts satisfactorily for the main features of the low pressure discharge, but requires considerable amplification when we come to details. We have, for example, seen that the discharge is maintained by the large field in the Crookes dark space, but this field is itself a consequence of the discharge. One result of this is that a discharge when once started can be maintained with a much smaller potential difference than that required to start the discharge. For a very complete summary of the subject the reader may be referred to Thomson's *Conduction of Electricity through Gases*.

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CHAPTER VII

CATHODE RAYS AND POSITIVE RAYS

42. Cathode rays. In addition to the glows described in the previous chapter close observation of the discharge tube will usually reveal another phenomenon, having the appearance of a stream of faint blue light proceeding normally from the cathode and passing along the axis of the tube. At moderate pressures this ends in the negative glow, but if the pressure is reduced until the Crookes dark space fills the whole tube, the stream impinges on the opposite wall of the discharge tube, its point of impact being marked by a greenish fluorescence on the surface of the glass. The fluorescence can be much increased by coating the glass with a layer of zinc blende, or willemite. The blueish light which marks the track of the rays through the gas is also a fluorescence effect and disappears when the gas pressure is greatly reduced.

The cathode rays are actually a stream of electrons proceeding from the cathode, as already described in § 41. The nature of the rays was, however, the subject of a long controversy. Goldstein, to whom the name is due, regarded them as some kind of disturbance in the ether. Crookes suggested that they were material in nature. As it was the researches made in connection with this divergence of opinion which resulted in the discovery of the electron, and the atomic nature of electricity, it will be worth while to discuss the evidence in some detail.

(1) *The rays travel in straight lines.* This can readily be shewn by constructing a discharge tube of the form of Fig. 33, in which some obstacle, generally in the form of a mica cross, is placed in the path of the rays. A shadow of the obstacle appears in the centre of the fluorescence caused by the rays on the further boundary of the tube.

(2) *The rays emerge normally from the cathode.* If a tube

such as that just described is constructed with a large plane cathode and a small obstacle such as a wire is placed near it a sharp shadow of the wire appears on the further wall of the tube without any sign of penumbra around it. If the rays were given off in all directions from the cathode (as, for example, light is emitted from a uniformly luminous disk) no shadow of the wire would be seen. Similarly if the cathode is concave the cathode rays come to a focus at some point along the axis. Owing to the mutual repulsion of the rays the focus is generally somewhat beyond the geometrical centre of the concave surface. This property of the rays is made use of in the construction of X-ray tubes.
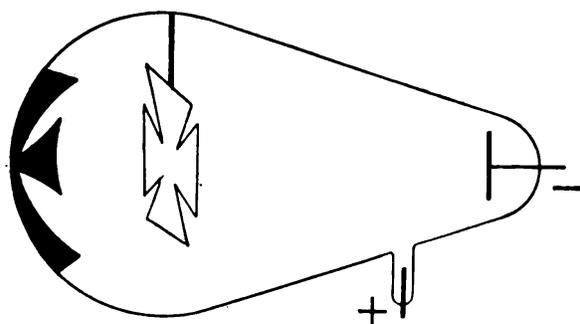
Fig. 33

(3) *The rays can penetrate small thicknesses of matter* such as sheets of aluminium foil or gold leaf without producing perforations in the metal. This discovery, which was due to Hertz, can be demonstrated by constructing a "window" of thin aluminium leaf in the end of the tube struck by the rays. The passage of the rays through the foil is demonstrated by luminous blue streamers in the air on the far side of the leaf. These are sometimes known as *Lenard rays*.

(4) *The cathode rays are deflected by a magnetic field.* If an ordinary bar magnet is held near a discharge tube the deflection of the rays by the magnet is made evident by the movement of the fluorescent spot which they produce on the further boundary. We shall return to this important point later. The direction of the deflection shews that the cathode rays experience the same deflection as would be experienced by a flexible conductor coinciding with the path of the rays and carrying

an electric current, the direction of the current being towards the cathode.

(5) *The rays carry a negative charge.* This was demonstrated by Perrin [1] in 1895. A slight modification of Perrin's original experiment is shewn in Fig. 34.

The cathode A is contained in a small side tube which also contains the anode B. The rays starting from the cathode pass through a small slit in a brass plate C across the larger bulb D, where they manifest themselves by phosphorescence of the walls of the bulb. Enclosed in this bulb but out of the direct line of fire of the cathode stream is a small cylindrical vessel E having a small aperture facing the centre of the bulb. This vessel is carefully insulated and connected by the electrode
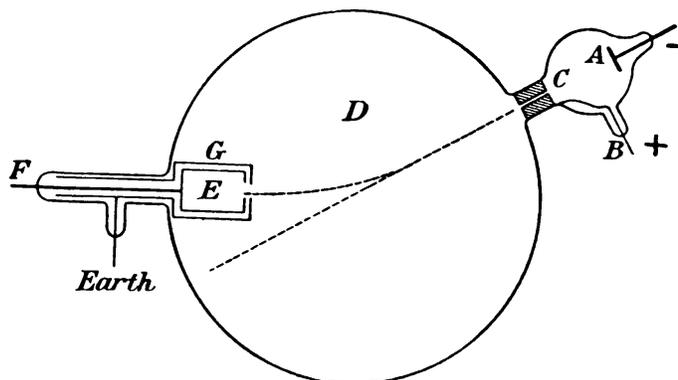
Fig. 34

F to an electrometer. The vessel is screened from the powerful electrostatic disturbances in the discharge tube by surrounding it with a nearly closed metal vessel G which is connected to earth. This arrangement forms what is known as a *Faraday cylinder*.

When the discharge was passed the inner cylinder received a very small negative charge. If, however, the cathode rays were deflected by a magnet so as to fall on the openings in the Faraday cylinder a very large negative charge was recorded by the electrometer. This charge increased for some little time but finally became constant owing to the fact that the cathode rays turned the residual gas in the discharge tube into a partial conductor. The charge on the vessel increased until the loss

by conduction through the ionized gas (which is roughly proportional to the potential of the Faraday cylinder) was equal to the gain from the cathode stream. This experiment proves conclusively that a negative charge is a necessary accompaniment of the cathode stream.

(6) *The rays are deflected by an electrostatic field.* This effect, which was a necessary consequence of the theory that the rays consist of charged particles, was for some time sought for in vain. The results just described gave a clue to the cause of the failure. We have seen that the cathode rays ionize the gas through which they pass, thus making it a partial conductor. In fact they move down the discharge tube through a sort of conducting cylinder of their own construction, and are thus screened from the action of any electric field applied to the tube. By exhausting the tube very completely of the residual gas J. J. Thomson[2] in 1897 succeeded in partially eliminating this effect and demonstrated the direct deflection of the cathode rays by an electrostatic field. The direction of the deflection shewed that the particles in the rays were negatively charged.

(7) In addition to these effects the cathode rays can exert mechanical pressure, and convey very considerable amounts of kinetic energy. A metal obstacle placed in the path of the rays quickly becomes incandescent, especially if the rays are focused upon it by using a concave cathode in the way already described. If the discharge is very powerful, portions of metal may be actually torn out of a solid plate by the impact of the rays.

A consideration of these facts leaves no doubt that the cathode rays consist of negatively charged particles. Determinations of the mass of these particles (§ 45) shewed (i) that they were much lighter than the lightest known atom and (ii) that all the particles, from whatever source, had exactly the same mass. They were given the name of "electrons."

43. Motion of a charged particle under the action of a magnetic field. Let us suppose that we have a stream of electrified particles each carrying a charge e and moving with velocity v along some line OX. Let us assume that the particles follow each other along the track at equal short intervals ∂t, so

that they are separated by distances ∂s given by $\partial s = v \cdot \partial t$. The current i along OX is, by definition, the charge conveyed per second past any point on OX; that is it is equal to $e/\partial t$. By Laplace's equation the mechanical force on a length ∂s of this current when placed in a magnetic field of strength H is $H \cdot i \cdot \partial s \sin \theta$, where θ is the angle between the direction of the field and that of the current. This becomes $Hev \sin \theta$, on substituting for i. But since a length ∂s of the track contains only one particle, this must be the mechanical force acting on that particle. Hence the mechanical force on the particle due to the magnetic field H is equal to

$$Hev \sin \theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

It acts at right angles to the plane containing the path of the particle and the direction of the field. It should be noted that both H and e are measured in the e.m. system of units.

The magnetic equivalence of a moving electric charge to a current was demonstrated experimentally by Rowland. A large insulating disk was furnished near its circumference with a number of conducting studs which could be charged to a known value by induction from a neighbouring charged plate. On rotating this disk at a rapid rate a magnetic field was produced, which was found to be, within the limits of experimental error, the same as that which would have been produced by a current of strength qn moving in a circuit coinciding with the path of the studs where q is the total charge on the studs, and n the number of revolutions of the disk per second.

Suppose for simplicity that the particle is projected at right angles to the magnetic field (the mechanical force in this case is equal to Hev). Since the mechanical force is always at right angles to the path of the particle the speed will remain unaltered. Let ρ be the radius of curvature of the path of the particle under the action of the field, and m its mass. The centrifugal force is equal to $\dfrac{mv^2}{\rho}$ and for equilibrium this must be balanced by the mechanical force due to the field. Hence

$$\frac{mv^2}{\rho} = Hev,$$

$$\rho = \frac{m}{e}\frac{v}{H}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

As v is constant the radius of curvature is constant, that is, the particle describes a circle of radius $\dfrac{m}{e}\dfrac{v}{H}$ in a plane at right angles to the magnetic field.

If the velocity of the particle has a component parallel to the magnetic field this component will remain unaltered since there is no mechanical force acting on the particle along this direction, and the particle thus moves forward through equal distances in equal times along this line, while at the same time describing a curved path around it. Its path is thus a helix, the axis of which is parallel to the field. If θ is the angle between the direction of projection of the particle and the field we have

$$\frac{mv^2}{\rho} = Hev \sin \theta,$$

$$\rho = \frac{mv}{eH \sin \theta} \, . \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (38)$$

Since v and θ are constant ρ is constant and the path of the particle is a helix wound on a circular cylinder with its axis parallel to the magnetic field and of radius $r = \rho \sin^2 \theta = \dfrac{mv \sin \theta}{eH}$.

When $\theta = \dfrac{\pi}{2}$ this helix contracts into a circle, the case we have already considered.

In the general case, when the field is not uniform, the particles will describe helices of varying amplitudes about the lines of the magnetic field.

44. Motion of a charged particle under the joint action of electric and magnetic forces. If the particle is moving in an electric field of intensity X it will experience a force equal to Xe, and in the absence of any resisting medium, as for example when it is freely moving through a vacuum, it will have an acceleration of Xe/m in the direction of the electric field.

If there is also a magnetic field it has, as we have seen, an acceleration $H (e/m) v \sin \theta$ due to the magnetic field H, and its actual acceleration at any instant is the resultant of these two. The path will evidently depend on the magnitudes of the

velocity, the magnetic, and the electric fields, and on their relative directions. The general solution has been obtained. It will, however, be sufficient to consider the cases which are of practical importance.

CASE 1. *The magnetic and electric fields act in the same line and the particle is projected at right angles to them.* In this case since the acceleration due to the magnetic field is at right angles to the field while that due to the electrostatic field is parallel to the field the two accelerations are at right angles to each other, and similarly the two deflections produced will also be at right angles to each other and to the path of the particle. Hence if the original velocity of the particle is so great that we may neglect the small change in its speed produced by the action of the electrostatic field on the particle, the deflection of the particle produced by one of the fields in the direction in which it acts will be independent of the action of the other. The final displacement of the particle will thus be the resultant of the two displacements which each would produce separately. For example if the fields are arranged with their lines of force vertical, the electric field if acting alone would produce a vertical displacement of the particle of, say, y cm., while the magnetic field alone would produce a horizontal displacement of, say, x cm. Then if they are both acting together the particle will by their joint action be displaced to a position the co-ordinates of which will be x, y. This is the arrangement most generally employed in experimental work.

CASE 2. *The electric and magnetic fields are at right angles to each other, and the particle is projected at right angles to the two fields.* In this case the mechanical force due to the two fields acts along the same line, and at right angles to the original velocity v. Thus the resultant force on the particle is equal to

$$Hev - Xe,$$

assuming that the fields are so arranged that the forces are in opposite directions, and acts along the direction of the lines of force of the electric field. This force will be zero if

$$Hev - Xe = 0$$

or $\qquad\qquad\qquad v = X/H. \quad . \quad . \quad . \quad . \quad . \quad (39)$

The motion of the particle will in this case be unaltered by the joint action of the electric and magnetic fields, an important relation, which has often been used to determine v.

CASE 3. *A charged particle, initially at rest, is exposed to the joint action of electric and magnetic fields at right angles to each other.* Suppose the electric and magnetic fields coincide with the axes of X and Z respectively. The particle being charged will begin to move in the direction OX. As soon, however, as it has acquired a velocity it will be acted upon by the magnetic field, and its path will therefore be modified.

Suppose that at any instant the component of its velocity parallel to the electric field is dx/dt. There is then a mechanical force acting on the particle at right angles to the magnetic field and to the electric field, that is, in the direction of OY, and equal by (36) to $He\,dx/dt$. Hence

$$m\frac{d^2y}{dt^2} = He\frac{dx}{dt}. \qquad \ldots \quad (40)$$

The electric force along OX is equal to Xe, and there will also be a mechanical force in this direction due to the magnetic field equal to $He\,dy/dt$, where dy/dt is the component of the velocity of the particle along OY. Hence

$$m\frac{d^2x}{dt^2} = Xe - He\frac{dy}{dt}. \qquad \ldots \quad (41)$$

The solution of equations (40) and (41) is

$$\left.\begin{aligned} x &= \frac{X}{\omega H}(1 - \cos \omega t) \\ y &= \frac{X}{\omega H}(\omega t - \sin \omega t) \end{aligned}\right\}, \qquad \ldots \quad (42)$$

where
$$\omega = \frac{He}{m}.$$

These are the equations to a cycloid, the curve traced out by a point on the circumference of a circle when the latter rolls along a straight line. The path therefore consists of a series of loops as shewn in Fig. 35, where the electrons are supposed to be liberated from the surface of the plate CD. It is obvious that the particle can never reach more than a certain distance in the direction of the electric field, and cannot

penetrate beyond the plane LL which is the common tangent to the curves. Since the minimum value of cos ωt is -1 this maximum distance is equal to $\dfrac{2X}{\omega H}$ or $\dfrac{2X}{H^2}\dfrac{m}{e}$.

Thus if AB and CD are two parallel plates, and an electric field of strength X is established between them, while a uniform magnetic field H is applied at right angles to the plane of the paper, then if ions are formed on the surface of the negative plate CD, either by the action of ultra-violet light, or by raising it to incandescence or otherwise, no charge will be received by the upper plate until it reaches the position LL in the diagram, at a distance d from the lower plate given by

$$d = \frac{2X}{H^2}\frac{m}{e} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (43)$$
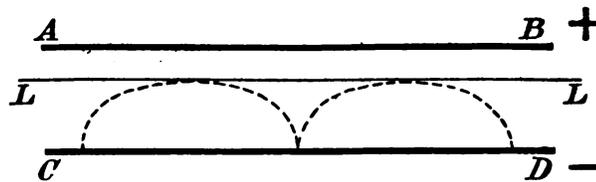
Fig. 35

At any smaller distance the whole of the ions will reach the upper plate which will thus receive a charge.

The arrangement has been used to determine the ratio e/m for photoelectrons (§ 64) and thermions (§ 57).

45. Thomson's method (2) of determining e/m and v for cathode rays. The apparatus used is shewn in Fig. 36. The cathode E is a small aluminium disk, the anode F being placed in a side tube. A brass disk pierced with a small slit along the axis of the tube limits the rays to a narrow pencil, and to narrow the pencil still further a second brass disk similarly pierced but with a still finer slit is placed at B some distance from A. A very fine flat pencil of rays is thus obtained which in the absence of any deflecting fields falls on a fluorescent screen of barium platino-cyanide or powdered willemite at the far end of the tube.

The electric field is applied by two parallel plate electrodes *J*, *K*, their planes being parallel to the path of the rays. The lower plate is earthed while the upper is charged to a suitable potential by means of a large number of small accumulator cells. The field can thus be calculated if the distance between the plates is known. The deflection produced by the field on the negative particles of the rays is in the direction of the field, that is, in the plane of the paper.
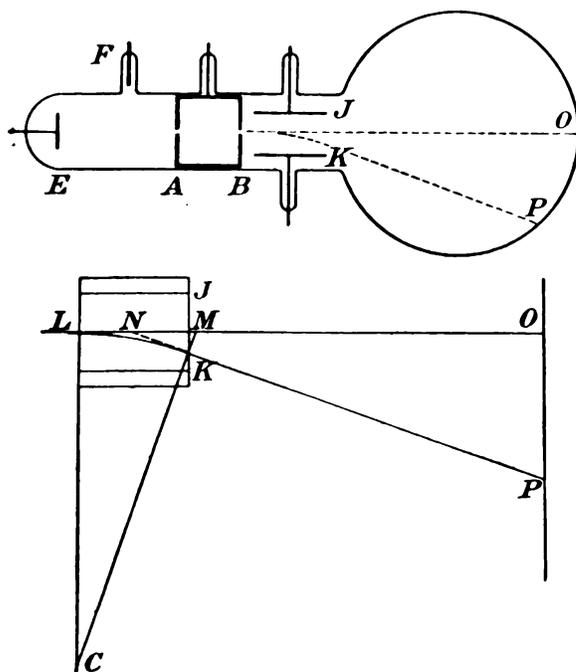
Fig. 36

The magnetic field is applied by a small electromagnet placed with its poles at right angles to the plates *J*, *K*. Since the magnetic deflection is at right angles to the magnetic field the magnetic deflection is also in the plane of the paper.

Suppose now that both the magnetic and the electric fields are uniform and coterminous being applied over a short length *LM* of the path of the particles. The two fields produce deflections in the same straight line and by properly adjusting the sign and intensity of the electric field these two deflections may be made to neutralize each other, a condition the fulfilment of which can be ascertained by the return of the spot of light

on the fluorescent screen to its undeflected position. Under these conditions we have by (39)

$$v = X/H.$$

To find e/m for the particles we must now measure the deflection produced either by the magnetic or the electric field acting alone. Taking the former case the path of the particles while in the uniform field is bent into the arc of a circle of radius ρ given by

$$\frac{1}{\rho} = \frac{He}{mv}.$$

On emerging from the field at K the particles will continue to move along the tangent to the circle at K. The angle PNO through which the rays are deflected is by the geometry of the figure equal to the angle LCM, that is, to LM/ρ. Thus $\dfrac{LM}{\rho} = \dfrac{OP}{ON}$ from which ρ can be determined when the deflection and the dimensions of the apparatus are known. Since the magnetic field and the velocity v are both known, e/m can be calculated.

The electrostatic deflection can also be calculated. The acceleration produced in this case is parallel to the field, that is, perpendicular to LO and equal to Xe/m. If the time during which the particle is in the field is t this produces a velocity $X(e/m)t$ or $\dfrac{Xe}{m} \dfrac{LM}{v}$ in a vertical direction. On leaving the field the particle moves with these two velocities. Hence if P' is the deflected position of the rays OP'/OM is equal to the ratio of the horizontal to the vertical velocity, that is, to

$$\frac{Xe}{m} \frac{LM}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad (44)$$

which can be evaluated for e/m since the field X and the velocity v are known.

It is obvious that under the conditions of the experiment neither of the fields can be perfectly uniform owing to the disturbances near the edges of the plates and the poles. A correction can be applied as follows.

Since the curvature of the path is small we have approximately, if x is the co-ordinate of the particle measured along

the undisturbed path LO and y the co-ordinate at right angles to it, $\dfrac{1}{\rho} = \dfrac{d^2y}{dx^2}$. Hence

$$\frac{d^2y}{dx^2} = \frac{He}{mv},$$

$$\therefore \quad OP = \frac{e}{mv} \int_0^{BP} [\textstyle\int_0^x H dx]\, dx. \quad . \quad . \quad . \quad (45)$$

Similarly the electric deflection OP'

$$= \frac{e}{v^2 m} \int_0^{BP} [\textstyle\int_0^x X dx]\, dx. \quad . \quad . \quad . \quad (46)$$

If these integrals are evaluated, which can be done when the distribution of the two fields is known, we have two equations for determining e/m and v.

46. Kaufmann's method [3] **of determining** e/m. A somewhat different method was used by Kaufmann. In order to obtain a very uniform magnetic field of calculable value he enclosed the whole of the path of the cathode rays from the limiting aperture to the screen in a uniformly wound solenoid (Fig. 37). The magnetic observations could thus be made with considerable accuracy. Instead of measuring the electrostatic deflection of the rays he assumed that the energy of the cathode particles was that due to a fall through the whole difference of potential between the cathode and the anode, that is, to Ve where V is the difference of potential between the electrodes of the discharge tube. V was measured by an electrostatic voltmeter.

Fig. 37

This assumption implies that the effect of the collisions of the rays with the residual gas is negligible. To test this point experiments were made for many different pressures of the gas in the tube. These different experiments
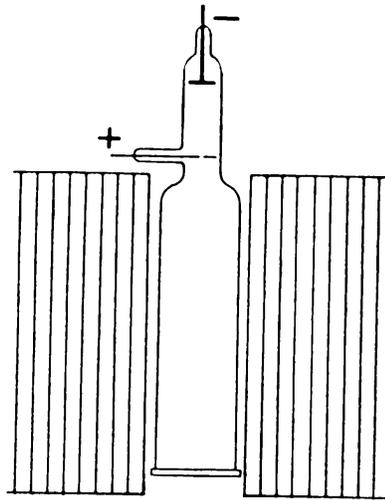
were found to yield exactly the same results and hence, since the collisions would be relatively more frequent at high pressures than at low, Kaufmann's assumption seems justifiable. Hence we may write $\frac{1}{2}mv^2 = Ve$;

$$v^2 = 2V\frac{e}{m}. \quad \ldots \ldots \quad (47)$$

A very careful investigation of the magnetic field was made and the integral (45) evaluated. In this way Kaufmann obtained a value for e/m of $1\cdot77 \times 10^7$ absolute e.m.u. per gm.; a value quite near the best recent observations.

47. Direct measurement of the velocity of cathode rays. The velocity of the cathode rays has also been determined by direct experiment by Wiechert [4]. The principle of the method
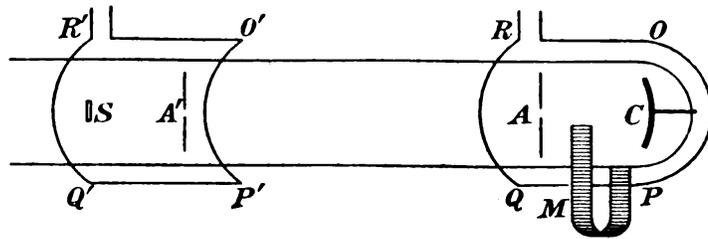
Fig. 38

is as follows. The cathode rays from a cathode C (Fig. 38) fall normally on a hole in a screen A, and through another hole in a screen A' on to a narrow fluorescent plate S. The rays are then deflected by a permanent magnet M placed near the cathode so that they all fall on the solid part of A, the screen S in consequence being dark. A circuit $OPQR$ carrying a rapidly alternating current such as that obtained by the discharge of a condenser is brought near AC, thus producing a rapidly alternating magnetic field. This will set the beam of rays swinging like a pendulum at right angles to the field, and if the force is sufficiently great the oscillations will be sufficiently large to reach to the hole in A. Thus rays will pass through intermittently, and the screen S will again become bright.

A second circuit $O'P'Q'R'$ is now brought up near $A'S$ carrying the same alternating current as that in the circuit

OPQR. If the time taken by the rays to pass from *A* to *S* is zero the two magnetic fields will produce at any instant fields of the same sign and intensity; hence the rays between *A'* and *S* will suffer the same deflection as between *C* and *A* and will be deflected off the screen which will thus be always dark. If, however, the time taken by the rays to pass from *A* to *S* is such that the current has changed its phase by one-quarter of a period during that time there will be no current in *O'P'Q'R'* when the rays reach *A'*. Thus the rays will suffer no further deflection and the screen will become bright.

Thus the screen will become bright if the time taken for the rays to describe a distance *AS* is equal to the time taken for the current in the wires to change by one-quarter of a whole period, that is, to $\frac{1}{4}L/c$, where *c* is the velocity of light and *L* the wave length of the current vibrations. The latter can be determined experimentally by any of the methods for determining wave lengths used in wireless telegraphy. Hence finally

$$v = AS \frac{4c}{L}.$$

The values thus obtained were of the order 3×10^9 cm./sec. or about one-tenth of the velocity of light. This result is of importance as proving directly that the cathode rays do not travel with the velocity of light and thus are not ether pulses. By substituting the measured value of *v*, obtained in this way in equation (47), the method can also be used to give a value for *e/m* for the particles.

48. Numerical value of *e/m*. Experiments by one or other of the methods outlined above have been made using discharge tubes with electrodes of many different metals, and containing residual gases of many kinds and at different pressures. All give substantially the same value for *e/m*, shewing that negatively charged particles of this kind could be produced from any kind of matter and were thus presumably a constituent part of all kinds of matter. Experiments on the principles outlined above have also been made on negative particles from other sources, such for example as a hot wire (§ 57), the action of ultra-violet

light on metals (§ 64), and from radioactive substances (§ 111). These also gave identical values for e/m. Modern theory enables us also to calculate values for this important ratio from the Zeeman effect (§ 151) and from the hydrogen and helium spectra (§ 143). A few of these numerous determinations are collected in Table IV. These results leave no doubt of the existence of the electron as a universal particle common to all kinds of matter, the mass and charge of which are independent of its mode of origin.

Recent observations, made with the utmost refinements, seem to agree in giving a value of e/m for the electron of $\mathbf{1 \cdot 760 \times 10^7}$ **e.m.u. per gm.** to an accuracy of about 1 in 1000. Taking e as $1 \cdot 590 \times 10^{-20}$ e.m.u., the mass of the electron is $9 \cdot 03 \times 10^{-28}$ gm.

TABLE IV

e/m for electrons from different sources

Observer	Source of electrons	e/m in e.m.u. per gm.
Classen	Cathode rays	$1 \cdot 775 \times 10^7$
Classen	Heated CaO	$1 \cdot 776 \times 10^7$
Dushman	Tungsten filament (§ 61)	$1 \cdot 76 \ \times 10^7$
Alberti	Ultra-violet light (§ 63)	$1 \cdot 756 \times 10^7$
Bucherer	Slow β rays (§ 113)	$1 \cdot 763 \times 10^7$
Perry and Chaffee	Cathode rays	$1 \cdot 761 \times 10^7$
Kirchner	Cathode rays	$1 \cdot 759 \times 10^7$
Babcock	Zeeman effect (§ 151)	$1 \cdot 761 \times 10^7$
Houston	H and He spectrum (§ 143)	$1 \cdot 761 \times 10^7$

The ratio of the mass to the charge for a hydrogen ion (or proton), i.e. the electrochemical equivalent of hydrogen is $1 \cdot 044 \times 10^{-4}$ gm. per e.m.u. The ratio of the mass of the proton to that of the electron is thus $(1 \cdot 044 \times 10^{-4}) \times 1 \cdot 760 \times 10^7$ or 1839. The electron thus has a mass which is very small compared with that of the lightest known atom.

49. The positive rays. Thomson's experiments. We have already seen that if the cathode of a discharge tube is pierced by a narrow hole, streamers appear behind the cathode. These streamers are formed by particles which travel from the discharge

towards the cathode, and which are, therefore, positively charged. They consist of atoms and molecules of the various gases present in the discharge tube, carrying positive charges which are either numerically equal to, or some small integral multiple of, the electronic charge.

The investigation of these particles proved to be a matter of some difficulty. Positive rays, owing to their relatively large mass, produce intense ionization in the residual gas in the tube. By combination with the negative electrons so liberated the particles may lose some or all of their charge, or may even
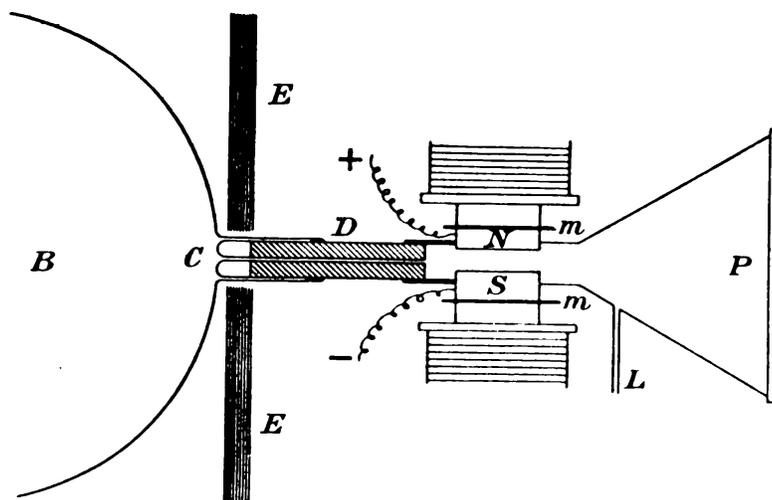
Fig. 39

acquire a negative charge. Also in any collision between a positive particle and a molecule of the residual gas it may easily be that it is not the original particle but the molecule struck which continues in the course of the rays. Should these effects occur when the particle is already in the deflecting fields, the deflection obtained will correspond neither to one kind of particle nor the other, and some very puzzling and misleading results may be obtained. The effect could be reduced by working at a very low gas pressure; on the other hand, if the pressure is too low no discharge can pass at all.

The difficulties were overcome by J. J. Thomson[5] with an apparatus, one form of which is shewn in Fig. 39.

7-2

The discharge takes place in the bulb B of some 4 litres capacity as the discharge passes more readily in a large volume than in a confined space. The cathode C is an aluminium rod pierced by an axial copper tube of 1/10th mm. or even 1/100 mm. diameter.

The tube is surrounded by a soft iron cylinder D, to screen it from stray magnetic fields which would deflect the rays and so cause them to strike the sides of the tube. The main discharge is similarly shielded by soft iron screens E, E. The anode is not shewn; its position is immaterial. The cathode is water cooled, to remove the large quantities of heat developed there by the discharge, and so preserve the numerous wax joints in this part of the apparatus from being melted.

The fine copper tube serves a double purpose. In the first place it produces a very fine pencil of rays, thus giving a minute and well defined spot on the fluorescent screen or photographic plate at P. In the second place it acts as a fairly efficient separator of the discharge tube from the measuring apparatus or camera. Diffusion takes place very slowly along a fine tube, particularly at the low pressures employed in these experiments. Thus by feeding the gas very slowly into the bulb, and removing it as rapidly as possible from the camera through the tube L, it is possible to have the camera at a really high vacuum, while the pressure in the bulb is sufficiently large to enable the discharge to pass. This device is essential to accurate measurement of positive ray deflections, and is embodied in the apparatus of later experimenters.

To measure the ratio of the mass to the charge for the mixed beam of positive rays, the method of parallel fields (§ 44) was employed. The pole pieces, N, S, of a small electromagnet are let into the sides of the apparatus, and are insulated from the core of the magnet by thin strips of mica m, m. The pole pieces can thus be charged, by a battery of accumulators, to any required potential difference, and can be used for applying the electrostatic as well as the magnetic field. The electrostatic deflection is in the plane of the diagram, the magnetic deflection is at right angles to it.

The deflections can be observed visually on a willemite screen,

at P, or can be made to record themselves on a photographic plate which can be let down, without breaking the vacuum, in front of P. Positive particles, like cathode rays and X-rays, affect a photographic emulsion in the same way as light, and a point struck by the particles shews as a black dot after development.

50. Positive ray parabolas. The equations for the deflection of a particle of charge E and mass m in an electric or a magnetic field have been developed in § 44. Taking either the approximate calculations, or the more elaborate formulae of (45) and (46) we have

$$\left.\begin{array}{l} \text{Electrostatic deflection } x = k_1 \dfrac{E}{m} \dfrac{X}{v^2} \\[2mm] \text{Magnetic deflection } \qquad y = k_2 \dfrac{E}{m} \dfrac{H}{v} \end{array}\right\}, \quad . \quad . \quad (48)$$

where k_1 and k_2 are constants which depend only on the geometry of the apparatus, and can be evaluated if its dimensions are accurately known. Combining these equations we have

$$\frac{y}{x} = \frac{k_2}{k_1} \frac{H}{X} v, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$$\frac{y^2}{x} = \frac{k_2^2}{k_1} \frac{H^2}{X} \frac{E}{m} . \quad . \quad . \quad . \quad . \quad (50)$$

If the fields are kept at a constant value, and if E/m is constant, then by (50) $y^2/x =$ constant, which is the equation to a parabola. Thus all particles, no matter what their velocity, which have the same value of E/m will lie on a single parabola.

The maximum velocity which a particle can acquire in the discharge is that corresponding to a free fall through the full potential difference V between the anode and cathode, and is given by $VE = \frac{1}{2}mv^2$. Since the electric deflection is given by $x = k_1 \dfrac{E}{m} \dfrac{X}{v^2}$ we see that the minimum deflection x_0 is given by

$$x_0 = \tfrac{1}{2}k_1 \frac{X}{V},$$

and is the same for particles of all kinds. If every particle entered the fields with the maximum energy each set of particles in the beam would be deflected to some definite spot on the ordinate

through x_0. As, however, the particles do not all originate at the anode, but in parts of the discharge nearer the cathode, many will not have fallen through the full potential difference V, and will thus have less than the maximum velocity; others will have lost energy in collisions with the residual gas molecules. The spots will thus be drawn out into a series of parabolic arcs, terminating on the ordinate through x_0.

Owing to the large number of particles which lose their charges before entering the deflecting fields, there is always intense blackening and diffusion round the point corresponding to the undeflected beam, and it is impossible to determine its position accurately. The magnetic field is, therefore, reversed half way through the experiment. This reverses the magnetic deflection, and gives a repetition of the parabolic arcs on the lower half of the picture. On development the plate will present the appearance shewn in Fig. 40, which represents the case of two sets of particles. This theoretical diagram may be compared with Fig. 41 (Plate II), which is reproduced from one of J. J. Thomson's plates.

51. Positive Ray Analysis. Equations (48) shew that the lightest particles will be the most deflected. Evaluating the constants k_1, k_2 for the apparatus it was found that the value of E/m for the most deflected parabola was 10^4 e.m.u. per gm. This is practically identical with the value for a hydrogen ion in solution. We may identify the corresponding particles as hydrogen atoms with a single electronic charge. Other particles may be identified most conveniently by direct comparison with this line. Draw any ordinate cutting the two parabolas (Fig. 40) in p, p', and q, q'. Then

$$\frac{(pp')^2}{(qq')^2} = \frac{(2y_1)^2}{(2y_2)^2} = \frac{y_1{}^2/x}{y_2{}^2/x}$$

(since x is the same for both)

$$= \frac{E_1/m_1}{E_2/m_2}.$$

Thus, if all the particles carry the same charge, we have

$$m_2/m_1 = (pp')^2/(qq')^2. \quad . \quad . \quad . \quad . \quad (51)$$

Matters are not quite as simple as this. A particle may lose more than one electron in the discharge and thus enter the fields with more than one positive charge. A particle which carries n times the normal charge will behave in the same way as a particle with a single charge and $1/n$th of the mass. Thus a doubly charged carbon monoxide molecule would give a parabola identical with that of a singly charged nitrogen atom, and it is not always possible to discriminate between such cases. In other instances the positive particles are not merely neutralized in passing through the ionized gas in the copper tube, but may even take
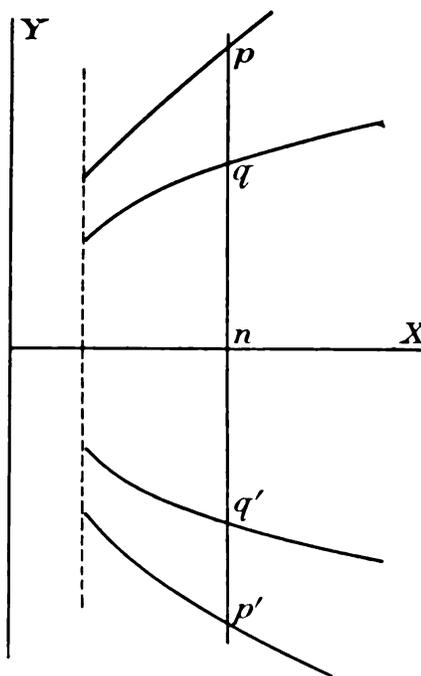
Fig. 40

up an extra electron, thus passing into the deflecting fields with a negative charge. These give rise to parabolas on the negative side of the Y axis. These negative parabolas are very common with elements of an electronegative character such as oxygen, and the halogens. Strangely enough they are also formed by hydrogen atoms. They have never been observed with nitrogen or helium.

The positive rays are always made up of atoms or molecules of the elements and compounds contained in the discharge tube. The method can, therefore, be employed to make a qualitative analysis of gases in the tube. The method is, for some gases, more sensitive than the spectroscopic method; it is possible for example to detect the helium present in 1 c.c. of air, an amount of the order of four millionths of a cubic cm. Some substances, however, seem to enter the positive rays only with difficulty. The metals, with the exception of mercury, are noticeably absent. On the other hand, owing to the fact that the particles register themselves on the plate in considerably less than one

millionth of a second, temporary combinations of atoms of extreme instability are often detected. Thus with methane (CH_4) in the tube parabolas are formed not only by methane itself, and its constituents, carbon and hydrogen, but also by the unstable compounds CH, CH_2, and CH_3 which are not otherwise known.

The uniqueness of the method, however, lies in the fact that it measures directly the masses of individual atoms. Chemical methods give only the average mass of the atoms of an element, the assumption being made that all atoms of the same element are identical. Thomson shewed that the neon line (atomic weight 20) is always accompanied by a fainter line corresponding to an atomic weight of 22. The substance forming this line is inseparable from neon by any chemical treatment. Radio-active theory (§ 171) had already suggested the possibility of the existence of substances identical in chemical properties, but differing in atomic weight. Such substances are called *isotopes*. Thomson's experiments suggested strongly that the existence of isotopes was not confined to the radio-active elements but that neon consisted of a mixture of two isotopes having atomic weights of 20 and 22.

Thomson's method is not sufficiently sensitive to separate atoms of higher atomic mass which differ by only one or two units. An ingenious modification of the method, due to Aston [6], enabled the necessary precision to be attained.

52. The mass-spectrograph. Aston's experiments. In the experiments already described the positive particles having the same value of e/m but differing in velocity are scattered along a parabolic curve of considerable length. The intensity at any point on the curve is therefore small, and if the original beam of rays is at all fine very prolonged exposures are required to obtain a measurable trace on the plate. If the particles of different velocity but the same mass could all be focused on the same spot it is obvious that a much finer pencil of rays could be employed, together with much greater dispersion, without at the same time making the necessary exposure unduly long.

This was achieved by Aston in the following way. A narrow

pencil of positive rays is passed first through the electric field between a pair of parallel plates and is thus spread out into what may be called an electric spectrum. The deflection θ of a given particle is given by equation (44), § 45. If the deflections are sufficiently small we may write $OP'/OM = \theta$, whence

$$\theta v^2 = X \cdot LM \cdot \frac{e}{m} = Xl \cdot \frac{e}{m} \text{ if } LM = l.$$

The deflected rays then pass through a magnetic field, arranged so as to produce a deflection of the rays in the opposite direction to that of the electrostatic field. The deflection ϕ produced is obviously equal to L/ρ where L is the length of the path in the magnetic field and ρ the resulting radius of curvature (see Fig. 36). Hence by equation (37) we have

$$\phi v = L \cdot H \frac{e}{m}.$$

Now in a given experiment X, H, L and l are constant. Hence for all particles which have the same value of e/m, we have, by differentiating, since e/m is constant,

$$\frac{\delta\theta}{\theta} + \frac{2\delta v}{v} = 0; \quad \frac{\delta\phi}{\phi} + \frac{\delta v}{v} = 0,$$

$$\therefore \frac{\delta\theta}{\delta\phi} = 2\frac{\theta}{\phi}. \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Now $\delta\theta$ and $\delta\phi$ represent the difference in the deviations produced by the electric and magnetic fields respectively for particles having the same e/m but differing in velocity by δv. These differences will be equal if the mean electric deflection θ is one-half the mean magnetic deflection ϕ. Since $\delta\theta$ and $\delta\phi$ are equal and in opposite directions the rays will emerge parallel to each other. Owing to the dispersion produced by the electric field, however, this beam will have a finite width. It can be brought to a focus by increasing the magnetic deviation.

Let us suppose for simplicity that the electric field can be supposed concentrated at a point Z (Fig. 42); the magnetic field acting at O. Then ZOP will be the path of one ray and $ZO'P$ that of another of the same mass but of different velocity.

Then since θ and ϕ are both very small angles in practice, we have

$$OO' = OZ \cdot \delta\theta = OP \cdot \delta(\phi - \theta),$$

$$\therefore \quad \frac{OP}{OZ} = \frac{\delta\theta}{\delta(\phi - \theta)} = \frac{2\theta}{\phi - 2\theta}$$

by equation (52). Now in all cases the particles are most numerous near the heads of the different parabolas. The mean kinetic energies of the different kinds of particles will be therefore very much the same (§ 50) and the average value of the electrostatic deflection will be the same for all kinds of particles. Thus θ is approximately constant and

$$OP(\phi - 2\theta) = OZ \cdot 2\theta = \text{constant.} \quad . \quad . \quad (53)$$
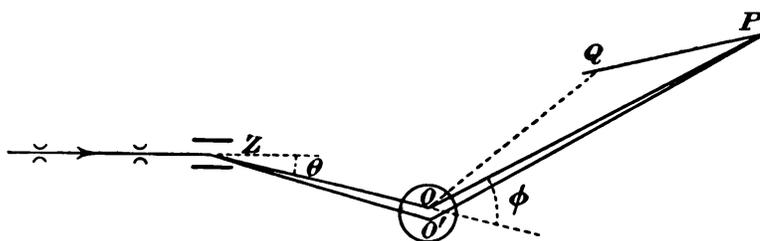
Fig. 42

This gives the locus of the foci of rays of different masses. This is approximately a straight line making an angle of 2θ with the direction ZO and passing through a point Q such that $OQ = OZ$ and the angle $Q\hat{O}Z$ equals $\pi - 4\theta$. A photographic plate placed along this line will be in focus for a very fair range of different masses. If a very fine slit is substituted for the circular tunnel in the cathode of the earlier experiments the different sets of particles will produce a corresponding set of fine lines on the photographic plate. The fineness of the focusing and the dispersion obtainable are shewn in Fig. 43 (Plate II) which is reproduced from one of Aston's plates.

53. The whole number rule. The first mass spectrograph gave an accuracy of the order of 0·1 per cent. Aston found that, to this order of accuracy, every particle registered on the photographic plates had a mass which could be represented by a whole number, if the mass of the oxygen atom was taken as 16·00.
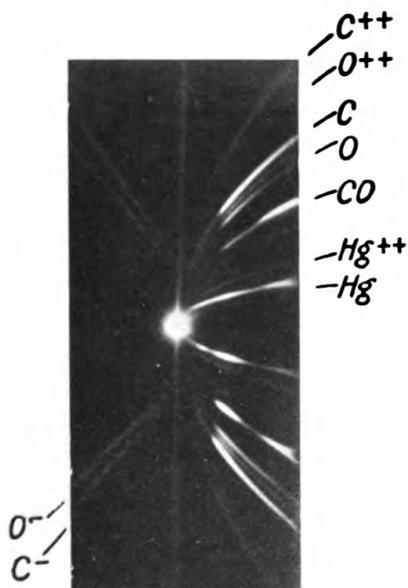
Sir J. J. Thomson.

FIG. 41. POSITIVE
RAY PARABOLAS.
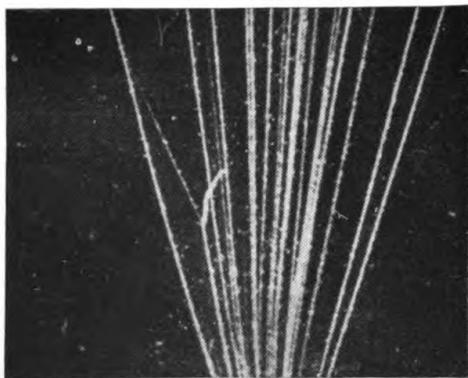
P. M. S. Blackett.

FIG. 83. DISINTEGRATION OF THE
NITROGEN NUCLEUS BY α-PARTICLES.
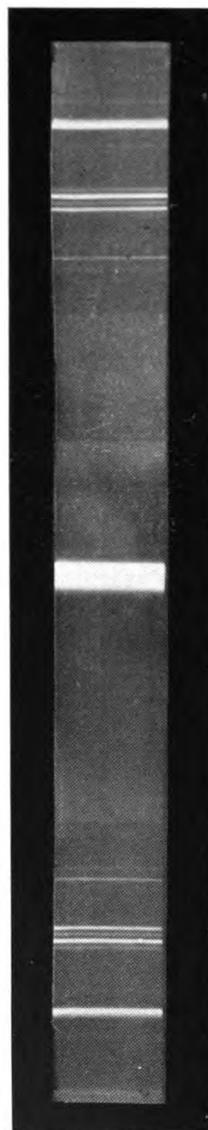
G. Shearer.

FIG. 68.
L SPECTRUM OF
TUNGSTEN.
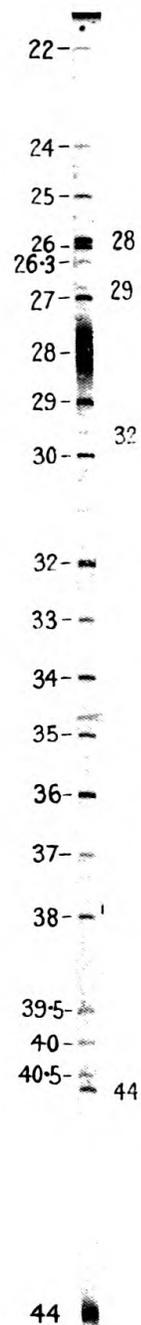
F. W. Aston.

FIG. 43.
MASS SPECTRUM
OF · BROMINE
WITH CARBON
DIOXIDE.

Thus chlorine, which has a chemical atomic weight of 35·4 appears as a mixture of particles of atomic mass 35 and 37 respectively. Neon (20·2) is a mixture of particles with masses 20 and 22 respectively. Xenon consists of a mixture of no less than 9 different isotopes with masses ranging from 124 to 136. All elements whose chemical atomic weights differ from whole numbers are found to be mixtures of isotopes of integral masses, and even elements whose atomic weights appear to be integral are sometimes found to contain minute proportions of some other isotope. Thus hydrogen contains about 0·003 per cent. of an isotope of mass 2. This "heavy" hydrogen, or diplogen, has recently been isolated in a comparatively pure state by the fractional electrolysis of water. Oxygen (16) is accompanied by 0·03 per cent. of an isotope of mass 17, and by 0·16 per cent. of an isotope of mass 18. Helium and fluorine so far appear to be pure.

Since the positive rays may contain compound molecules, as well as atoms, and since very small traces of impurities register themselves on the plates, the mass spectra, as we may call them, are usually very rich in lines, and often nearly every integral position is occupied. Fig. 43 (Plate II), which is reproduced, by permission, from Aston's *Mass Spectra and Isotopes*, is a typical example. The gas in the tube was a mixture of bromine and carbon dioxide. The doubly charged carbon dioxide molecule (giving an effective mass of 22) appears at the top of the plate, and the singly charged molecule (44) at the bottom. In the middle we have the two chlorine isotopes 35 and 37, and their corresponding hydrogen compounds HCl (35) and HCl (37) at 36 and 38 respectively. The oxygen molecule appears at 32, and several other lines can also be identified on the plate.

Of the lines on the plate which are not represented by integers 39·5 and 26·3 are the doubly and trebly charged atoms of bromine (79). The line 40·5 is the doubly charged atom of a bromine isotope (81). Its triply charged atom is seen at 27. The numbers on the right of the diagram refer to a second spectrum taken on the same plate with rather less dispersion.

Results of this kind afford the strongest possible proof of the unitary structure of matter. Prout's suggestion that all the

elements were built out of hydrogen atoms was negatived, for the time, by the fact that the chemical atomic weights were not whole numbers, and were thus not integral multiples of any chemical unit. The possibility that the atoms of a given element might not all be alike was overlooked. These results have cleared the way for a theory of matter in which the nuclei of the different elements are regarded as being collections of an integral number of hydrogen nuclei or protons.

54. The packing effect. The one exception to the whole number rule was hydrogen itself. The experiments shewed quite definitely that the mass of the hydrogen atom was 1·008, if that of oxygen is taken as 16·00. The unit brick of the whole atomic structure is thus slightly, but definitely too large.

The discrepancy can be explained on the electromagnetic theory of mass, which is developed in a later chapter (§ 112). It can be shewn that the electrical mass of a number of small charged particles diminishes if the particles are brought together in a very confined space. The nucleus of the helium atom (mass 4) contains presumably four protons packed in a volume, the radius of which is certainly less than 10^{-12} cm., so that it is not surprising that its mass is somewhat less than four times that of the hydrogen nucleus, or proton. The loss of mass which takes place is known as the *packing effect.*

Einstein has suggested that under certain circumstances matter and energy may be mutually convertible, the disappearance of mass m being accompanied by the production of an amount of energy W given by

$$W = mc^2,$$

c being the velocity of light. The condensation of four protons to form a helium atom involves a loss of mass of

$$(4 \times 1·008 - 4·000) \times 1·66 \times 10^{-24} \text{ gm. or } 0·054 \times 10^{-24} \text{ gm.}$$

and should be attended by an evolution of energy of

$$(0·054 \times 10^{-24}) \times (9 \times 10^{20}) \text{ ergs or } 4·8 \times 10^{-5} \text{ ergs.}$$

The condensation of 4·032 gm. of hydrogen into 4 gm. of helium should evolve $2·88 \times 10^{19}$ ergs or $2·88 \times 10^9$ Kilojoules of energy.

To investigate the packing effect with greater accuracy Aston[7] has constructed a new mass spectrograph with larger distances between the fields and the photographic plate, which is capable of giving an accuracy of 1 in 10,000. He finds that when measured to this degree of accuracy all the atoms shew slight departures from the whole number law, thus shewing, as might have been expected, that the packing effect is not quite identical in magnitude for all atoms. Thus if oxygen is taken as 16·0000, helium has a mass 4·00216, nitrogen (14) a mass of 14·008, and
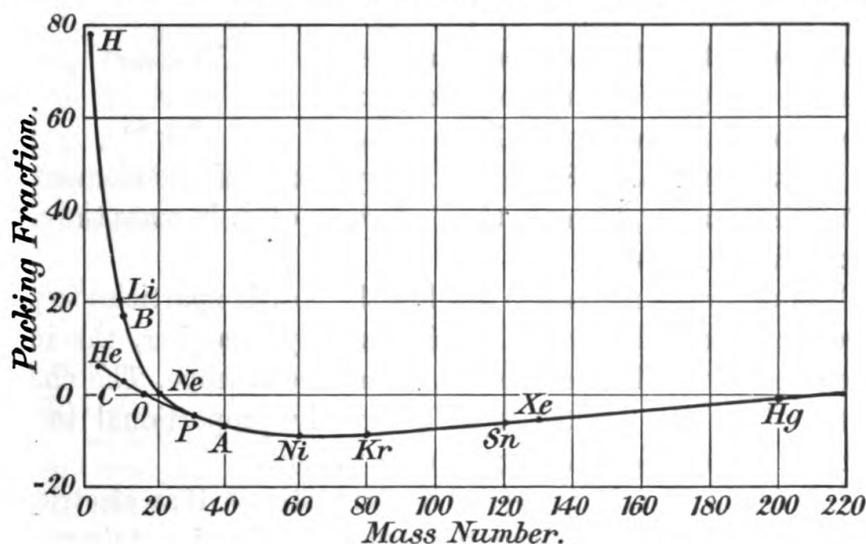
Fig. 44

argon (40) a mass of 39·971. To express such numbers conveniently Aston has defined a "packing fraction" which is the divergence of the atom from the whole number rule divided by the whole number which most nearly represents the mass of the atom (on the scale O = 16·0000). It is usually expressed in parts per 10,000. The relation between the packing fraction and the mass number of the element is indicated in Fig. 44.

As will be seen from the diagram, the packing effect is a maximum for elements in the neighbourhood of nickel. Thus while elements of low atomic weight should give out energy if condensed into atoms of higher atomic weight, elements of high atomic weight should yield energy on disintegration. The energy given out by radioactive substances (§ 174) is probably to be ascribed to this cause.

55. Relative abundance of isotopes. Electrical methods of measurement. The relative abundance of the different isotopes of a given element can be estimated from the relative intensity of the corresponding lines on the mass spectrogram. The method is only approximate, as the degree of blackening depends not only on the number but also on the nature of the particles. The hydrogen line, for example will often be the most intense line on the plate when the hydrogen atoms form no more than 1 per cent. of the whole beam. Since the isotopes of a single element do

Fig. 45

not differ, usually, by more than a few per cent. in mass the error is probably not great.
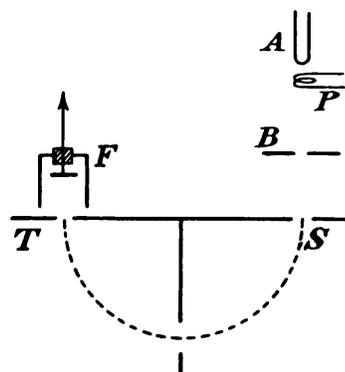
A more certain method is to allow the positive particles to pass through a fine slit into a small Faraday chamber, the inner electrode of which is connected to an electroscope. The charge collected by the electroscope is directly proportional to the number of particles passing through the slit.

This method has been applied by Dempster[8]. If an electrically heated wire A (Fig. 45) is coated with the salts of certain metals positively charged atoms of the metals are emitted (see § 57) with negligible velocities. The emission is greatly increased if the wire is bombarded by electrons from a heated platinum wire P at a negative potential of about 100 volts. These particles are accelerated in the known potential difference V between the anode A and a perforated cathode B, so that they pass into the deflecting magnetic field through the slit S with a definite known energy. The magnetic field, applied perpendicular to the plane of the diagram is arranged to bend the rays through exactly 180°, and the field is adjusted until the particles fall on the slit T, and are collected in the Faraday cylinder F. The radius of curvature ρ of the path is thus $\frac{1}{2}ST$. Thus $e/m = v/H\rho$, and $\frac{1}{2}mv^2 = Ve$, from which the ratio e/m can be determined since V, H and ρ are known. The whole apparatus is, of course, exhausted to the highest possible vacuum.

The method has since been extended by Bainbridge (9) to the particles from a gas discharge. The positive rays emerging through a fine slit in the cathode of the discharge tube are passed between a pair of parallel plates charged to a known potential difference. A magnetic field H is applied at right angles to the electric field. If the plates are close together, only particles which are undeflected in the crossed fields can emerge on the further side, as the rest will be deviated in one or other of the plates. The velocity of the particles emerging is thus given by $v = X/H$ (39) for all particles. The value of E/m can be determined from the magnetic deflection as in Dempster's method. If the collecting cylinder is replaced by a photographic plate with its plane lying along TS, the photographic method of registering the deflections of the particles can be employed, and very accurate measurements of the masses of the particles obtained.

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CHAPTER VIII

EMISSION OF ELECTRICITY BY HOT BODIES

56. Loss of charge from a hot body. The fact that heated bodies are unable to retain electric charges has been known for nearly two centuries. Thus it was found that a red-hot iron ball was unable to retain a positive charge but would retain a negative one, while at higher temperatures still it was unable to retain a charge of either sign. The early experiments were not made under very definite conditions and most of our knowledge of the phenomena is due to experiments made since 1900, and very largely to the work of O. W. Richardson, who has given the name *thermionics* to this branch of the subject. The current from a heated body is thus known as the *thermionic current*, while the carriers by which the discharge is carried are known as *thermions*.

The phenomena are in general very complex, the current depending on the nature and pressure of the surrounding gas, and on the nature and previous treatment of the heated substance. To simplify matters as far as possible we will take the case of a metallic wire which has been carefully treated to remove impurities, heated in a high vacuum so as to eliminate all effects due to the presence of gas. The effect can be studied conveniently with the apparatus shewn in Fig. 46. The wire AB to be heated is surrounded by an outer metal cylinder CC which remains cool during the experiment, the whole being enclosed in a glass vessel which can be evacuated. The wire is heated by a current from an insulated battery of cells and the temperature of the wire can be estimated by measuring its electrical resistance and thus making it serve as its own resistance thermometer. If the wire is raised to a suitable small potential a current flows from the hot wire to the cool cylinder. This current can be measured either by the electro-

meter method, or in many cases simply by allowing it to flow to earth through a galvanometer.

Initially with a new wire the current will flow through the tube whether the wire is negatively or positively charged shewing that thermions of both signs are emitted. If, however, the wire is kept glowing for some time and the gases evolved from the heated wire are continually removed by pumping, or better still by sweeping them out with pure oxygen, it is found that the positive current rapidly decreases and finally becomes negligibly small. The negative emission is also much reduced by this process but finally settles down to a steady value. The temperature to which the wire must be raised for an appreciable current to flow depends on the nature of the substance. For platinum a temperature of about 1000° C. is required; for sodium
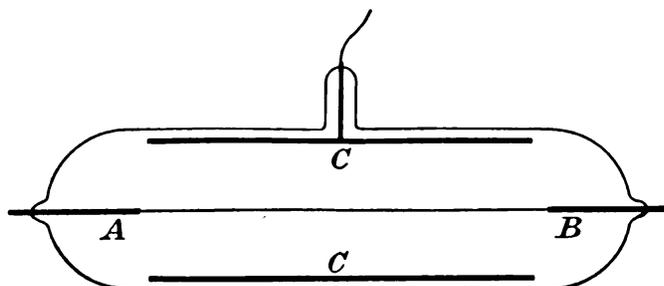
Fig. 46

on the other hand there is a very considerable thermionic emission at temperatures as low as 300° C.

Other conditions being constant, the thermionic current increases, with increasing potential difference until a maximum, or saturation value is reached. The potential difference required to produce the saturation currents depends on the intensity of emission of the heated wire. If the emission is large the saturation potential difference may rise to several hundred volts.

57. Nature of the thermions. The nature of the thermions can be determined by measuring the value of e/m for the particles by any of the methods described in the previous chapter. The arrangement employed by Dempster, and described in § 55, is convenient and accurate.

When a clean metal wire is heated in vacuo the positive emis-

C I   8

sion consists initially of particles of mass 39, on the scale O = 16. They are presumably atoms of potassium. After further heating particles of mass 23 are obtained which are presumably sodium atoms. The results seem to be independent of the nature of the wire, and are due to minute traces of alkali impurity in the wire. The emission fades away to zero with prolonged heating, but can be restored again by exposing the wire to the atmosphere of the laboratory for a few days. The emission of these particles can be greatly increased by coating the wire with a salt of the corresponding metal. The ions of other alkali metals can be obtained in the same way, and the effect has been used for studying the isotopes of these elements. Certain phosphates also give large initial positive emissions; in this case the carriers appear to be molecules of carbon monoxide, which is presumably occluded in the salt.

If the residual gas in the tube has an appreciable pressure a continuous positive emission is obtained, consisting of ionized atoms and molecules of the gas. In high vacuo the positive emission gradually ceases, and only negative carriers are emitted. When this stage is reached current can only pass across the apparatus when the hot wire is negatively charged, and the system serves as a rectifier or valve. Thermionic rectifiers are now employed for many purposes, and can be constructed to carry currents of twenty amperes or more.

The negative thermions give values of e/m identical with those obtained for cathode rays. Some of the results obtained are included in Table IV. They are, therefore, simply negative electrons. In the succeeding sections we shall confine our attention to the negative, or electronic emission.

58. Theory of thermionic emission. It can be shewn that the conduction of electricity through metals is due to the motion of electrons through the metal, and the fact that the current is directly proportional to the applied E.M.F., however small, shews that these electrons are free. If the electrons were bound to the atoms an electrical field of finite magnitude would be required to remove them from the atom, and until this field was reached no current could flow.

The electrons, however, though moving freely through the metal are retained within it by forces at the surface of the metal. An electron escaping from the surface of a metal will, for example, induce a positive charge immediately beneath it which will tend to attract it back to the surface. There may also be other intrinsic fields acting in the same direction. To separate an electron from the surface, a certain amount of work w must be done against these forces, and an electron will only be able to escape if its kinetic energy normal to the surface is greater than w.

If we could assume that the free electrons in the metal behaved like the molecules of a perfect gas at the temperature of the surrounding metal, we could calculate the probability of an electron reaching the surface with energy greater than w. Richardson developed a theory of the effect on these assumptions, which agreed satisfactorily with the experimental results.

Measurements on the specific heats of metals are, however, inconsistent with the assumption that a metal contains any appreciable number of free electrons sharing the thermal energies of the molecules. According to Sommerfeld, the electrons must be regarded as forming a "degenerate system" (p. 289). Fortunately we can evade these uncertainties by resorting to thermodynamical considerations.

Suppose we have an evacuated enclosure at a constant temperature containing a body emitting electrons. Electrons will accumulate in the vacuous space, forming an electronic gas, until the electron density becomes so great that the number of electrons returning to the metal from the electronic atmosphere becomes equal to the rate of emission of electrons from the metal. A state of dynamical equilibrium will thus be reached, similar to that between a liquid and its saturated vapour.

The analogy holds in another respect. Since work is done when an electron escapes from the surface heat will be absorbed in the process. The absorption of heat from an incandescent filament during thermionic emission has actually been measured by Richardson[4], as has also the reverse effect, the emission of heat when thermions are reabsorbed. We can thus speak of the latent heat of evaporation of the electrons, and apply the usual latent heat equation to the problem.

8-2

Thus, if p is the pressure of the electron atmosphere when equilibrium is established, V and U the volume of one gram-molecule of electrons in the free space and in the metal itself, and L the energy absorbed during the evaporation of one gram-molecule of electrons,

$$L = \theta \frac{dp}{d\theta}(V - U) = \theta \frac{dp}{d\theta} V$$

approximately, since the volume of the electrons in the metal is very minute compared with that outside.

Now the energy absorbed is used up in two ways: (a) in providing the work necessary to allow of the escape of the electrons from the surface; this is equal to Nw where N is the number of electrons in a gram-molecule, that is Avogadro's number, (b) in overcoming the pressure of the electronic atmosphere into which the electrons evaporate. This is equal to pV where p is the pressure. Since the electrons in the free space behave as a gas $pV = N.R\theta$ where R is the gas constant for one molecule, i.e. Boltzmann's constant. Thus

$$L = Nw + NR\theta, \quad \ldots \ldots \quad (54)$$

$$\therefore V\theta \frac{dp}{d\theta} = N (w + R\theta),$$

or substituting for V from the relation $pV = NR\theta$,

$$NR \frac{\theta^2}{p} \frac{dp}{d\theta} = N (w + R\theta),$$

$$R \frac{dp}{p} = \frac{w + R\theta}{\theta^2} d\theta,$$

$$p = K\theta\epsilon^{\int \frac{w}{R\theta^2} d\theta}. \quad \ldots \ldots \quad (55)$$

If n is the number of electrons per unit volume in the free space, we can write $p = \beta n\theta$ where β is a constant, and thus

$$n = C\epsilon^{\int \frac{w}{R\theta^2} d\theta}, \quad \ldots \ldots \quad (56)$$

where C is a constant.

The electrons in the free space will behave as molecules of a rarefied gas, and the ordinary kinetic theory of gases can thus be applied. It is true that as they are negatively charged they will repel each other and thus possess a negative intrinsic

pressure. The actual pressure of the electronic gas is, however, so minute under ordinary conditions that the effect may be neglected. The root mean square velocity of the free electron is thus given by $\frac{1}{2}mv^2 = \alpha\theta$, where θ is the absolute temperature and α is a constant which is the same for all gases, or

$$v = \sqrt{\frac{2\alpha\theta}{m}}. \quad \ldots \ldots \quad (57)$$

If we make the usual elementary assumption that the electrons may be regarded as travelling in six streams parallel to the six faces of a cube, and that all the electrons possess the same velocity v, the number n_0 striking unit area per second will be all the electrons in the stream normal to the surface whose distance from it is less than v, that is $nv/6$. The correct value, allowing for the distribution of velocities among the electrons, can be shewn to be $\dfrac{nv}{\sqrt{6\pi}}$. Substituting for v its value as given by (57) we have

$$n_0 = \frac{n}{\sqrt{6\pi}} \sqrt{\frac{2\alpha\theta}{m}} = Cn\theta^{\frac{1}{2}} \quad \ldots \ldots \quad (58)$$

where C is a constant.

If all the electrons which fall upon the metal surface are absorbed by it, n_0 is the number entering, and thus, when equilibrium has been established, the number leaving the surface per sq. cm. per second. Experiment shews that a certain number (possibly 50 per cent.) of the returning electrons are reflected back from the surface. The number emitted will thus be n_0 multiplied by an appropriate fraction; e.g. one half, if the reflection is 50 per cent. This fraction can be included in the constant C, so that the emission is still given by an equation of the form of (58).

Substituting for n from (56) we have finally

$$n_0 = A\theta^{\frac{1}{2}}\epsilon^{\int \frac{w}{R\theta^2}d\theta}. \quad \ldots \ldots \quad (59)$$

If we assume that the electrons within the metal have the same energy of thermal agitation as when in the free space outside the metal we can regard w as independent of the tempera-

ture, as it is unlikely that the electrical forces will vary with temperature. Taking w as constant, equation (59) obviously reduces to

$$n_0 = A\theta^{\frac{1}{2}}\epsilon^{-\frac{w}{R\theta}}, \quad . \quad . \quad . \quad . \quad . \quad (60)$$

which was the form first given by Richardson.

If, on the other hand, we assume that the electron has no energy in the metal, then the total work done in extracting the electron from the metal will include the work done in giving it the energy $\frac{3}{2}R\theta$ which it has in the space outside the metal, and w will be of the form

$$w = w_0 + \tfrac{3}{2}R\theta.$$

It can be shewn that this is equivalent to assuming that the "specific heat of electricity" in the metal, i.e. the Thomson effect, is zero. Substituting this value of w in (59) and integrating we have

$$n_0 = A_1\theta^2\epsilon^{-\frac{w_0}{R\theta}}. \quad . \quad . \quad . \quad . \quad (61)$$

Since each electron carries a charge e, the saturation current is n_0e per square centimetre of surface. The experimental curve for platinum is shewn in Fig. 47.

At first sight it might appear to be an easy matter to distinguish experimentally between the relations (60) and (61). In practice, however, the variation in the exponential term produced by small changes in θ completely overshadows any variation due to changes in $\theta^{\frac{1}{2}}$ or θ^2, and the experimental results can be expressed almost equally well, though

Fig. 47

of course with different constants, by either relation. Recent experiments are rather in favour of the second form of Richardson's law.
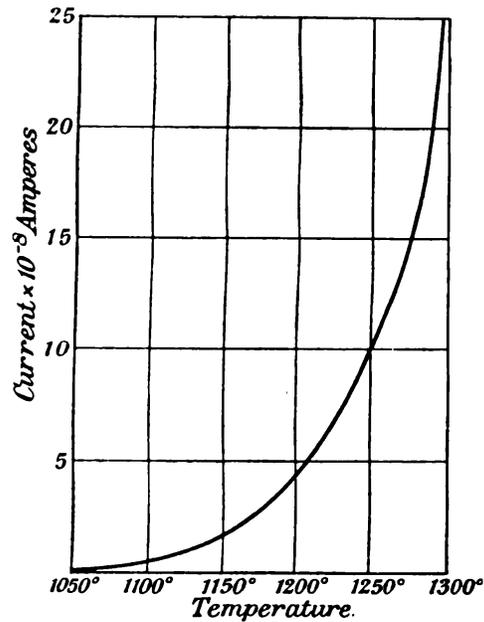
59. The thermionic work function. The thermionic emission is very largely controlled by the value of w. This quantity, which measures the work which must be done to extract an electron from the metal, is known as the thermionic work function. Like other electron energies it is most conveniently measured in electron-volts. Its value can be deduced from the experimental curve relating temperature and emission, since R, the gas constant per molecule, or Boltzmann constant, is known.

Table V gives the values of w for a few commonly used wires. The corresponding values of A are also given. The figures have been calculated using the second form of Richardson's law.

<div align="center">

TABLE V

Some thermionic constants

</div>

	A in amp. per sq. cm.	w_0 in volts
Carbon	5·9	3·92
Molybdenum	60·2	4·59
Tantalum	60·2	4·51
Tungsten	60·5	4·52
Platinum	27·1	4·24
Mixture of BaO and SrO	3·2	1·79

Some of these values are very uncertain. The presence of minute traces of an impurity which has a small work function will increase the emission many fold. Thus the carbon filament of an electric lamp gives a very large negative emission—the well-known Edison effect adopted by Fleming to rectify wireless signals. The effect is, however, mainly due to impurities, as pure carbon does not differ very markedly from platinum in its emissive power.

Owing to the very low value of the work function the emission from wires coated with oxides of calcium, barium, strontium or thorium, or mixtures of these oxides, may be many thousand times greater than that from a bare tungsten wire at the same temperature. Conversely, for the same emission the coated wire may be run at a much lower temperature, with a corresponding saving in electrical energy. Coated filaments are, therefore, now

used almost exclusively in thermionic valves. The emission follows Richardson's law, the increased effect being due solely to the low value of the work function.

Similarly a strip of platinum carrying a speck of barium oxide (such as can easily be obtained by placing a speck of sealing wax on the strip and burning off the lacquer) forms a convenient point source of electrons, the emission from the platinum being negligible in comparison with that from the oxide. The electrons are emitted with small energies, of the order of a volt, and can be speeded up to any desired velocity by applying a suitable negative potential to the strip. The arrangement is known as a Wehnelt cathode.

The thermionic emission is generally increased by the admission of gas at low pressures, or even by its previous absorption in the wire. Hydrogen at a pressure of no more than 0·0006 mm. was found to increase the emission from platinum at 1350° C. no less than 2500 fold. The emission still follows Richardson's law, but with a smaller value for the work function.

The effect is probably due to the condensation on the platinum of a layer of hydrogen. Hydrogen is a very electro-positive element, and if we assume that the hydrogen atoms in the condensed layer are positively charged their presence will produce a field between the gas and the metal tending to assist the escape of the electrons from the metal. Less work will thus be required to extract an electron from the metal. Since w_0 is a measure of this work the value of w_0 will be decreased, as is actually found to be the case.

60. Distribution of velocities among the thermions. The distribution of velocities among the electrons emitted from a hot wire has been investigated by Richardson [4] by a method based on the following principle. Let the cool electrode be maintained at a definite negative potential V. The work done by the negative electron in passing from the surface of the hot strip to the negative electrode will thus be Ve, and the electron will only succeed in reaching the electrode and imparting its charge to it if the kinetic energy $\frac{1}{2}mv^2$ is greater than Ve.

Thus the current reaching the electrode is a measure of the number of thermions whose kinetic energy perpendicular to the strip is greater than Ve. In this way the distribution of normal velocities of the thermions can be studied. A slight extension of the method can be used to measure the distribution of the velocities of the thermions in a direction parallel to the surface of the hot strip. In both cases the distribution found agreed very closely with that given by the Maxwell-Boltzmann law for the distribution of velocities among the molecules of a perfect gas. The electrons thus escape from the metal not only with the mean velocity but also with the velocity distribution of gas molecules at the same temperature. These results are very interesting as they supply a very direct experimental verification of the Maxwell-Boltzmann distribution law.

61. The current through a thermionic valve. Langmuir's Law. Richardson's law (61) gives the relation between the temperature and the saturation current from a heated filament. In the earlier experiments where the currents measured were small saturation was easily obtained with potential differences of a few volts only. This is by no means the case in a modern thermionic valve. Langmuir[5] has shewn that if a constant potential difference is maintained between the electrodes and the temperature of the hot wire is gradually increased the current at first increases in accordance with the law of Richardson. Soon however the rate of increase with temperature becomes rapidly smaller than that given by the law and eventually the current reaches a maximum value which then remains constant however much the temperature may be increased, as illustrated in Fig. 48. This constant current, however, increases with the potential difference employed. If V is this potential difference the value of the constant current i is given by

$$i = kV^{\frac{3}{2}}. \qquad \ldots \ldots \quad (62)$$

This is known as Langmuir's law.

This limitation of the current is due to the presence between the electrodes of the negative electrons which are carrying the current. These negative charges will repel the negative electrons

which are tending to emerge from the hot cathode and, as the current grows bigger and hence the number of electrons in the space becomes more numerous this repulsion increases until finally it counterbalances the applied field, and the actual field at the surface of the cathode becomes zero or may even be reversed. At this point further emission from the hot wire ceases. The maximum current which can pass for a given potential difference is thus limited by the space charge due to the electrons between the electrodes.
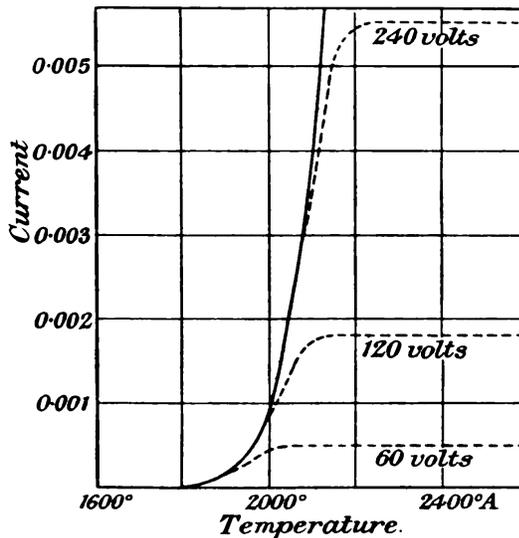
Fig. 48

We may take as a simple case a pair of parallel plates at a distance d apart, the heated plate being at potential zero and the cold plate at a positive potential. Then if ρ is the negative space charge (charge per cubic cm.) at some point between the electrodes, V the potential at that point, then by Poisson's equation

$$\frac{d^2V}{dx^2} = 4\pi\rho.$$

Also the current i per sq. cm. at right angles to the direction of the field is clearly equal to the charge per unit volume into the velocity, v, with which the charges move, i.e.

$$i = \rho v,$$

where v is given by the equation

$$\tfrac{1}{2}mv^2 = Ve.$$

Hence
$$\frac{d^2V}{dx^2} = 4\pi i \sqrt{\frac{m}{2Ve}}.$$

Now if we neglect the small intrinsic velocities with which the electrons are emitted from a hot cathode (usually a fraction of a volt), we have seen that the maximum current will be attained when the field at the surface of the cathode has been reduced to zero by the space charge effect. Hence for the maximum current we have $dV/dx = 0$ when $x = 0$, if we measure our distances from the surface of the cathode; and integrating our equation with this condition we have

$$\left(\frac{dV}{dx}\right)^2 = 8\pi i \sqrt{\frac{2Vm}{e}}.$$

Integrating again, and remembering that V is zero when x is zero, i.e. at the surface of the cathode, we have finally

$$i = \frac{\sqrt{2}}{9\pi} \sqrt{\frac{e}{m}} \frac{V^{\frac{3}{2}}}{d^2}. \quad \ldots \quad \ldots \quad (63)$$

If i and V are measured and the distance apart of the plates is known this equation can be used to determine the ratio e/m for the thermionic carriers. This experiment has actually been carried out[6], the result obtained being $1\cdot76 \times 10^7$, a very satisfactory agreement.

In the ordinary thermionic valve the filament is maintained at a constant temperature, and owing to its high thermionic emissivity saturation conditions are not approached with the potentials normally applied to the valve. The current is thus governed by the space charge effect and should thus vary with the applied potential difference in accordance with (63). A correction, however, is required on account of the intrinsic velocity of emission of the thermions. If the electrons were all emitted with the same velocity v they would still escape from the filament unless a reverse potential difference were applied greater than some value V where $Ve = \tfrac{1}{2}mv^2$. The current will thus commence to flow when the collecting plate is at a small negative potential, and will increase as this potential is decreased to zero.

The velocities of the electrons are, however, not constant but are distributed according to the Maxwell-Boltzmann relation. As the retarding potential is decreased the emission will increase rapidly as electrons with smaller and smaller velocities will be able to emerge. The first portion of the current-voltage curve (Fig. 49 (1)) will thus be complex, and will be governed mainly by the Maxwell-Boltzmann relation. As the applied potential difference is increased, however, and becomes large in comparison with the retarding

Fig. 49

voltage necessary to stop the emission of electrons, the preliminary effects become comparatively negligible and the curve merges into that given by Langmuir's equation (Fig. 49 (2)). Finally if the potential is sufficiently increased it may be sufficient to produce saturation for the temperature at which the filament is being run. The current then remains constant with further increase in voltage (Fig. 49 (3)) and its value is given by Richardson's law.
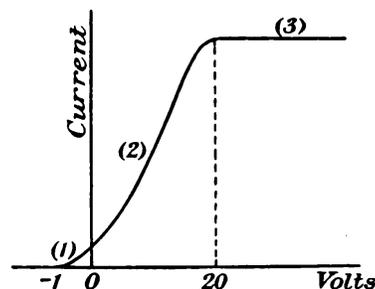
62. Conductivity of flames. If two platinum plates are placed a few centimetres apart in a wide Bunsen flame and one of them is raised to a moderately high potential by a battery of accumulators a current passes between the plates through the flame. The current is usually large enough to be measured by a galvanometer, one terminal of the instrument being connected to the insulated plate and the other to earth. The current is maintained by the thermionic emission from the heated electrodes. In these circumstances both positive and negative thermions are produced. The relation between the current and the applied potential difference is complicated by the presence of the gas molecules, and if the potential is large ionization by collision may also come into play. The current is approximately proportional to the square root of the applied potential difference. The current is greatly increased if salts, particularly those of the alkali metals, are vaporized in the flame, the effect being

the greatest when the salt vapour comes into contact with the negative electrode. A theory of the effect has been worked out by J. J. Thomson(7), but the effect is not of much practical importance.

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CHAPTER IX

PHOTO-ELECTRICITY

63. The photo-electric effect. If a metal plate is illuminated by the light from an arc or spark it emits negative electricity. If the plate is carefully insulated the emission continues until the plate has acquired a small positive potential, usually of the order of a volt. When this potential is reached the emission stops. If, however, the plate is connected to earth through a sensitive galvanometer so that its potential is always less than this critical value, a continuous negative current flows from the plate to earth, which continues as long as the plate is illuminated. The effect, which was discovered by Hallwachs in 1888, is known as the photo-electric effect, or more rarely, as the Hallwachs effect.

For most metals the photo-electric emission is only excited by ultra-violet light, and is stopped if a glass plate is interposed between the source of light and the metal plate. The alkali metals are, however, peculiarly sensitive and respond to rays from the visible part of the spectrum. They can be excited even by the light from a candle.

If the experiments are conducted in air, or other gases, the rate at which electricity escapes from the illuminated plate depends on a large number of conditions, such as the pressure and nature of the gas, the state of polish of the surface and even on the time which has elapsed since the plate was last polished. A very considerable amount of experimental work was expended on the problem before it was finally realized that these variations were mainly due to condensed gas films on the surface of the metal which retarded the escape of the negative electricity. It was only when experiments began to be made on surfaces not only maintained but actually prepared in vacuo, and which had never been exposed to gas at appreciable pressure that consistent results were obtained.

The photo-electric effect can be shewn to be due to the emission of comparatively slowly moving negative electrons, which are often spoken of as photo-electrons, to indicate their mode of production. The value of the ratio e/m for the photo-electrons has been determined by Thomson, Lenard and others, the experiment being most conveniently carried out by applying the relations (42) and (43) of § 44. The value of the ratio e/m for the photo-electrons is the same as that for electrons produced in other ways. The photo-electric emission is, therefore, simply an emission of negative electrons under the stimulus of the light.

It has been found that for each substance there is a definite wave length at which the photo-electric emission commences; rays of wave length longer than the critical value producing no effect. This critical wave length is greater according as the element is more electro-positive and shorter as the element becomes more electro-negative. Thus for the alkali metals which are extremely electro-positive, the maximum or *threshold* wave length which will excite photo-electricity is actually in the visible spectrum being greater for caesium than for potassium and sodium; for other metals the critical wave length lies between 4000×10^{-8} and 2500×10^{-8} cm. For the non-metals light of still shorter wave length is necessary.

64. Velocity of emission of the photo-electrons. It is found that a plate illuminated by ultra-violet light gives electrons of all velocities from a certain maximum downwards. The velocity is most conveniently measured by measuring the difference of potential necessary to prevent the escape of electrons from the plate. Suppose the metal plate emitting the electrons is at a positive potential V. The negative electron will experience a force attracting it backwards to the plate and by the time it reaches a place of zero potential it will have lost energy equal to Ve, where e is its charge. If the original energy with which it left the plate was E it will now have energy equal to $E - Ve$. If this is equal to or greater than zero the electron will escape being dragged back to the plate. If its initial energy is less than Ve its motion will be reversed and

it will return to the plate again. Thus the minimum velocity an electron can have to escape is given by

$$\tfrac{1}{2}mv^2 = Ve,$$

$$v^2 = 2V\,\frac{e}{m}.$$

If the active plate is surrounded by conductors at zero potential and carefully insulated it will gradually acquire a positive potential owing to loss of negative electricity. This potential will grow until it is just sufficient to prevent the escape of the fastest electrons which the plate emits. Thus a measurement of the potential acquired by a plate exposed under these circumstances to ultra-violet light will enable us to estimate the velocity of the swiftest electrons emitted. Similarly the current flowing from the plate when its potential is maintained at some value V less than the maximum is a measure of the number of electrons which leave the plate with initial energies greater than Ve.

On this account the objectionable practice has grown up of stating the velocity in terms of the voltage acquired by the plate, and thus phrases like "a velocity of one volt" have become common. As will be seen from the formula the velocity is not proportional to the potential but to its square root. The actual electronic velocity can readily be calculated from the potential, since e/m is equal to $1\cdot77 \times 10^7$ e.m.u. Thus a "velocity of one volt" or 10^8 e.m.u. is equal to about $5\cdot9 \times 10^7$ cm./sec. The objection does not apply to the measurement of energy in volts, since the energy acquired by an electron is directly proportional to the potential through which it has fallen, and conversely, the minimum potential which will prevent its escape is a measure of its energy.

Experiments on the maximum velocity of emission of electrons from a metal under the action of light yielded unexpected results. It was shewn, in the first place, that the maximum velocity was absolutely independent of the intensity of the light, even when the intensity varied in the ratio of 10^8 to 1. It varied with the nature of the metal, and, in particular, it depended on the frequency of the radiation. If V is the positive potential difference

necessary to prevent the escape of electrons, and ν the frequency of the exciting radiation,

$$V = k\nu - V_0, \quad \ldots \ldots \quad (64)$$

where V_0 depends on the nature of the substance, but k has the same value for all substances. Both k and V_0 are independent of the intensity of the light. This result was first stated by Lenard. The most accurate proof of it has been provided by Millikan(2).
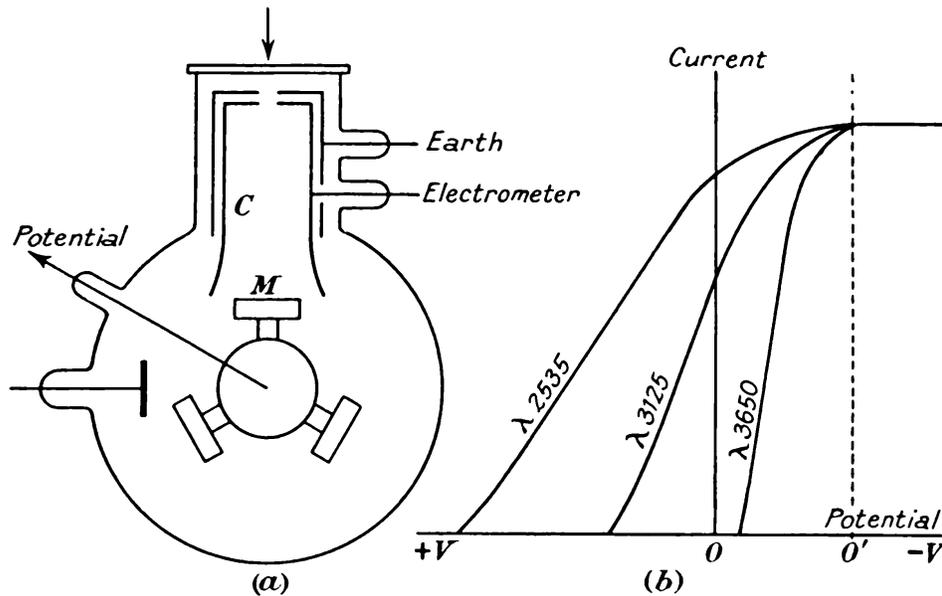
Fig. 50

65. Millikan's experiments on the photo-electric effect. In order to be able to employ as wide a range of frequencies as possible Millikan worked with the alkali metals for which the photo-electric effect begins in the visible spectrum, and his observations extended over a range of frequencies of nearly three octaves. The experiments were carried out in an exceedingly high vacuum, and in order to obtain really clean surfaces, the surfaces were actually turned up in the vacuum itself, by means of a tool which could be operated from outside by an electromagnet.

The clean metal surface M (Fig. 50 a) was illuminated in turn with various monochromatic beams of light, picked out spectroscopically from among the lines in the spectrum of a

mercury arc. The escaping electrons were collected in a Faraday cylinder C of oxidized copper; this material being chosen because it does not itself emit photo-electrons for light of the frequency employed. The current collected by the cylinder for different values of the applied potential difference V between the cylinder and the illuminated metal was measured by an electrometer, for a series of different wave lengths, and a series of curves plotted (Fig. 50 b) from which the value of V at which the emission ceased could be determined with accuracy, for each frequency ν of the light employed. Plotting this critical value against the corresponding frequency ν, Millikan obtained a series of points which lay accurately on a straight line. His results thus confirmed the relation (64) to an accuracy of at least one per cent. The value of k is given by the slope of the line, and was found to be $4\cdot128 \times 10^{-15}$, when V is measured in volts. If a second metal was substituted for the first (e.g. potassium for sodium) a second straight line was obtained parallel to the first. The value of k is thus identical for both metals, while that of V_0 changes from metal to metal.

It will be seen from Fig. 50 b that the maximum photo-emission was only obtained when a negative, i.e. an accelerating potential was applied to the metal. The actual potential difference between the metal M and the collecting cylinder differs from the potential difference applied. If the plates of a condenser are of different metals and are joined by a wire of one of the metals there will actually be a field across the space between the plates owing to what is known as the contact potential difference. In Millikan's experiments it acts from the alkali metal to the copper oxide, and thus tends to prevent the escape of electrons from the former, even when the two are connected together and the applied potential difference is zero.

The existence of this effect does not change the form of the relation (64), as the contact potential, unless corrected for, will be included in V_0. By subsidiary experiments Millikan was able to measure the contact potential difference, and so the actual potential difference through which the electron escaped. The effect of the correction is to move the zero from O to O' (Fig. 50 b) where OO' is the contact P.D. It was found that the photo-

emission was complete when the actual P.D. between the plate and cylinder was zero. In the discussion which follows we shall suppose that this correction has been applied and that V measures the real potential difference between the illuminated metal and the collector. $V_0 e$ is thus the work which must be done by an electron in passing from the metal to the collector, and is thus the energy with which the fastest electrons leave the surface.

The significance of the experimental relation (64) can be made clear by multiplying the equation throughout by the electronic charge e, and transposing. Thus

$$Ve + V_0 e = kev. \quad \ldots \ldots \quad (65)$$

Now Ve is the energy with which the fastest electron escapes from the illuminated surface. $V_0 e$ has also the dimensions of energy and can only be interpreted as measuring work done by the electron in escaping from the metal. This work may conceivably take two forms, work done in escaping from the parent atom, and work done in escaping through the surface. By ingenious experiments and arguments Millikan was able to shew that, for a metal, no energy is used in extracting the photo-electron from the atom. The electrons ejected are those which are already in the free state in the metal. $V_0 e$ should thus be identical with the thermionic work function, w_0 (p. 115), and V_0 should have the same value as w_0 if both are expressed in volts. Comparison of recent determinations of the two quantities are, in fact, in very good agreement. Thus for tungsten $V_0 = 4\cdot52$ volts, and $w_0 = 4\cdot52$ volts; for platinum we have $4\cdot40$ and $4\cdot24$; and for molybdenum, $4\cdot33$ and $4\cdot30$ volts respectively.

$V_0 e$ is thus the energy used up by the electron in escaping, and thus the left-hand of equation (65) is the total energy with which the electron starts its career. Thus if monochromatic light of frequency ν falls upon any substance the initial energy, W, imparted to the electrons is given by the relation

$$W = \tfrac{1}{2}mv^2 = h\nu, \quad \ldots \ldots \quad (66)$$

where h is a constant which is independent of the nature of the

9-2

substance, and is equal to ke. Taking Millikan's value for k and converting volts to electrostatic units, we have

$$h = 4 \cdot 770 \times 10^{-10} \times \frac{4 \cdot 128 \times 10^{-15}}{300} = 6 \cdot 56 \times 10^{-27} \text{ ergs sec.}$$

It will be seen that equation (66) is merely an expression of well-ascertained experimental facts.

Further, if ν_0 is the minimum frequency which will stimulate photo-electric emission in the metal (the *threshold frequency* as it is called), it is found experimentally that $V_0 e = h\nu_0$ where h is the same constant as before. The relation (64) can thus be written

$$Ve = h\,(\nu - \nu_0). \quad . \quad . \quad . \quad . \quad (67)$$

66.   The quantum theory. In order to explain the laws governing the thermal radiation from a perfect radiator Planck had been led to formulate the hypothesis that an accelerated electron did not radiate energy continuously, as demanded by the classical electromagnetic theory of light (see § 75), but only intermittently, each emission consisting of a definite burst or *quantum* of energy (4). The energy, w, in one of these quanta was supposed to be directly proportional to the frequency of the radiation emitted. Thus if ν is the frequency of the radiation the energy associated with each quantum of it is given by

$$w = h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

where h is a universal constant, known as Planck's constant. The value deduced for this constant from radiation data was

$$h = 6 \cdot 55 \times 10^{-27} \text{ ergs sec.}$$

It is therefore numerically identical with the h of the previous section.

We can illustrate Planck's law quite readily from phenomena which we have already considered. We have seen (§ 35) that an electron may be transferred from its normal position in the atom to some other condition of greater energy by the impact upon it of another electron if the latter has a certain minimum energy, measured by Ve, where V is the radiation potential for the atom. This minimum energy is clearly the difference in energy of

the atomic electron in its two conditions. Thus the potential energy of the electron in its abnormal condition will be Ve units greater than in its normal state, and Ve units of energy will be set free when the electron falls back into its stable condition (5). This energy, as we mentioned, is radiated as monochromatic light of definite frequency, only one line appearing in the spectrum. The frequency of this radiation, by Planck's law, should be given by the relation

$$Ve = w = h\nu, \text{ or } \nu = Ve/h.$$

If we take the case of mercury vapour the first radiation potential is 4·9 volts or $1·63 \times 10^{-2}$ e.s.u. and the radiation emitted should thus be given by

$$\nu = \frac{1·63 \times 10^{-2} \times 4·774 \times 10^{-10}}{6·55 \times 10^{-27}} = 1·17 \times 10^{15}.$$

The frequency of the light actually emitted is $1·18 \times 10^{15}$. The agreement is perfect, considering the possible errors of the measurement of resonance potentials.

In Planck's original form of the theory only the emission occurred in quanta, the atom or electron being supposed to absorb radiation continuously until its energy reached that of the quantum for the radiation concerned. In 1905 Einstein (6) made the further assumption that the radiation actually travelled in minute bundles each possessing the quantum energy corresponding to its frequency, and that the atom absorbed either the whole of this quantum or none at all. This assumption leads immediately to our experimental relation (67). From monochromatic light of frequency ν the atom will absorb a whole quantum of energy $h\nu$, and this energy when transferred to an electron will give it kinetic energy $\frac{1}{2}mv^2 = h\nu$. At the time the data for testing this equation did not exist, and the suggestion was not well received, as the idea of a definite quantum of radiation travelling through space as an entity appeared to be completely irreconcilable with the wave theory of light (4).

So drastic an assumption is not absolutely necessitated by the results of § 65. It is possible to conceive that the atom absorbs energy from the radiation continuously until the quantum energy is reached and then ejects this superfluous energy in the form

of a photo-electron. This mode of escape is, however, made impossible by the following considerations. However weak the incident light may be the emission of photo-electricity commences as soon as the light falls on the surface. The lag, if any, is certainly less than 3×10^{-9} sec. Now the photo-electric effect for sodium can easily be detected with an ordinary candle at a distance of 3 metres. This corresponds to an energy of 1 erg per sq. cm. per sec. falling on the surface of the metal, and of this not more than one-third is of sufficiently short wave length to excite the photo-electric effect. Now the area of cross section of an atom is of the order of 10^{-15} sq. cm. and the maximum energy which could be absorbed by the atom from the beam, if uniform, would be therefore about $\frac{1}{3} \times 10^{-15}$ ergs per sec. But the energy of the electron emitted is of the order of 5×10^{-12} ergs. To accumulate this energy the atom would have to go on absorbing for about 15,000 seconds or more than four hours. The suggestion of a gradual absorption from a uniform beam is therefore inconsistent with the facts, and we are driven back on Einstein's assumption.

Again, we have seen that the photo-electric emission ceases for a threshold frequency ν_0 given by $h\nu_0 = V_0 e$. No matter how intense the radiation may be an electron is only ejected if the value of $h\nu_0$ is greater than the work necessary to eject an electron. Absorption, therefore, can only take place in complete quanta. If the energy in a single quantum is insufficient to provide the work necessary for the escape of an electron, no electron will escape.

The only possible conclusion from the facts outlined in this section is that when energy is interchanged between matter and radiation, the interchange is effected in definite units, the value of which is expressed by $h\nu$. Planck's relation (68), originally derived in a highly speculative manner, is thus found to express a highly important and well authenticated law in atomic physics; the exchange of energy between matter and radiation takes place in quanta. This is called the quantum theory.

The quantum theory in reality is not a theory: no theoretical basis has yet been found for it. It is a fundamental law governing the exchange of energy between radiation and matter, and in all

cases in which it has been tested it is found to express the phenomena with great exactitude. We shall meet with further examples in the following chapter. The question as to how the quantum relation is to be reconciled with the electromagnetic theory of light is an interesting problem. The formal reconciliation of the two ideas is however not beyond the reach of mathematics, and is dealt with in what is known as Wave Mechanics.

67. Distribution of velocities among the photo-electrons. So far we have considered only the maximum velocity with which the electrons escape from the metal. If we maintain a constant difference of potential V between the radiator and its surroundings less than the maximum positive potential which would be acquired by the plate, the rate of loss of electricity from the plate, that is, the negative current from it, will be proportional to the number of electrons which leave the plate with an initial energy greater than Ve. In this way the proportion of the electrons which emerge with various velocities less than the maximum can be measured.

We have seen that the maximum current is only reached when the illuminated plate is at the potential of its surroundings, that is when there is no retarding field. Electrons emerge with all velocities from zero up to the maximum. It is indeed very improbable that they actually commence their course with different velocities. Electrons will be projected at different depths in the metal (since light can penetrate small thicknesses of metal) and hence will have different thicknesses of metal to traverse before escaping from the surface. Now in passing through matter electrons lose velocity owing to collisions with the molecules Thus those electrons which start at the surface, having no matter to traverse, will escape with the actual velocity given them by the radiation. Those starting deeper in the metal will lose some of their velocity before reaching the surface, until at last a layer is reached the electrons from which will be unable to penetrate to the surface at all.

68. Magnitude of the photo-electric effect. The magnitude of the photo-electric effect may be defined as the total

current from unit area of the illuminated surface when its potential is favourable to the escape of negative electricity. Its value is only definite for surfaces not only kept but also prepared in the highest vacua obtainable and never exposed at any period to the action of a gas at a perceptible pressure.

An apparatus (7) suitable for the preparation and investigation
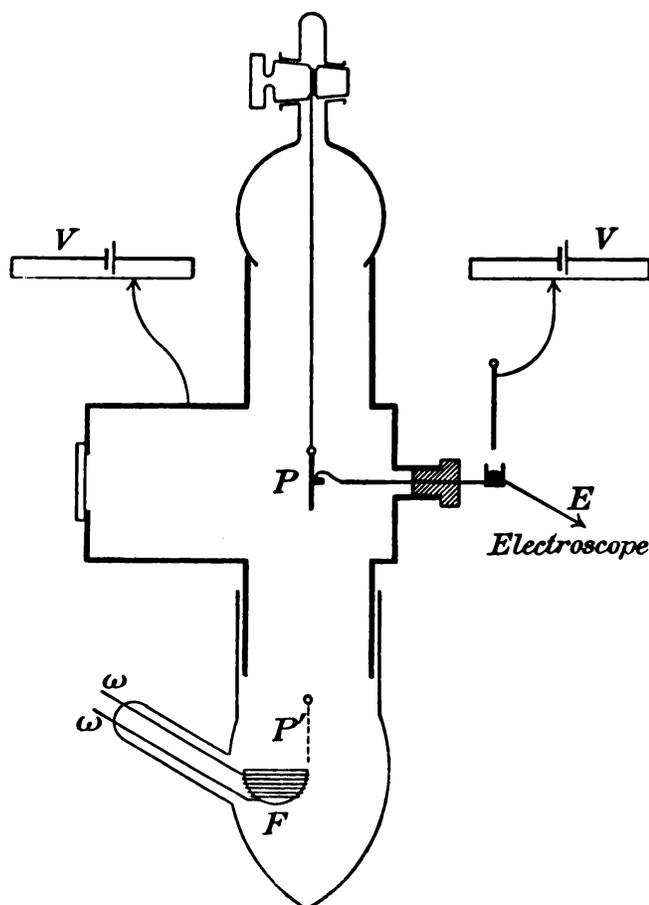
Fig. 51

of a metallic surface in vacuo is shewn in Fig. 51. The thick lines represent the metallic part of the apparatus which extends far enough on all sides to screen the plate P from external electrostatic effects. When in the position shewn the plate makes metallic contact with a Wilson electroscope E, while the two potentiometers V, V can be adjusted so as to maintain a constant measured difference of potential between

the radiator and its surroundings. To obtain a film on the radiator P it is lowered to the position P' opposite the mouth of a small quartz crucible F, which contains the metal under investigation and can be electrically heated by the wires ω, ω passing through the walls of the tube. The metallic vapours condense on the cold plate forming a film which, as the whole apparatus is maintained at a high vacuum, has never been in contact with gas and so is free from the disturbing surface layer. If the outer case is earthed the maximum potential acquired by the plate P as measured by the electroscope gives the maximum velocity of emission of the photo-electrons, as already explained. By applying a small accelerating potential sufficient to ensure the maximum emission, the total photo-electric effect can be measured.

With films prepared and kept in vacuo, the total photo-electric effect is found to be directly proportional to the intensity of the light for intensities varying in a ratio of as much as 1 to 10^6. On account of its importance with respect to the quantum theory of radiation experiments with exceedingly small intensities of illumination have been made, but even when the energy was as small as 10^{-7} ergs per sq. cm. per sec. no departure could be observed from the proportionality between the intensity and the current. The current is also independent of whether the light is continuous or is given out in a series of brief flashes. As long as the average energy remains constant the emission remains the same.

69. Variation of the photo-electric effect with wave length and state of polarization. For the majority of metals the photo-electric effect increases as the wave length of the exciting radiation diminishes. The alkali metals for a certain part of the spectrum and with oblique incidence of the light form an exception; the current rising to a fairly sharp maximum at a definite wave length. In these metals the effect also depends on the plane of polarization of the incident light.

Let light be incident obliquely on a surface, say, of a liquid alloy of sodium and potassium. These liquid alloys are convenient since they give perfectly plane surfaces. The plane containing

the ray and the normal to the surface is known as the plane of incidence. According to the electromagnetic theory of light, if the light is plane polarized in the plane of incidence the electric field in the pulse will be perpendicular to this plane, that is, parallel to the surface of the radiator. We will denote this state as the $E_{\parallel}$ plane to indicate that the electric force is parallel to the radiating surface. On the other hand, if the light is plane polarized at right angles to the plane of incidence the electric field will be parallel to the plane of incidence and thus will have a component if the ray is oblique, perpendicular
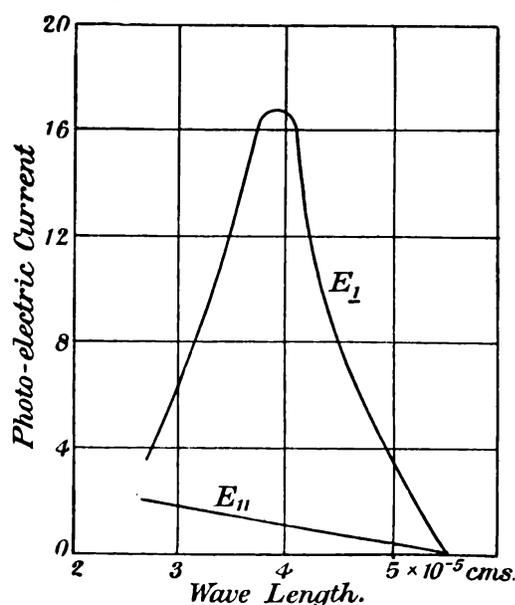

Fig. 52

to the surface. The more oblique the incidence the greater this component. We will denote this state of polarization by $E_{\perp}$.

If now experimental curves are drawn between the photo-electric intensity and the wave length of the incident light for the two states of plane polarization the results shewn in Fig. 52 are obtained. It will be seen that when the electric field in the light waves is parallel to the surface of the radiator the emission decreases uniformly as the wave length is increased. When, however, the light is polarized so that the electric field in the radiation has a component perpendicular to the radiator, the emission rises rapidly as the wave length decreases, reaches a maximum for a certain definite wave length and then decreases

until it joins the other curve. The maximum intensity increases with the obliquity of the rays, but the corresponding wave length is constant. The ratio of the maximum to the normal effect differs widely for different surfaces even of the same alloy. It is normally as much as 15 to 1, but has been observed as high as 300 to 1, with an angle of incidence of 60°. The velocity of the electrons emitted is the same in the two cases.

So far as is yet known this selective effect is confined to the alkali and alkali earth metals and is only apparent over a comparatively short part of the spectrum. In the diagram (Fig. 52) which represents the case of a sodium-potassium alloy the maximum effect is reached at a wave length of 3900×10^{-8} cm.; for potassium the corresponding wave length is 4490 and for rubidium about 5000, that is, in the yellow green of the visible spectrum. If the light is incident normally on the surface the effect, of course, disappears, since the light has then no component normal to the surface.

70. Photo-electric cells. The photo-electric effect is largely employed both for the accurate measurement of light intensities, and for the conversion of light energy into electrical energy. One form of photo-electric cell is shewn in Fig. 53. The light enters through a quartz window W and passing through the ring-shaped anode A falls on the cathode C.


Fig. 53

The sensitive surface is deposited by evaporation in vacuo on the surface of the cathode. If the cell is required to respond to the visible part of the spectrum the metal employed is usually potassium or rubidium, and in this case the quartz window can be replaced by one of glass. If the ultra-violet only is to be measured, cadmium is often employed as the sensitive surface. The photo-electric emission can be largely increased by treating the surface in various ways, and notably by admitting hydrogen at low pressure to the cell and passing an electric discharge for a short time. This probably transforms the alkali metal into a hydride.
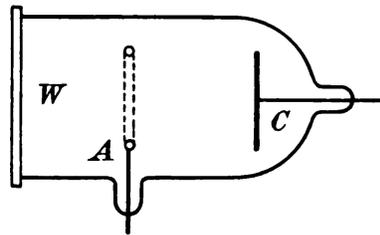
If the cell is to be used for accurate photometry it is evacuated as completely as possible. The saturation current through the cell is then, for light of given wave length, accurately proportional to the intensity of the light. Unless the light is intense, however, the current is usually too small to be measured by a galvanometer, and an electrometer method must be employed.

Much larger currents can be obtained by including an inert gas at low pressure in the cell, and applying potentials not much less than that necessary to produce an ordinary gas discharge through the cell. The photo-electrons are thus accelerated so that ionization by collision occurs, and the current can thus be multiplied many fold. Cells of this type are not suitable for accurate measurements as their sensitivity is very variable, and they also suffer from fatigue, owing to the condensation of the gas on the sensitive surface. They are used largely in sound film projection. Light is passed through the sound film on to the photo-electric cell. Variations in the density of the film produce corresponding variations in the intensity of the transmitted light, which in turn produces variations in the current through the cell. This current, which may be of the order of several microamperes can be amplified by a thermionic valve amplifier, and so transmitted to the loud speaker where the electrical fluctuations are converted into sound.

For fuller details the report on *Photo-electric cells and their Applications* [8] published by the Physical Society may be consulted.

71. Photo-electric effect in non-metals. The photo-electric effect can also be detected in non-metals, but owing to their more electro-negative character the frequency at which the effect commences is greater than in the case of metals. For carbon, for example, the emission of electrons begins when the wave length is reduced to 2550×10^{-8} cm. The observations are still more difficult to make if as usually happens the non-metal is also a non-conductor. In this case the charge on the surface is not conducted to a wire leading to the electrometer, and the positive charge accumulates until its potential is sufficient to stop the emissions of the photo-electrons. The

accumulated charge can be measured by transferring the substance bodily into a Faraday cylinder connected with an electrometer. The charge measured by the electrometer is by the ordinary laws of electrostatics equal to that on the substance.

The emission of electrons takes place throughout the mass of the substance as far as the light penetrates it. Owing to the presence of these free electrons in the substance a certain conductivity is imparted to those layers of it which actually come under the action of the light which lasts so long as the illumination is continued. Thus if a sheet of sulphur is enclosed between two electrodes and illuminated by the light from a quartz mercury lamp a current passes which increases uniformly with the voltage between the two electrodes. The conductivity is independent of the applied field up to 400 volts per mm. With a field of this intensity currents of the order of 2×10^{-9} amps. were observed when the sulphur was illuminated.

As there are no free electrons in non-conductors, the absorbed quantum must have sufficient energy not merely to pass an electron through the surface, but also to extract the electron from its parent atom. $h\nu_0/e$ must, therefore, exceed the ionization potential of the atom, and for this reason alone we should expect the threshold frequency to be high. The same considerations apply to metallic oxides, the conductivity of which in the solid state is electrolytic. For oxides and non-conductors $V_0 (= h\nu_0/e)$ is thus greater than the thermionic work function, the difference being the ionization potential of the substance.

72. Ionization of gases by ultra-violet light. The photo-electric effect in the case of a gas would take the form of simple ionization, the ejection of the photo-electron leaving the gaseous molecule positively charged. As there is no surface effect to be considered, we should expect that ionization would begin for a frequency of the radiation ν_0 given by $h\nu_0 = V_0 e$, where V_0 is the ionization potential; that is for light of wave length λ given by $\dfrac{hc}{V_0 e}$. These wave lengths, for most of the permanent gases, are situated in the extreme ultra-violet. The value of λ corre-

sponding to an ionization potential of 15 volts is 820×10^{-8} cm. The limit of transparency of quartz is 1450×10^{-8} cm. Fluorspar goes somewhat further, perhaps down to 1000×10^{-8} cm. for very transparent specimens.

Great care is necessary to avoid spurious effects due to stray light falling on the walls of the ionization chamber. Traces of dust or impurities in the gas may also give rise to spurious effects. It is not surprising that the results obtained by different experimenters are very conflicting.

Hughes obtained ionization in air, using the light transmitted by an exceptionally transparent crystal of fluorspar, and of estimated wave length 1250×10^{-8} cm.; and ionization has been detected in carbon dioxide and ammonia using light transmitted through a quartz window. If these results may be regarded as established, the effect must be regarded as connected with the radiation potentials, rather than the ionization potentials of the molecules. It is possible that if two molecules, each of which has passed into the excited state by the absorption of radiation, come into collision, their joint energies may be given to a single electron, which would then have sufficient energy to escape from the atom. Effects of this kind are known to occur among molecules stimulated by electron bombardment.

73. Phosphorescence and the photo-electric effect. No connection can be traced between photo-electricity and fluorescence, many fluorescent compounds being quite inactive. On the other hand, phosphorescent substances always shew a well-marked photo-electric effect. Thus calcium sulphide with a trace of powdered bismuth and a flux of sodium borate yields a very actively phosphorescent substance. On testing this it was found to be exceedingly photo-electric also, giving a photo-electric effect nearly as large as brightly polished magnesium. The three substances taken separately and also in pairs were found to be neither phosphorescent nor markedly photo-electric. By using absorbing screens it could also be shewn that light which did not produce phosphorescence did not produce a photo-electric effect. The two effects, therefore, seemed to run parallel to each other.

It has been shewn that phosphorescence is due to certain active centres in the "phosphor." In all probability these centres under the action of light emit an electron which if the centre is sufficiently near the surface escapes as a photo-electron. If the centre is too deep for this the electron remains embedded in the substance, which is always a non-conductor. Eventually, however, under the action of the attraction of the now positively charged centre the electron finds its way back into the "centre," producing disturbances there which cause the emission of the phosphorescent light. The photo-electric effect is thus connected with the excitation of phosphorescence, and not with the phosphorescence itself. The photo-electric effect itself ceases as soon as the exciting radiation is cut off.

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CHAPTER X

X-RAYS

74. Production of X-rays. Röntgen, in 1895, discovered that if a discharge tube at low pressure was worked in the neighbourhood of a cardboard screen covered with crystals of barium platinocyanide the crystals glowed with their characteristic yellowish green fluorescence. The effect was traced to radiation of some kind proceeding from those portions of the walls of the discharge tube on which the cathode stream impinged. The luminosity was not appreciably diminished if the tube was completely enclosed in black paper, and it was therefore not due to ordinary light. This new type of radiation was labelled X radiation, pending further enquiry as to its nature. It is sometimes, but more rarely, called Röntgen radiation.

The radiation can be detected by the luminosity it excites in certain fluorescent materials, by its action on a photographic plate or by the ionization it produces in any gas through which it passes. The latter effect is commonly employed to measure the intensity of the radiation.

X-rays have the property of penetrating many substances which are opaque to ordinary light. The absorbing power of a substance for X-rays depends partly on the density, and partly on the atomic weight of the elements contained in it. Light substances, and those containing only elements of low atomic weight are comparatively transparent, while substances of high atomic number, and great density are comparatively opaque. Thus if an experimenter places his hand between the source of X-rays and a fluorescent screen the shadows cast by the relatively opaque bones are clearly visible, surrounded by the much fainter shadow cast by the relatively transparent flesh. This property of the rays renders them an extremely valuable asset in medical diagnosis, and is also being widely applied in metallurgical and other technical investigations.

For medical and commercial purposes the original type of X-ray tube, in which the cathode rays were produced by means of a low pressure gas discharge have been replaced by a design originally due to Coolidge, one form of which is shewn in Fig. 54. The cathode C consists of a spiral of tungsten wire which can be heated by passing a current through it either from an insulated battery, as shewn in the diagram, or, more conveniently, from a specially designed transformer. The tungsten wire, when raised to incandescence emits large numbers of thermions, which can be projected towards the anode A with any desired velocity by applying a suitable potential difference
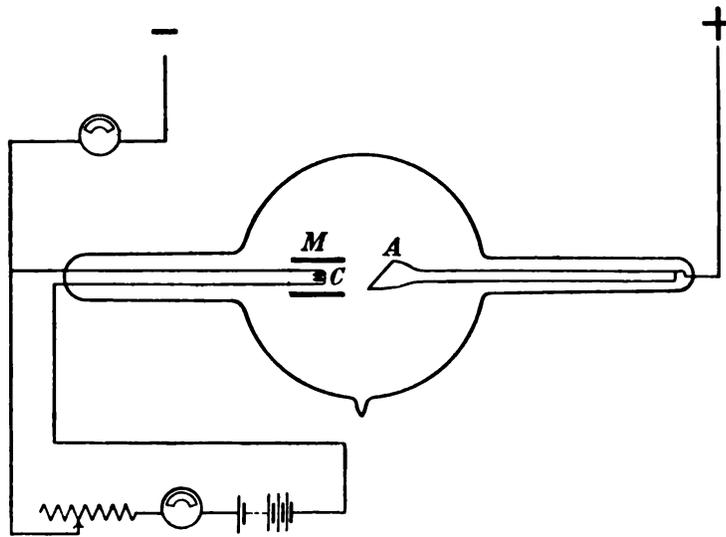
Fig. 54

between the anode and the cathode. The cathode stream thus produced can be focused to a fine spot by surrounding the cathode with a molybdenum shield M.

The tube is exhausted as completely as possible, so that no discharge passes when the wire is cold. As the P.D. across the tube is always greatly in excess of the saturation potential, the current through the tube depends only on the thermionic emission of the filament, which in turn is governed by the temperature of the filament. This can be controlled by a rheostat in the heating circuit. The current through the tube can thus be regulated independently of the P.D. across it.

The anode A is a massive block of tungsten. The efficiency of

C I   10

a target in converting the energy of the cathode rays into X-ray energy increases with the atomic weight of the target, while the hardness and high melting point of tungsten are also valuable qualities. In modern practice currents of 30 m.a. at a P.D. of 100,000 volts are quite commonly employed in X-ray production. Only a minute fraction of this energy, usually about 0·2 per cent., is converted into X-radiation. The remainder is transformed into heat in the anode. As will be seen from the figures quoted above this production of heat may amount to 700 calories per second, and in tubes designed for prolonged running, special cooling devices have to be employed to remove it from the tube.

The high potential supply for the tube is almost invariably obtained from a high tension transformer. The tube itself acts as a rectifier, since current can only pass when C is negatively charged. A practically constant unidirectional current can, however, be obtained from the high tension transformer by the use of thermionic rectifiers and high tension condensers, and the larger X-ray plants generally adopt this plan.

75. Radiation emitted by the stoppage of a moving electrified particle. Classical Theory. The fact that the X-rays have their origin at the point struck by the cathode rays led Sir G. Stokes to suggest that they are electromagnetic waves set up by the sudden stoppage of the rapidly moving electrons which make up the cathode stream. This view is now generally accepted.

The effect is most readily understood by a consideration of the Faraday tubes of force. If a charged cathode particle is moving with a speed which is small compared with that of light, its electric field will be the same as that for a particle at rest, and the tubes will be therefore distributed uniformly round the particle. Assigning all the effects in the field round the charge to the action of the Faraday tubes it can be shewn that the motion of a single Faraday tube of force produces a magnetic field in the medium which is perpendicular to the length of the tube and to its direction of motion, and equal to $4\pi v$, where v is the velocity of motion of the tube in a direction perpendicular to its length. (See J. J. Thomson, *Elements of Electricity and Magnetism*, Chap. XIII.)

Consider a single charged particle moving along a direction OX with a velocity v. This particle will carry with it a number of Faraday tubes of electric force, which when the motion has become steady will travel along as if rigidly attached to the particle.

Suppose the particle is suddenly stopped by striking a solid obstacle at the point A (Fig. 55 a), and let us suppose that disturbances are propagated along the Faraday tubes with a finite velocity c. It can be shewn that this velocity is the velocity of light.
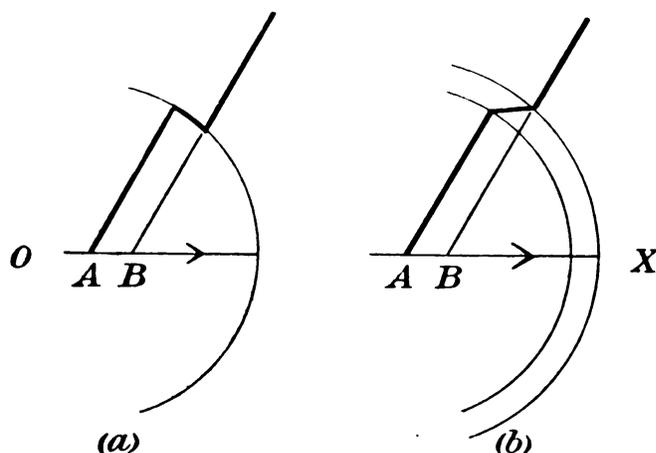
Fig. 55

Let t be the time that has elapsed since the particle was stopped. Describe round A a sphere of radius ct. Then all the portions of the tubes inside this sphere will be radiating from the stationary position of the particle at A. Outside this sphere however the disturbance produced in the Faraday tubes by the stoppage of the particle will not have arrived. They will thus be still moving in the direction OX with their original velocity v, and will be radiating from the position which the particle would have reached if it had not met the obstacle, that is, from a position B along OA produced where AB is equal to vt.

There will thus be a relative displacement between the two portions of the tube of force, and as we must regard the tube as continuous it is evident they must wrap themselves round the surface of the sphere.

10-2

This sphere is expanding with a velocity c, and we thus have a sheet of electric force travelling out with a velocity c from the position of the particle. But the motion of the Faraday tubes at right angles to their length produces a magnetic field perpendicular to the Faraday tubes and to the direction in which they are moving, that is to say, also in the surface of the sphere. Thus a sheet of electromagnetic disturbance spreads out from the particle. This, on Stokes' theory, constitutes an X-ray pulse.

It will not in general be possible to stop the particle abruptly. If τ is the time taken to reduce the particle to rest, the disturbance will be enclosed by two spheres of radii ct and $c (t + \tau)$ (Fig. 55 b). The thickness of the disturbance or pulse will thus be $c\tau$ and will be smaller the more quickly the particle is stopped.

Let Fig. 55b represent this state of affairs. Then, since $AB = vt$,

$$\frac{\text{tangential electric polarization}}{\text{normal electric polarization}} = \frac{vt \sin \theta}{\delta},$$

where δ is the thickness of the pulse and θ is the angle between the direction of the tube and AX. But the normal polarization is $e/4\pi r^2$ and thus since $r = ct$ the tangential electric polarization

$$= \frac{e}{4\pi r\delta} \frac{v \sin \theta}{c} . \quad . \quad . \quad . \quad . \quad (69)$$

Now since this is moving at right angles to its direction with a velocity c it will produce a magnetic force H, equal to $4\pi c$ times the polarization, that is

$$\frac{ev \sin \theta}{r\delta} . \quad . \quad . \quad . \quad . \quad (70)$$

Since these fall off inversely as the distance from the particle while the normal polarization falls off as the inverse square of the distance, the intensity in the pulse except for points near the particle will be great, compared with the intensity outside it. We shall thus get a pulse of electromagnetic disturbance travelling out from the particle, and behaving in many respects like ordinary light. The chief differences are that in the first place the thickness of the pulse is found to be small compared with the wave length of visible light, while

in the second place the X-rays lack that regular periodic character which occurs in a train of waves of constant wave length.

The energy in a pulse of this kind being equally divided between the electric and magnetic fields is equal to $2 \times \dfrac{\mu H^2}{8\pi}$ per unit volume, i.e. $\dfrac{\mu e^2 v^2 \sin^2 \theta}{4\pi r^2 \delta^2}$.

The energy radiated is thus zero along the direction of motion of the particle, and rises to a maximum at right angles to this direction. The volume of shell included between radii, making angles θ and $\theta + d\theta$ with the axis AB, is $\delta . 2\pi r \sin \theta . r d\theta$, and the total energy in the shell is therefore

$$2 \int_0^{\frac{\pi}{2}} 2\pi r^2 \sin \theta \, \delta \, \frac{\mu e^2 v^2 \sin^2 \theta}{4\pi r^2 \delta^2} \, d\theta$$

$$= \frac{2}{3} \frac{\mu e^2 v^2}{\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

on substituting for H from (70) and evaluating the integral. The energy is thus inversely proportional to the thickness of the pulse. Thus the more suddenly the particle is stopped the greater the energy radiated.

The method can easily be extended to the case of the acceleration of a charged particle which is not actually brought to rest. If f is the acceleration then the time τ which would be taken for the particle to be brought to rest is given by

$$v = f\tau.$$

Substituting this value for τ, and the value $c\tau$ for δ in equations (69) and (70) we have

tangential polarization $D = \dfrac{ef \sin \theta}{4\pi r c^2}$ . . . (72)

∴ Magnetic field $\quad H = \dfrac{ef \sin \theta}{rc}$ . . . (73)

The rate of flow of energy across unit area (by Poynting's Theorem) is $c^2 DH$. Hence

intensity of the radiation $= \dfrac{e^2 f^2 \sin^2 \theta}{4\pi r^2 c}$ . . (74)

Integrating over the area of the sphere of radius r we have

$$\text{total energy of the radiation} = \frac{2}{3} \frac{e^2 f^2}{c} . \quad . \quad (75)$$

76. The scattering of X-rays by matter. Suppose the radiation from one electron falls upon another. The second electron while the pulse is passing over it will be subject to an electric field X and will thus have an acceleration

$$f_1 = X \frac{e}{m} = \frac{4\pi e D}{m} = \frac{e^2 f \sin \theta}{mrc^2} \quad . \quad . \quad . \quad (76)$$

substituting for D from (72). This electron will, therefore, give out radiation which, since f_1 is proportional to f, will have the same wave form and thus the same quality as the radiation exciting it.

Thus if a beam of primary X-rays falls on a material substance, since all matter contains electrons, secondary X-rays will be given out in all directions which, since they are found to be of the same quality as the rays exciting them, have been called "*scattered radiation*," in order to distinguish them from another type of secondary radiation which may also be emitted, the quality of which depends not on the primary radiation but on the chemical nature of the radiator. This latter type is often called "*characteristic*" radiation, since it is characteristic of the radiator used for the experiment.

These effects can easily be observed by allowing a narrow pencil of X-rays to fall on a thin sheet of aluminium, or paper. An electroscope placed near the radiator, but out of the direct line of the primary pencil, will lose its charge, shewing that ionizing radiations are being given out by the radiator. If the radiator is removed the rate of loss of charge becomes very small. If, however, a sensitive electroscope is employed it is possible to observe a residual effect due to the action of the primary pencil on the molecules of the air.

The scattered radiation is not uniformly distributed about the radiator. The simple theory already outlined leads to the conclusion that I_θ the intensity of the radiation emerging from

the radiator at an angle θ with the primary rays should be expressed in the form

$$I_\theta = I_{\frac{\pi}{2}} (1 + \cos^2 \theta) \quad . \quad . \quad . \quad . \quad . \quad (77)$$

where $I_{\frac{\pi}{2}}$ is the intensity of the scattered radiation at right angles to the primary beam. The scattered radiation is thus a minimum in this direction, and approaches twice this value as the direction of the primary beam is approached.

Careful experiments have shewn that this relation is not strictly true. In every case the intensity of the radiation on the side of the radiator from which the primary rays emerge is greater than that given out at a similar angle from the face by which the rays enter(1). The distribution is thus unsymmetrical about a plane through the radiator at right angles to the primary beam. This is shewn by the thick line curve in Fig. 56, which represents the author's results for the actual distribution of the scattered radiation around a thin aluminium radiator placed at R. The dotted line gives the theoretical distribution as determined by (77).
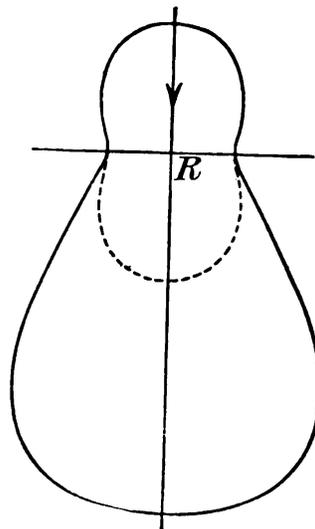
Fig. 56

77. **Polarization of the scattered radiation.** Consider a beam of cathode rays falling on an anti-cathode at O in the direction DO (Fig. 57). If the first impact of the electrons produced an X-ray the acceleration of the electrons would be in the direction OD, and the electric force in the resultant pulse at any point along the ray OP would be parallel to the plane of the paper. Actually the fact that the distribution of the primary rays round the anti-cathode is almost uniform, shews that many of the cathode particles must experience considerable deviations owing to collisions with the electrons in the anti-cathode before producing an X-ray pulse, but at any rate we may expect a preponderance of direct collisions and therefore a maximum electric force parallel to the plane of the paper.

Since there is an excess of electric field in the pulses in a definite direction the emerging beam may be said to be partly polarized.

Suppose now that this partially polarized radiation falls on a radiator at P. The electric force will cause the electrons in the gas molecules to have an acceleration (§ 76), which if the beam is completely polarized will be in the direction PQ since the field must be in the plane of the paper and also perpendicular to the direction of the ray. Thus the electrons will be set vibrating in the direction PQ, and will emit radiation which as we have seen will be zero in the direction of motion of the electron, and a maximum at right angles to it. Thus if the primary rays were completely polarized there would be no
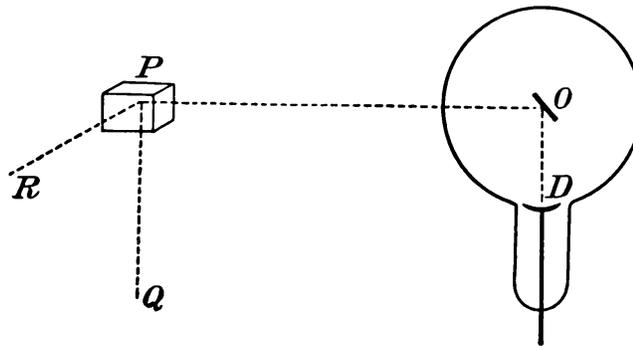
Fig. 57

scattered radiation in the direction PQ while it would reach a maximum in a direction PR through P perpendicular to the plane containing OD and OP. In other words if we allow the rays from an X-ray tube to fall on a radiator we should expect that the scattered radiation would be a minimum in a line through the radiator parallel to the incident cathode rays, and a maximum in a direction at right angles to this. The experiments were carried out by Barkla (2) in 1904 and shewed a very marked effect, the polarization often reaching as much as 20 per cent. The actual amount depends on the hardness of the rays and the nature of the anti-cathode.

The matter can, however, be pursued further. The electrons in the radiator are all moving in the plane RPQ. Since the component of motion parallel to PR produces no radiation in the direction PR the scattered radiation proceeding along PR will

clearly be completely polarized, the electric displacement being parallel to the direction PQ. Thus if a second radiator of low atomic weight is placed at R, no radiation should be scattered from it in a direction parallel to PQ, the maximum scattering being in a direction at right angles to this. The relation will only hold exactly if the different beams are infinitely narrow, so that they can be regarded as lines. Compton, using very narrow slits to limit the beams, was, however, able to shew that the radiation scattered from R in a direction parallel to PQ was less than 1 per cent. of that scattered at right angles to this direction. The complete polarization of the beam scattered along PR has thus been demonstrated.

78. Energy of the scattered radiation. The total energy scattered by a single electron when a primary X-ray pulse passes over it can easily be calculated. Let the electron be situated at a distance r from the point of origin of the X-ray pulse and in a direction making an angle θ with the direction of the acceleration of the primary electron producing the pulse. The acceleration of the scattering electron is then given (76) by

$$f_1 = \frac{e^2 f \sin \theta}{m r c^2},$$

and the total energy S radiated by it is, by (75), given by

$$S = \frac{2}{3} \frac{e^2}{c} \int f_1^2 dt = \frac{2}{3} \frac{e^6 \sin^2 \theta}{m^2 r^2 c^5} \int f^2 . dt,$$

where the integration extends over the whole time that the primary pulse is passing over the electron. But, by (74), I the energy per unit area in the primary pulse at the scattering electron is given by

$$I = \frac{e^2 \sin^2 \theta}{4 \pi r^2 c} \int f^2 . dt,$$

from which we have immediately

$$\frac{S}{I} = \frac{8\pi}{3} \frac{e^4}{m^2 c^4}, \quad . \quad . \quad . \quad . \quad . \quad (78)$$

where e is measured in electrostatic units.

If there are N electrons in unit mass of the radiator, and if we can assume that they scatter independently, so that there is no

constant phase relation between the secondary wavelets from the different electrons, the total energy of the scattered radiation will be the sum of the intensities from the individual electrons. Thus if S is the total intensity of the radiation scattered from unit mass of a radiator when in a primary beam of intensity I

$$\frac{S}{I} = \frac{8\pi}{3} \frac{Ne^4}{m^2c^4}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (79)$$

This result is historically important as it forms the basis of by far the earliest method of estimating the number of electrons in the atom. Since the primary and scattered radiations have the same pulse form it is legitimate to assume that their energies are proportional to the ionization produced by them in unit volume of air. The ratio S/I can thus be determined by making suitable observations with an ionization chamber. Experiments showed that for elements of low atomic weight and for radiation of medium wave lengths, the mass coefficient of scattering was approximately constant at a value of about 0·2.

If Z is the number of electrons per atom, and W the atomic weight of the radiator, the number of atoms per gm. of the radiator is $1/Wm_0$ and the number of electrons is Z/Wm_0 where m_0 is the mass of an atom of unit atomic weight. Hence substituting in (79) we have

$$0·20 = \frac{8\pi}{3} \frac{Z}{Wm_0} \frac{e^4}{m^2c^4} = 0·40 \frac{Z}{W}$$

on evaluating. The number of electrons per atom is thus approximately equal to half the atomic weight.

We can express this result in a more fundamental manner. The existence of isotopes shews that the chemical atomic weight of an element is not a fundamental property as different atoms of the same element differ in mass. If we arrange the elements in the order of ascending atomic weights, and number them consecutively, beginning with hydrogen = 1, the number assigned to any element is called its *atomic number*. All isotopes of the same element have the same atomic number, though they differ in atomic weight. Except in the case of hydrogen the atomic number is not far removed from half its atomic weight. Hence the result we have just arrived at may be stated in the form that

the number of electrons in an atom is equal to its atomic number. This suggestion is amply confirmed by phenomena with which we shall deal later.

For primary radiation of long wave length, and for elements of high atomic number the mass coefficient of scattering increases above its classical value of 0·2. The effect may be ascribed to the interaction of the scattered waves from the different electrons. Suppose that the pulse thickness, or wave length, of the primary pulse is large compared with the diameter of an atom. The different electrons in the atom will as the pulse passes over them be all moving simultaneously in practically the same phase, and the radiations they give out will also be in phase. In this case ordinary optical theory shews that the amplitude of the resulting wave is the sum of the separate amplitudes, the intensity being the square of the resultant amplitude. The intensity of the radiation scattered by the atom will thus vary as Z^2 not as Z. We may call this "coherent" scattering, and we should expect it to set in when the wave length of the radiation became comparable with the average distance between the electrons in the atom. Thus for long wave length radiation and for elements of high atomic number, where the number of electrons per atom is large, the scattering is greater than that given by the simple theory.

It is also found that for very short wave length radiation the scattering per electron falls gradually far below the classical value. This phenomenon is not explicable on the classical theory.

79. The Compton effect. The scattered radiation is found to be somewhat less penetrating than the primary radiation which produces it. In a brilliant series of experimental researches Compton succeeded in analysing spectroscopically the scattered radiation from a radiator illuminated by a beam of monochromatic X-rays. The experiments were difficult partly owing to the very small intensity of the scattered radiation, and partly owing to the smallness of the difference in wave length to be detected. He found that the scattered radiation consisted of two components, the one of precisely the same wave length as that of the primary beam; the second, known as the modified

radiation, of somewhat greater wave length. The difference $\Delta\lambda$ in wave length between the two radiations was found to vary with the direction in which the scattered radiation was viewed, in fact $\Delta\lambda$ was proportional to $\sin^2\frac{1}{2}\theta$, where θ is the angle between the directions of the primary and secondary beams. The actual value of $\Delta\lambda$ when measured in a direction at right angles to the primary beam was $0 \cdot 024 \times 10^{-8}$ cm. ($0 \cdot 024$ A.U.). The value was independent of the nature of the radiator and of the wave length of the primary beam.

The distribution of energy between the two wave lengths, however, varies with the nature of the radiator. For elements of low atomic number the scattered radiation is mainly of the modified type. For elements of high atomic number it is nearly all unmodified radiation.

To explain these effects, Compton suggested that the un-modified line represented the scattering of electrons which were firmly bound in the atom; the modified line being due to the scattering by "free" electrons. An electron may be regarded as free if the energy binding it in the atom is much smaller than that in the primary X-ray pulse. On the average, electrons are much more firmly bound in elements of high atomic number, and it is thus the elements of low atomic number which would be expected to give the maximum proportion of the modified radiation.

80. Compton's theory of scattering. To account for the observed change in wave length Compton made a somewhat daring, but very successful application of the quantum hypothesis. He assumed that the quanta of energy in the primary X-ray beam were so highly localized that they might be regarded as particles of negligible size, and further, that the collision between one of these quanta and an electron might be treated by the ordinary laws of dynamics, in exactly the same way as the collision between two perfectly elastic particles.

From the fact that radiation exerts a pressure it can easily be shewn that it possesses momentum equal to its energy divided by the velocity of light. The momentum of the "quant" as we may call the localized quantum is, therefore, $h\nu/c$. Consider a quant travelling in the direction AB (Fig. 58), and meeting an

electron at B. After the collision the quant is scattered in some direction BC, the electron itself moving in a direction BD. It is assumed that the electron is free to move, and is not rigidly attached to an atomic structure.

Since the electron has received energy the quant must have lost an equal amount. Its energy is no longer $h\nu$, but must be written $h\nu_1$, where ν_1 is less than ν, since h is a universal constant. In other words the frequency of the quantum is diminished by collision with the electron, that is its wave length is increased. This is, in essence, Compton's theory of the Compton effect.
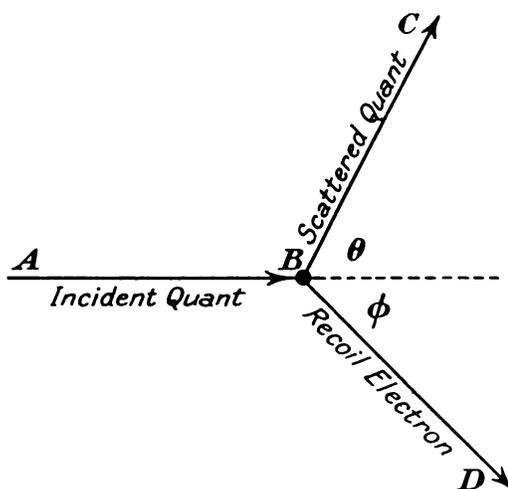
Fig. 58

We can easily put this in mathematical form. Let θ (Fig. 58) be the angle between the original and deflected directions of the quant, and ϕ the angle between the original direction of the quant and that of the electron; m the mass of the electron and v its velocity. To obtain a solution we must express the kinetic energy and momentum of the electron, not in their usual form, but in the form given by the relativity principle. The kinetic energy of the electron thus becomes $mc^2 \left(\dfrac{1}{\sqrt{1-\beta^2}} - 1 \right)$, and its momentum $\dfrac{m\beta c}{\sqrt{1-\beta^2}}$, where $\beta = v/c$. By the principle of the conservation of energy we have

$$h\nu = h\nu_1 + mc^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1 \right). \quad . \quad . \quad . \quad (80)$$

From the conservation of momentum we have further

$$\frac{h\nu}{c} = \frac{h\nu_1}{c}\cos\theta + \frac{m\beta c}{\sqrt{1-\beta^2}}\cos\phi,$$

$$0 = \frac{h\nu_1}{c}\sin\theta - \frac{m\beta c}{\sqrt{1-\beta^2}}\sin\phi,$$

from which we can readily deduce

$$\left(\frac{m\beta c}{\sqrt{1-\beta^2}}\right)^2 = \left(\frac{h\nu}{c}\right)^2 + \left(\frac{h\nu_1}{c}\right)^2 - 2\frac{h\nu}{c}\cdot\frac{h\nu_1}{c}\cos\theta. \quad . \quad (81)$$

Combining (81) with (80) and eliminating β we have

$$\nu_1 = \nu \Big/ \left(1 + \frac{2h\nu}{mc^2}\sin^2\tfrac{1}{2}\theta\right).$$

Since $\nu = c/\lambda$, and $\nu_1 = c/\lambda_1$, where λ is the wave length of the primary radiation and λ_1 that of the radiation scattered in the direction θ, the equation, in terms of wave lengths instead of frequencies, becomes

$$\lambda_1 - \lambda = \frac{2h}{mc}\sin^2\tfrac{1}{2}\theta. \quad . \quad . \quad . \quad (82)$$

The change in wave length thus depends on the angle θ, and a factor involving only universal constants. Substituting the accepted values of h, m and c,

$$\lambda_1 - \lambda = \Delta\lambda = 0\cdot 0484\sin^2\tfrac{1}{2}\theta,$$

which, for radiation scattered at right angles to the primary beam, gives us

$$\Delta\lambda = 0\cdot 0242 \text{ A.U.},$$

a value identical with that found by direct experiment.

If, instead of being free to move, the electron with which the quant collides is rigidly attached to an atom, m becomes the mass of the whole system, i.e. the atom, and $\Delta\lambda$ thus becomes vanishingly small. The quant is then scattered without loss of energy, and without change in wave length. On Compton's theory this accounts for the unmodified radiation.

The scattering by free electrons involves a loss of energy from the beam which is transferred to the electron with which the quant collides, which is therefore projected with a definite velocity. The short tadpole-shaped tracks seen along the line of the X-ray track in Fig. 59 (Plate I) are those of the Compton

recoil electrons. The longer tracks are those of the photo-electrons ejected when a quant is completely absorbed in the atom.

81. Interference phenomena with X-rays. The identification of X-rays with light of short wave length naturally led to many attempts to detect diffraction or interference effects. Haga and Windt[3] in 1901 made experiments with a V-shaped slit, a few thousandths of a mm. wide at its narrowest end, and obtained certain variations of intensity in the resultant photograph which if really due to diffraction would indicate a wave length of the order of $1 \cdot 3 \times 10^{-8}$ cm. The experiments are difficult and have never been accepted as decisive, although it is only just to say that the value obtained by these experiments has been confirmed by the method of crystal reflection which we are about to describe.

The difficulty in demonstrating diffraction for X-rays lies in the shortness of their wave lengths. A beam of sodium light of wave length $5 \cdot 89 \times 10^{-5}$ cm. is deflected through an angle of some 19° by a grating with 5500 lines to the cm. To produce a similar deviation in X-rays would require each of these spacings to be divided into ten thousand spaces, a process mechanically and physically inconceivable. It was not until 1912 that Prof. Laue[4] conceived the idea that the regular grouping of the atoms in a crystal, as affirmed by modern crystallography, might provide a natural grating of suitable spacing for the experiment. The problem is of course more complicated than that of the ordinary grating in which the spacings are all parallel and all in one plane. Since the regularity of the crystal grating is in three dimensions instead of only one Laue was able to shew that if a narrow pencil of X-rays was made to pass symmetrically through a crystal diffracted rays should emerge in various directions from the crystal and would form a symmetrical pattern of spots on a photographic plate placed perpendicular to the beam.

The theory was put to the test by Friedrich and Knipping in 1913. Their apparatus is indicated in Fig. 60. F is the anticathode of a powerful focus tube, and the rays are limited to a narrow pencil by passing through a series of slits in the lead screens A, B, C. They then pass along one of its axes of sym-

metry through a small crystal X. A sighting screen S enables
the adjustment to be made. A photographic plate is then in-
serted at P and an exposure made lasting for some hours. On
developing the plate it was found that the very black central
patch made by the undeflected beam of rays was surrounded
by a symmetrical pattern of spots as indicated by the theory,
some of the spots being deviated by nearly 40° from the direct
line of the primary beam. A Laue pattern for nickel sulphate
is reproduced in Fig. 61 (Plate III).
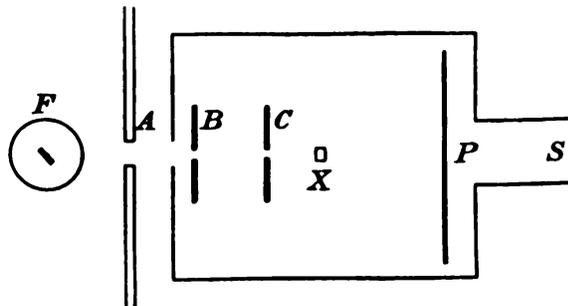
Fig. 60

82. Theory of Laue's experiment. Modern crystallo-
graphers, following Bravais, have been led to regard the atoms
in crystals as arranged with a definite spacial symmetry. All
the atoms of the same sort are regarded as forming a regular
system of points in space, the different systems belonging to
the different atoms of course interpenetrating. This net-like
arrangement is known as a space lattice.

In order that a set of points shall form one of these space
lattices they must satisfy certain geometrical conditions.
These conditions can be worked out irrespective of any definite
knowledge of crystalline structure merely from the general laws
to which all regular patterns in space must conform.

It has been shewn that the only method of dividing up space
which will satisfy the conditions is as follows. A series of three
sets of parallel planes is taken intersecting each other. All the
planes in each set are parallel and equally spaced, but the
spacings of the different sets need not be the same, and the
planes may intersect at any angle. The space is thus divided
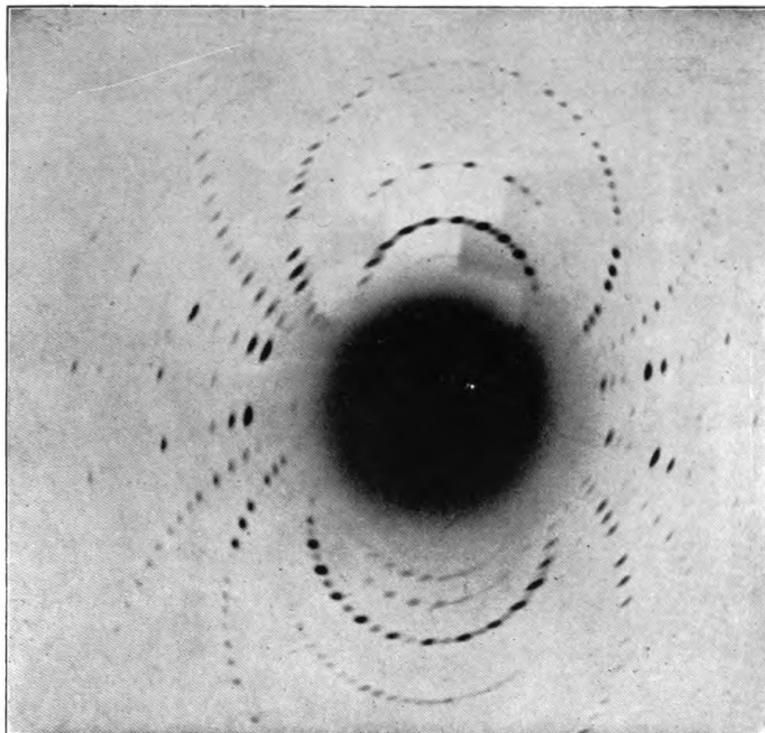
Sir William Bragg.

FIG. 61. LAUE PATTERN OF NICKEL SULPHATE.
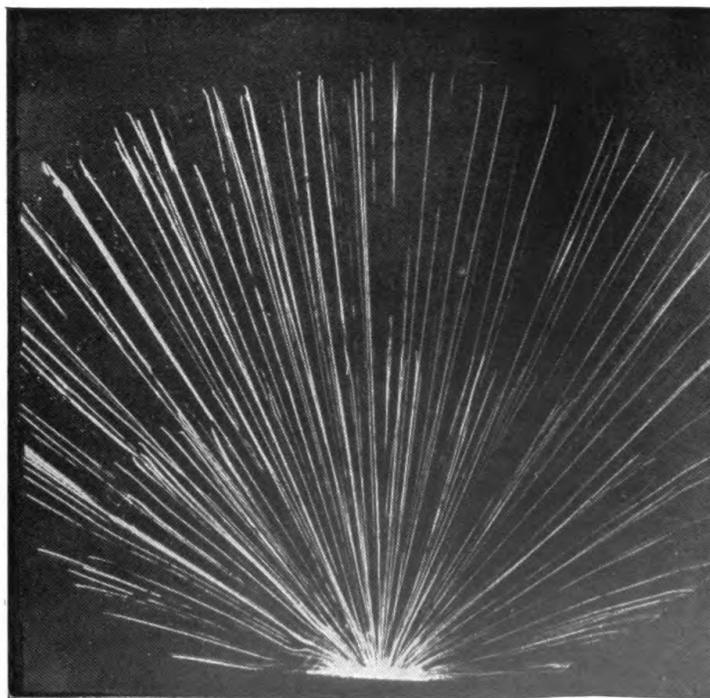
Lord Rutherford, J. Chadwick and C. D. Ellis.

FIG. 80. TRACKS OF α-PARTICLES FROM THORIUM C AND THORIUM C'.

up into a series of parallelepipeds (Fig. 62) the corners of which
form a space lattice. The atoms are supposed to be placed at each
of these corners. The three directions parallel to the three edges
of the parallelepiped form the axes of the crystal. We have seen
that an atom under the action of a Röntgen pulse becomes the
centre of a secondary wave of disturbance which spreads out
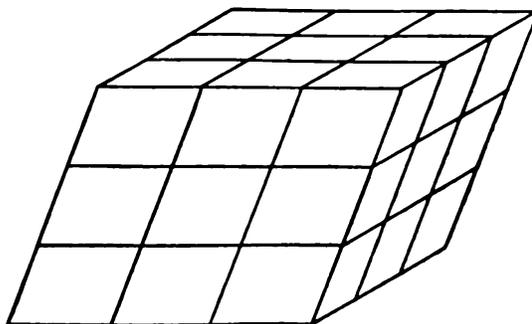
Fig. 62

through space. Consider a series of atoms A, B, C, ... (Fig. 63)
all equally spaced along a line parallel to one of the axes of the
crystal. By the ordinary
theory of optical diffraction
a wave front EB travelling in
the direction EA will give rise
to a diffracted wave front
AF travelling in the direction
BF if the optical path dif-
ference $BF - EA$ is an integral
number of wave lengths of the

Fig. 63

radiation used, that is if $AB (\cos \phi - \cos \phi_0) = p\lambda$, where p is
an integer. Writing $AB = a$, $\cos \phi_0 = \alpha_0$ and $\cos \phi = \alpha$ we have
for all the atoms along the line ABC to co-operate to form a
diffracted wave, $a (\alpha - \alpha_0) = p\lambda$.
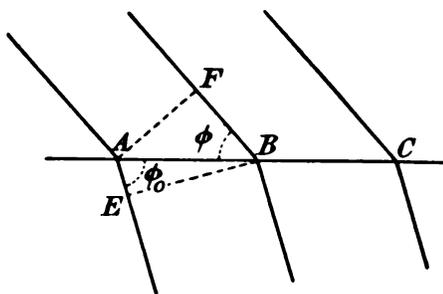
Exactly similar conditions apply to the atoms equally spaced
parallel to the other axes of the crystal. Thus if a, b, c are the
distances apart of the atoms in the three directions parallel to the
axes α_0, β_0, γ_0 the cosines of the angles between the incident ray
and these three axes, and α, β, γ the cosines of the angles made
by the diffracted ray and the axes, the conditions which must

C I   II

be simultaneously fulfilled in order that there may be a diffracted ray are

$$\left. \begin{array}{l} a\,(\alpha - \alpha_0) = p\lambda \\ b\,(\beta - \beta_0) = q\lambda \\ c\,(\gamma - \gamma_0) = r\lambda \end{array} \right\} \quad . \quad . \quad . \quad . \quad (83)$$

where p, q, and r are any integers.

If the radiation employed were strictly monochromatic so that λ is fixed, then since a, b, and c are fixed by the crystal structure it would not, in general, be possible to satisfy these three equations with finite values of the integers, p, q, and r. The X-rays from an X-ray tube, however, form a continuous spectrum and the crystal picks out, as it were, the particular components of the radiation which are suitable for diffraction. Thus the different diffracted rays differ in wave length, and the exact interpretation of the pattern is not always easy. Fortunately a slight modification of the experiment due to W. L. Bragg[5] gives not only a much simpler method of regarding the phenomena but also results capable of yielding more definite information.

83. Reflection of X-rays by crystal planes. Experiments of Bragg. Shortly after the publication of the work of Laue, W. L. Bragg[5] discovered that X-rays could be regularly reflected by the cleavage planes of crystals when the rays were incident on the surface at nearly glancing angles. If we return to Fig. 62 it will be noticed that along certain planes drawn in the crystal, the construction planes, for example, the atoms are thickly studded, that is to say, these planes pass through a considerable number of atoms. It is possible to draw other planes in the crystal, such for example as those drawn through opposite edges of the elementary parallelepipeds, which contain somewhat smaller but still considerable numbers of atoms. These planes are closely related to the surfaces of the natural crystal. They represent lines along which the crystal will cleave or split with comparative ease, and all are parallel to possible faces on the crystal.

Consider now a parallel beam of X-rays falling on one of these thickly studded planes represented in section by the dots

in Fig. 64. As the wave front passes over each atom in turn, it becomes the source of a secondary pulse similar in character to the primary radiation. These secondary pulses will combine to form a plane wave front inclined to the reflecting plane at an angle equal to that of the incident wave. We have, in fact, a reproduction of Huygens' construction for the reflection of a plane wave at a plane surface, except that the reflecting "elements" are now discontinuous.

There is, however, an important distinction between the specular reflection of light, and the so called "reflection" of X-rays by crystal planes. The fraction of the incident energy
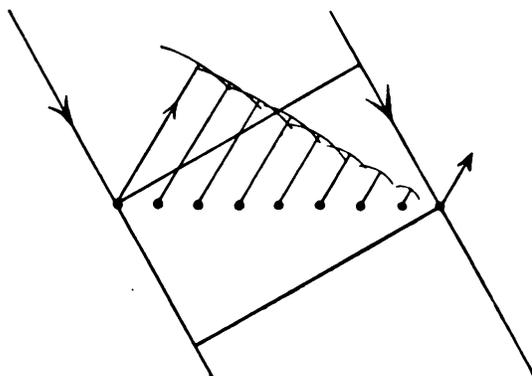
Fig. 64

which is reflected from a single plane of atoms is infinitesimally small. Most of the radiation is transmitted to be reflected again at the series of parallel planes through which it passes while penetrating into the crystal. If the waves reflected from these successive planes of atoms are in phase with each other when they reach some point outside the crystal they will co-operate to form a measurable reflected beam. If they are out of phase they will, by the ordinary laws of interference simply cancel each other and there will be no reflected beam. The effect, when it occurs, is thus a volume not a surface reflection. It depends on the internal structure of the crystal, not on its surface, and will occur even if the crystal exhibits no actual facet parallel to the planes we are considering.

Let pp, qq, rr, ... (Fig. 65) be a series of parallel planes of atoms and PP' be a wave front advancing on the crystal in the

11-2

direction PQ, making an angle θ with the surface pp. The reflected ray must travel in a direction QR making the same angle with the surface pp as the incident ray PQ. The waves reflected from the surfaces pp, qq, will be in phase at a point R if their path difference, $P'Q'R - PQR$, is an integral number of wave lengths of the radiation. Draw QSN perpendicular to pp and QD perpendicular to $P'N$. Then since PQ and QR make equal angles with the line pp, and QN is perpendicular to pp, $Q'Q$ is equal to $Q'N$ and the path difference between the two rays under consideration is $P'Q' + QQ' - PQ = P'Q' + Q'N - P'D$

$$= DN = QN \sin \theta$$

$$= 2d \sin \theta, \quad . \quad . \quad . \quad . \quad (84)$$
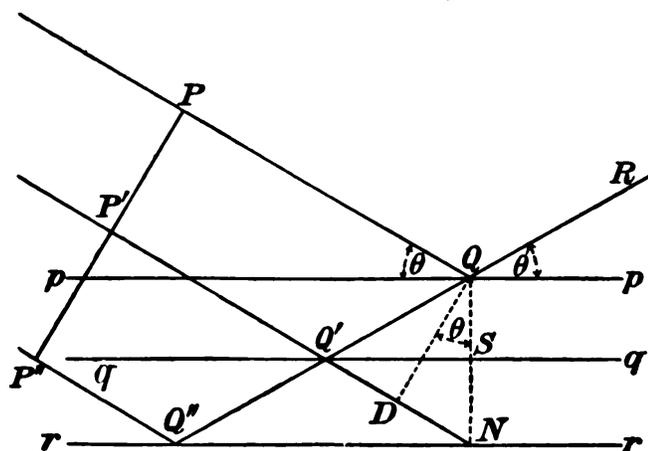
Fig. 65

where d is the perpendicular distance between the planes. Hence the condition for maximum reflection at any crystal face is that $2d \sin \theta$ shall be an integral number of wave lengths of the radiation used.

It will be noticed that the problem is exactly analogous to that of the diffraction grating, the various parallel planes acting as lines in the grating. Applying the usual optical principles it can be shewn that a very small discrepancy from exact agreement in phase between the separate elements such as would be introduced by a very slight change in the angle θ, will result in the almost complete extinction of the radiation by interference. The angle at which reflection occurs is, therefore, very sharply defined.

If the incident X-radiation is homogeneous there will obviously be a series of angles at which the radiation can be reflected, these being obtained by making n successively equal to $1, 2, 3, \ldots$ in the general equation

$$2d \sin \theta = n\lambda, \quad \ldots \quad \ldots \quad (85)$$

where λ is the wave length. These will correspond to the spectra of different orders produced by a grating, and may be alluded to as the first, second, etc., order reflection spectra. These spectral lines can be identified as belonging to the same primary wave length by the fact that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 :$ etc. $:: 1 : 2 : 3. \ldots$

The method obviously gives us a means of comparing the wave lengths constituting our primary beam. For if we allow two beams of wave length λ and λ' to fall on the same face of the same crystal they will suffer reflection at angles θ and θ' respectively, such that $2d \sin \theta = n\lambda$, $2d \sin \theta' = n\lambda'$. Hence for the same crystal and the same order of reflection we have

$$\frac{\lambda}{\lambda'} = \frac{\sin \theta}{\sin \theta'} . \quad \ldots \quad \ldots \quad (86)$$

Thus if our primary beam is made up of a number of definite wave lengths, there will be a series of definite angles at which we shall obtain sharp reflection of the rays, each angle corresponding to some definite wave length. If on the other hand the X-rays form a continuous series of wave lengths, there will be a certain range of angles between which reflection will take place. This corresponds to the case of the continuous spectrum formed by a grating with white light, and the radiation may conveniently be referred to as "white" X-radiation.

It is obvious that the phenomenon is confined to certain definite small limits. Since the maximum value of $\sin \theta$ is unity, then $n\lambda/2d$ must be less than 1. Thus reflection will only take place when n is sufficiently small and d sufficiently large. In very favourable cases, using the principal planes of the crystal d may be as much as five times λ, in which case as many as ten spectra may be observed. The intensity however as in the case of an ordinary grating decreases rapidly with the order of the spectrum. It is found experimentally that the

distance apart of the planes decreases rapidly as the planes become less fundamental, and eventually becomes so small that there are no values satisfying equation (85) for the wave lengths generally present in a Röntgen beam.

It is evident that if we keep λ constant and use different planes as reflecting planes we can find the relative values of d for the various crystal systems and thus obtain much light on crystal structure.

84. The X-ray spectrometer. The different angles at which reflection can occur mav be investigated either by a photographic or by an ionization method, and each has been
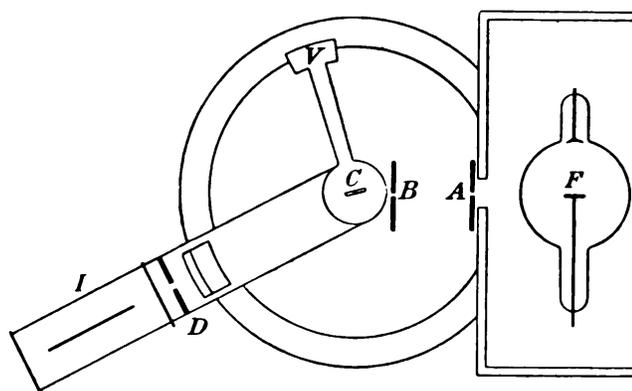
Fig. 66

used by different investigators. The apparatus needed for the ionization method has been perfected by W. H. Bragg and is indicated in Fig. 66. The rays from the anti-cathode of the X-ray tube are limited to a narrow pencil by two adjustable lead slits A and B. The arrangement may be compared to the collimator of a spectroscope. The crystal is mounted on the table of the spectrometer, as we may call it, at C, and its orientation may be read by the vernier V on the circular scale of the instrument. The ionization chamber I is carried by an arm also pivoted at the centre of the instrument, and the reflected beam can be limited by a third lead slit D. The current through the ionization chamber can be measured by an electroscope or electrometer in the usual way. As the intensity of the reflected ray is usually small the ionization chamber is generally filled with some heavy

gas such as methyl iodide, in which the ionization produced by a given beam of X-rays is more intense than it is in air.

In using the apparatus the crystal and the chamber are moved together, the latter of course being always moved through twice the angle of the former. As the glancing angle between the crystal face and the incident beam is gradually increased a point is reached where the electroscope shews a deflection, and the ionization current can be plotted against the glancing angle. If the rays are homogeneous the X-rays will only enter the
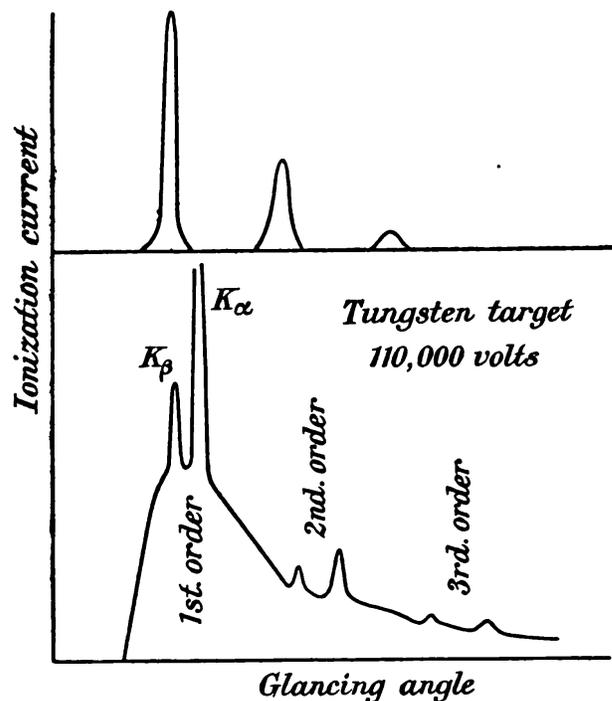
Fig. 67

chamber and the current will only flow at certain definite angles corresponding to the different order of spectra for that particular wave length, and the curve will be discontinuous.

This case is represented by the top curve of Fig. 67, which shews the current through the chamber against the glancing angle θ. It will be seen that the curve shews three peaks or "lines," and these three peaks can be identified as being due to the same waves by the fact that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3$ as $1 : 2 : 3$. In general, however, if the radiation is that from an ordinary X-ray tube, it will be made up of certain rays of

definite wave lengths together with more or less "white" radiation or radiation of continuous wave length. The curve will then be a continuous curve rising to various peaks or maxima, the height of which affords a rough measure of the intensity of the corresponding wave length in the primary beam. This is shewn in Fig. 67 the bottom curve of which gives the spectrum of the radiation from a tungsten anti-cathode. It will be seen that in this very important practical case we have a series of peaks which are characteristic of tungsten, on a background of "white" radiation. At larger angles peaks appear again in the second order reflections, and again in the third order. It will be noticed that the intensity decreases with the order of the spectrum. These peaks are characteristic of the tungsten anti-cathode. They appear whatever the nature of the crystal used for the reflection; rock salt, calcite and fluorspar, all yielding the same result. The curves are in fact exactly similar in the three cases, only the scale of the curve depending, as might be expected from the theory, on the nature of the crystal used.

85. X-ray spectrometry. Photographic methods. In the photographic method of X-ray spectroscopy the ionization chamber is replaced by a photographic film, which is usually bent round a former into a circular arc concentric with the axis carrying the crystal. The crystal itself is slowly rotated, by a clockwork mechanism, throughout the exposure. When, in the course of rotation, the reflecting planes in the crystal make with the incident beam an angle which is the reflecting angle for one of the constituent wave lengths in the incident radiation, a reflected ray is momentarily produced which records itself on the photographic film. The rotation of the crystal is continued until the weak images so formed are sufficiently exposed.

A photograph of the L-spectrum of tungsten, taken by Dr G. Shearer, is reproduced in Fig. 68 (Plate II). The central bright band is due to radiation which has passed straight through the crystal. The characteristic lines of the tungsten spectrum show as bright lines standing out on a much fainter background due to the general radiation from the tube. Since the photograph was taken with the crystal describing complete revolutions, the

spectrum appears symmetrically on each side of the central bright band. The photographic method is generally employed when measurements of wave length of the highest order of accuracy are required.

An alternative method, due independently to Hull, and to Debye and Scherrer, is to powder the crystal very finely, and to use this powder enclosed in a thin walled tube in place of the single crystal. Since the millions of minute fragments are orientated entirely at random, the incident radiation is sure to meet some of the crystal planes at the critical angle for reflection. Since only a few of the crystal grains are effective for any given radiation the reflected beams are weak, but the difficulty can be overcome by prolonging the exposure. The method is used with homogeneous incident radiation, and has the advantage that this radiation will be reflected during a single exposure from all the possible reflecting planes in the crystal. A single photograph will thus give a complete picture of the crystal structure, and the method is chiefly employed for this purpose.

86. Determination of the wave length of X-rays. The theory so far developed only enables us to compare wave lengths. To determine them in absolute units we must know the distance apart of the planes in our crystal grating. The discussion involves some acquaintance with elements of crystallography, but the argument is briefly as follows.
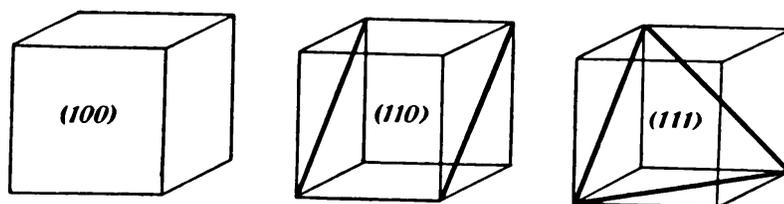
Fig. 69

Taking the case of a simple cube (Fig. 69), the most important faces are (1) the face of the cube itself, (2) the face parallel to a plane through opposite edges of the cube, (3) the face parallel to a plane including one corner of the cube and passing through the diagonal of the opposite face. The development of this face gives rise to regular octahedra and is exceedingly

common on cubic crystals. The three sets of planes are denoted in crystallography as {100}, {110}, and {111}, respectively.

Now crystallographers recognize three classes of cubic symmetry,

(1) the simple cube arising from a simple cube lattice such as we have already described,

(2) a cube with a single particle at the centre, known as the cube centred lattice,

(3) a simple cube with a particle at the centre of each face: this is known as the face centred lattice.

Now the ratios of the distances between two successive planes in the three sets of planes corresponding to the systems {100}, {110}, {111} will not be the same for the three kinds of lattices. It can be shewn by simple geometry that

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}}$$

$$= 1 : \sqrt{2} : \sqrt{3} \text{ for simple cube lattice}$$

$$= 1 : \frac{1}{\sqrt{2}} : \sqrt{3} \text{ for a cube centred lattice}$$

$$= 1 : \sqrt{2} : \frac{\sqrt{3}}{2} \text{ for a face centred lattice.} \quad . \quad (87)$$

Now by using the same homogeneous X-radiation for the three faces {100}, {110}, {111} respectively we can by (85) find the ratios of $d_{100} : d_{110} : d_{111}$. We can thus identify for any given crystal, by applying the above results, the particular order of cubic symmetry to which the crystal belongs.

Let us apply these results to the important sylvine group, comprising rock salt (NaCl), sylvine (KCl) and the corresponding bromides and iodides. These are chemically and crystallographically similar and may reasonably be expected to have the same structure. In the case of sylvine the measurements would indicate that it has the simple cubic structure. With rock salt, however, we meet a new phenomenon. The reflections from the {100} and the {110} faces are similar to those from sylvine. The reflections from the {111} faces give a weak first order spectrum, a strong second, a weak third, a strong

fourth, and so on. Judging only by the strong spectra we should assign to rock salt the simple cube lattice. Judging by the weak first order spectrum it would be a face centred lattice. How are the two results to be reconciled with each other and with the result for the crystallographically identical sylvine?

W. L. Bragg made the suggestion that the points making up the crystal structure were not molecules of the salt but atoms of its constituent elements. Since the intensity of the radiation scattered is proportional to the atomic number, reflection from a plane of sodium atoms (Na = 11) would be appreciably less than that from a plane of chlorine atoms (Cl = 17). A set of planes alternately made up of all sodium atoms, and all chlorine atoms would thus resemble a grating in which every odd ruling was somewhat wider than the even ones. Such a grating, as is well known, gives in addition to its normal spectra a set of weaker spectra with half the normal deviations. The experimental observations will thus be explained if the {111} planes are composed alternately of sodium atoms and chlorine atoms, while the {100} and {110} planes are each composed of equal numbers of the two kinds of atoms.

These conditions are satisfied if the atoms are arranged as in Fig. 70. Here the black dots indicate the metallic atoms, the circles the atoms of chlorine. It is easy to shew that the same structure will serve for the sylvine crystal. Potassium has an atomic number 19, very close to that of chlorine. In fact, since the compound KCl is formed by the passage of an electron from the potassium atom to the

Fig. 70

chlorine atom, the number of electrons in each will be the same, and their radiating powers will be identical. The structure of Fig. 70 obviously reduces to a simple cubic lattice if the dots and the circles become identical. The pattern of Fig. 70 must, of course, be regarded as repeating in every direction.
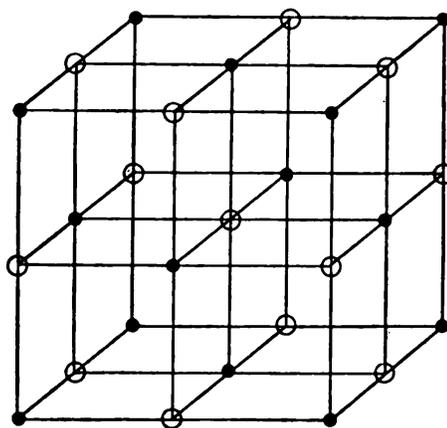
Accepting this structure for the rock salt crystal we see (considering the adjacent cubes in all directions) that each sodium atom is associated with eight of the small cubes into which the figure can be divided, and assuming its mass to be equally divided among the cubes, one-eighth of the mass is included in each cube. There are four sodium atoms associated with each small cube and thus each small cube includes the mass of half an atom of sodium, and therefore half a molecule of the compound sodium chloride. Thus the whole structure of Fig. 70 represents four molecules.

The distance apart of the planes bounding the small cubes is obviously d_{100}, all the planes being exactly similar. Hence the volume of each small cube is $(d_{100})^3$. The mass associated with each small cube is one half that of the sodium chloride molecule, that is $\frac{1}{2}$ (23 + 35·5) × (the mass of an atom of unit atomic weight), i.e. 1·65 × 10^{-24} gm.

Hence if ρ is the density of the rock salt crystal (= 2·17) the mass of the cube = ρ $(d_{100})^3$ = 29·3 × (1·65 × 10^{-24})

and $$d_{100} = 2·814 \times 10^{-8} \text{ cm.}$$

For the most pronounced radiation from platinum the glancing angle for the first order spectrum using the d_{100} planes of rock salt is 11·4°. Hence substituting in the equation $\lambda = 2d \sin \theta$ the wave length of this particular X-radiation is given by $\lambda = 1·10 \times 10^{-8}$ cm.

87. The X-ray spectra. The continuous background. We have seen that the X-ray spectrum emitted when cathode rays impinge on a target consists, to use optical phraseology, of a series of bright lines superimposed on a continuous luminous background. The lines are characteristic of the substance forming the target and constitute its X-ray spectrum. The background is independent of the nature of the target except for the fact that its intensity is proportional to the atomic number of the element of which the target is made. For a given target the intensity of the radiation is proportional to the square of the P.D. across the tube, and to the current passing through it. The energy in the radiation is, however, only a minute fraction (about $\frac{1}{1000}$) of

that of the incident cathode rays, the remaining portion of the energy appearing in the target in the form of heat.

The distribution of intensity in the spectrum is indicated in Fig. 71 (6). The form of the curves is reminiscent of the distribution of energy in the spectrum of black-body radiation, but there is still considerable doubt as to the equation to the curves. The maximum of the curve moves in the direction of shorter and shorter wave lengths as the P.D. across the tube is increased.
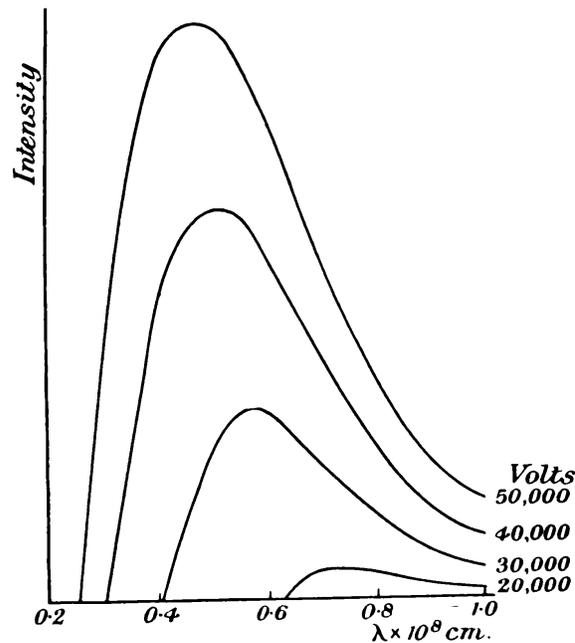
Fig. 71

It will be noticed that the curve falls to zero at some definite wave length, which depends on the P.D. used to excite the tube. There is thus for each P.D. a minimum value for the wave length of the radiation emitted, or in other words a maximum frequency, which cannot be exceeded. Very careful investigation of this end part of the spectrum by Hull (7) and others has shewn that this frequency ν is directly proportional to the applied P.D. If V is the potential difference in volts it was found that over the whole range of potentials employed (from 24,000 to 100,000 volts) the relation could be expressed by the formula

$$V = 4 \cdot 131 \times 10^{-15} \nu,$$

or converting volts to absolute e.s.u. and multiplying both sides by e, we have

$$Ve = (1 \cdot 377 \times 10^{-17}) \times (4 \cdot 774 \times 10^{-10}) \, \nu$$

$$= 6 \cdot 55 \times 10^{-27} \, \nu.$$

Thus the maximum frequency of the radiation emitted is related to the maximum energy of a cathode particle in the tube by the quantum relation, *energy* $= Ve = h\nu$, and the value of Planck's constant h obtained in this way agrees accurately with that determined from photo-electric phenomena. It will be noted that in the present case we are dealing with the transference of energy from an electron to radiation; in the photo-electric effect we have the reverse phenomenon, but the same law governs both.

The fact that most of the radiation has a frequency less than the maximum, is due to the exciting electrons losing energy owing to collisions in the target, before making the type of collision which results in X-radiation.

88. The X-ray spectra. The characteristic radiations. The characteristic spectrum of an element may be mapped by making it the target in an X-ray tube. Special demountable tubes, which can be rapidly opened up for changing the target and then re-evacuated, are generally employed for the purpose. The rotating crystal method described in § 85 gives the most accurate results. If the position of the line to be investigated is known approximately it is unnecessary to rotate the crystal through 360°. It is sufficient to set the crystal at approximately the correct angle, and to rock it backwards and forwards through a few degrees on each side of the expected value. In this way the relative wave lengths of the different lines can be compared to an accuracy approaching one part in a million. The absolute values, which depend on the determination of the lattice constant for rock salt and hence ultimately on the value of the electronic charge, are not known to an accuracy greater than 1 in 1000.

Experiments made prior to the development of X-ray spectroscopy had indicated that the characteristic radiations from an X-ray tube fell into certain groups known as the K and L radiations. Elements of high atomic number gave indications of a

still more absorbable group known as the M radiation. A study of the absorption of these radiations indicated that they were approximately homogeneous.

When examined by the spectrometer it is found that neither the K nor the L radiations are homogeneous. The K radiation consists of four principal lines; the L radiation shews ten or more. Thus the K spectrum of tungsten, the element most often employed in the target of an X-ray tube, shews four K lines:

$$K_{a_2} = 0{\cdot}21345; \quad K_{a_1} = 0{\cdot}20862; \quad K_{\beta_1} = 0{\cdot}18422; \quad K_{\beta_2} = 0{\cdot}17898;$$

all in Ångström units, and an L spectrum (Fig. 68) of thirteen distinct lines ranging from $1{\cdot}6750$ to $1{\cdot}0963$ A.U. Some lines of an M series of wave length between $6{\cdot}969$ and $6{\cdot}076$ A.U. have also been observed [11].

The outstanding feature of the X-ray spectra is their great similarity to each other. In fact, with some minor exceptions, the characteristic spectrum of one element differs from that of another only in being displaced bodily in the spectral scale, the wave length of the various lines becoming smaller as the atomic number of the element becomes greater. Moseley [8], to whom the first extensive series of observations is due, found that if ν is the frequency of some particular line in the spectrum, say the K_{a_1} line for example, then its value for any element can be expressed by the equation

$$\nu = a\,(Z - b)^2, \quad \ldots \quad \ldots \quad (88)$$

where Z is the atomic number of the element, and a and b are constants for that particular line. The value of a varies as we pass from one line to another, say from the K_{a_1} to the K_{a_2} line. The value of b is the same for all lines of the same series. For the K series it has a value very nearly equal to unity; for the L series its value is about $7{\cdot}4$. These relations are not quite exact, but if $\sqrt{\nu}$ is plotted against Z a perfectly smooth line is always obtained, which, however, shews a slight curvature for large values of Z.

It is interesting to note that when plotting his original observations Moseley found that it was necessary (in order to avoid definite breaks in the curves) to postulate that four elements, of atomic number 43, 61, 72, and 75, remained to be discovered.

These missing elements have since been discovered and identified by their X-ray spectra.

89.   The absorption of X-rays. If a sheet of any substance is interposed in the path of a homogeneous beam of X-rays the intensity of the beam is diminished, and falls off exponentially with the thickness of the sheet. Thus if I_0 is the initial intensity of the beam, I its intensity after passing through a thickness d of material,

$$I = I_0 \epsilon^{-\mu d}, \quad . \quad . \quad . \quad . \quad . \quad (89)$$

where μ is the coefficient of absorption of the radiation in the particular absorbing substance. The value of μ for radiation of any wave length can be measured conveniently with Bragg's spectrometer. The instrument is adjusted so that radiation of the desired wave length falls on the slit of the ionization chamber, and the absorbing substance, in the form of thin sheets, is placed in the path of the reflected ray, between the crystal and the ionization chamber.

It is found experimentally that the absorption depends only on the number of atoms of the substance in the thickness of the absorbing layer, and is independent of their state of aggregation. Thus μ/ρ, where ρ is the density, is constant for a given substance and independent of any changes in density due to its physical condition. μ/ρ is called the mass coefficient of absorption. The absorption can obviously be expressed in the form $I = I_0 \epsilon^{-\frac{\mu}{\rho} m}$, where m is the mass of unit area of the absorbing sheet.

It is necessary to distinguish carefully between the portion of the energy of the incident beam which is actually absorbed or transformed in the absorbing substance, and that portion which is merely scattered in radiation of the same quality as that of the incident beam. As the scattered radiation is dispersed in all directions, only a fraction of it, depending on the angle subtended at the absorbing sheet by the aperture of the ionization chamber, will enter the latter, and the beam will thus suffer a diminution in intensity from this cause alone. If the experiment is arranged so that only an inappreciable fraction of the scattered radiation enters the measuring chamber the coefficient μ as thus

measured is the sum of two distinct coefficients, the one τ measuring the actual absorption, the other σ the scattering. Thus

$$\mu = \sigma + \tau.$$

For light elements we have already seen that σ/ρ has a value of about 0·2, and is independent of the wave length of the incident radiation.

If we take some definite absorbing substance and a beam of homogeneous radiation of large wave length, so large, in fact that it does not excite the characteristic L radiation of the absorbing substance, it is found that the coefficient of absorption τ diminishes rapidly with diminishing wave length, the relation being approximately of the form

$$\frac{\tau}{\rho} = C\lambda^3.$$

This is shewn by the portion M of the curve in Fig. 72. At a certain perfectly definite wave length, however, there is a sharp and very marked discontinuity in the curve relating τ and λ and the absorption rises abruptly to
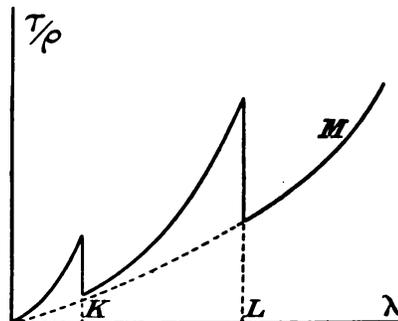
Fig. 72

a high value. At this identical wave length the absorbing substance begins to emit its characteristic L radiation. The energy of this characteristic radiation must be abstracted from the primary beam, and hence the sudden increase in the coefficient of absorption. The particular frequency for which this phenomenon occurs is known as the critical absorption frequency for the given substance. These absorption limits are so sharp that their position can be determined with an accuracy equal to that of the emission lines.

After passing the L discontinuity the absorption again decreases with the wave length, and again according to a third power law, but with a different coefficient of proportionality, until the wave length is reached at which the K radiation of the absorber is excited. This gives rise to a K discontinuity, and the phenomena described above repeat themselves. For elements of very high atomic number an M discontinuity is observed in the

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long wave region corresponding to the excitation of the characteristic M radiation. The absorption curve for varying wave lengths thus has the appearance shewn in Fig. 72 and the relation may be expressed by the formula

$$\frac{\tau}{\rho} = (C_K + C_L + C_M \ldots)\lambda^3, \quad \ldots \quad \ldots \quad (90)$$

where C_K, C_L, and C_M are constants for the given substance, which come into action when the wave length of the incident radiation is less than the corresponding K, L, M, ... absorption limits.
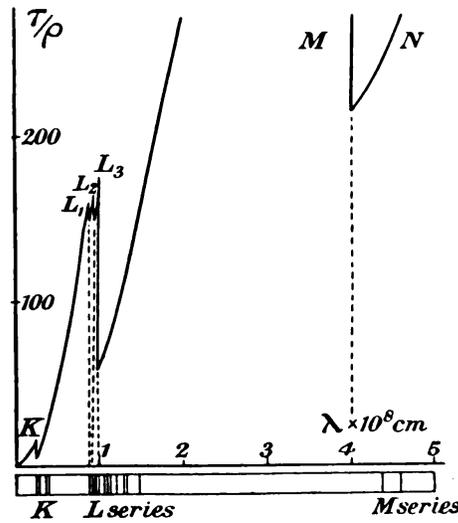
Fig. 73

It may be mentioned, in passing, that the absorption limit has a wave length slightly shorter than that of any of the lines in the corresponding series. No line of the K series is excited until the K limit is reached, but on reaching it all the lines are produced simultaneously. Close investigation has shewn that the L limit is, in fact, a triple one consisting of three peaks very close together (Fig. 73), while the M discontinuity consists of no less than five such peaks. The relation between the frequencies of the same absorption limit for absorbing elements of different atomic number is given by Moseley's relation

$$\nu = a\,(Z - b)^2. \quad \ldots \quad \ldots \quad (91)$$

90. Characteristic secondary radiation. As we have seen in the last section the characteristic radiation of an element may be excited not only by the impact of cathode rays in a discharge tube but also by the action of a beam of X-rays, providing that the latter is of suitable wave length. The rays so excited may be described as characteristic secondary rays, to distinguish them from the purely scattered secondary radiation already described (§ 76).

Much work had already been done on these characteristic secondary rays by Barkla[12] and others, before the phenomena of crystal reflection gave us a means of actually measuring their wave lengths. In order to identify the different radiations their absorbability in a light substance such as aluminium, which has no discontinuities within the range of wave lengths usually employed, was used as a test both of their homogeneity and of their wave length.

If the absorption of a beam of X-rays is measured using different thicknesses of the absorbing substance we can get a rough test of the homogeneity of the beam. If we have a primary beam of rays containing both hard and soft rays the latter will be absorbed by the first few thicknesses of material while the former being more penetrating will be largely transmitted. The beam will thus become relatively richer in the more penetrating components as it passes through greater thicknesses of material, and hence its absorption will not follow an exponential law.

It was found by Barkla that the absorption of the primary rays from an ordinary focus tube was not exponential, and the rays were thus presumably complex. It was found, however, that the secondary radiation given out by a copper radiator for example when illuminated by a beam of primary X-rays was absorbed fairly accurately according to an exponential law, and was, therefore, homogeneous. For this reason the characteristic secondary radiation from a radiator is often described as its "*homogeneous radiation.*" As we have seen, neither series of characteristic radiations is strictly homogeneous. As, however, the lines in the same series do not differ very widely in wave length we should not expect

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to disentangle them by the comparatively crude absorption method.

Since the radiation is only excited when the primary beam has a wave length shorter than the corresponding absorption limit, and thus shorter than its own wave length, it is sometimes referred to as "fluorescent" radiation. Unlike the scattered radiation, the fluorescent radiation is emitted uniformly in all directions round the radiator.

91. Conditions for the direct excitation of characteristic radiation. As we should expect from the quantum relation the characteristic radiation of a given element when used as an anti-cathode is only excited if the incident cathode rays reach a sufficiently high velocity. For cathode rays of smaller velocity than this only the "general" radiation is given out. The matter was first investigated by Whiddington[13] and subsequently by Webster[14], who used a spectrographic method of determining the presence of characteristic radiation. The experiments were carried out with an X-ray tube having a rhodium target and excited by means of a battery of a large number of accumulators. The applied potential was thus constant and could be measured with high accuracy. The maximum energy Ve of a cathode particle in the discharge was thus accurately known. The radiation emitted by the rhodium target was analysed by a spectrometer. It was found that for a potential difference of 23·2 kilovolts no lines of the rhodium K spectrum were excited, but that when the potential difference was raised to 23·3 kilovolts all the lines of the series appeared simultaneously.

Now the wave length λ for which Ve is the quantum of energy is given by the relation $Ve = hc/\lambda$. Substituting in this equation, the value of λ corresponding to a P.D. of 23·3 kilovolts is found to be $0·533 \times 10^{-8}$ cm. which is the value found directly for the K discontinuity of rhodium by absorption experiments. The wave lengths of the K lines of rhodium range from $0·616$ to $0·534 \times 10^{-8}$ cm. Thus a given line in the spectrum is not excited when the energy in the cathode particle becomes the quantum for the ray concerned, but only when it reaches that of the critical absorption frequency.

92. The theory of X-ray spectra. The application of the quantum principle to the phenomena described in the preceding sections leads at once to a very convincing explanation of the characteristic X-ray spectra. The work which must be done to extract an electron from the atom will depend on the forces which hold it bound, and hence on its position within the atom. Let us suppose that for the most firmly bound electrons, which we will call the K electrons for short, this work is equal to w_K. The smallest frequency which the incident radiation may have for it to be able to effect this removal is therefore $\nu_K = w_K/h$, where h is Planck's constant. We may assume that if the quantum of energy is insufficient to produce this ionization the electron will be unaffected by the radiation, and will absorb no energy from it. Thus if the wave length of the incident radiation is greater than that corresponding to a frequency ν_K, no energy will be absorbed from it by the K electrons. As soon, however, as the frequency increases to the critical value, absorption by the K electrons begins, and there is thus a sudden marked increase in the coefficient of absorption at this critical frequency. Thus the K absorption discontinuity marks the point at which the K electrons are capable of abstracting energy from the incident X-radiation. Similar considerations apply to the other absorption discontinuities.

Thus each discontinuity corresponds to some definite position, or level, within the atom where electrons are to be found, the "level" being characterized by the work which must be done to extract an electron from it. This energy is calculable, without ambiguity, from the critical absorption frequencies by the relation

$$w_c = h\nu_c ,$$

where ν_c is the critical frequency, and this calculation is confirmed by the direct measurements made with cathode particles and described in the previous section (§ 91). The comparatively small number of discontinuities and their great sharpness indicates that the levels which may be occupied by electrons are comparatively few, and their position very sharply defined. The existence of such levels is thus a necessary deduction from the phenomena of X-ray absorption, and does not depend on any theory of atomic structure.

The expulsion of an electron from, say, the K level will leave a vacancy which will be filled up by some electron, either from outside the atom or more probably, and hence more frequently, by an electron from one of the higher levels. Let us suppose, for example, that the electron falls into the vacant space from the L_1 level. Energy will thus be liberated, in amount equal to the difference between the work necessary to extract an electron from the K level, and that necessary to extract an electron from the L_1 level, that is to say, to $w_K - w_{L_1}$. On the quantum theory this will be radiated in the form of homogeneous radiation the frequency of which will be given by

$$hv = w_K - w_{L_1} = hv_K - hv_{L_1}. \quad . \quad . \quad . \quad (92)$$

v should thus be the frequency of a line in the K series of the element. Now, as we have seen, all the quantities in this equation can be determined to an accuracy of at least one part in ten thousand. It provides, therefore, a very searching test of the validity of our reasoning.

The experimental data are most complete for tungsten, since this metal is the usual target in an X-ray tube. The values of the K and L_1 discontinuities are respectively $0 \cdot 1785 \times 10^{-8}$ and $1 \cdot 2136 \times 10^{-8}$. We can put equation (92) in the form $\dfrac{1}{\lambda} = \dfrac{1}{\lambda_K} - \dfrac{1}{\lambda_{L_1}}$, where λ is the wave length of the radiation which should be emitted. The value of $\dfrac{1}{\lambda_K} - \dfrac{1}{\lambda_{L_1}}$ is $4 \cdot 792 \times 10^8$, and the value of λ should thus be the reciprocal of this, that is $0 \cdot 2086 \times 10^{-8}$. The wave length of the K_{a_1} line is found, by direct measurement, to be

$$0 \cdot 2086 \times 10^{-8} \text{ cm.}$$

Equally satisfactory agreement is obtained for the other lines of the K spectrum. Fig. 74 indicates the origin of the different K lines, the levels being indicated diagrammatically by horizontal lines. This theory, which is due to Bohr, has been applied with equal success to the more complicated L radiations. In the case of the L radiation we have three possible final levels corresponding to the three L discontinuities.

The energy characterizing each level in the atom of a given

element can, as we have seen, be determined experimentally either from the critical absorption frequencies, or from the critical energy which a cathode particle must possess to be able to eject an electron from the given level. The results obtained by the two methods are in good agreement. A third method, which promises equal accuracy, is provided by the phenomena of corpuscular secondary radiation described in the following section. The values for the different levels are thus experimental data, and are independent of any particular theory of the structure of the atom. They provide in fact a series of tests which any such theory should be able to satisfy.
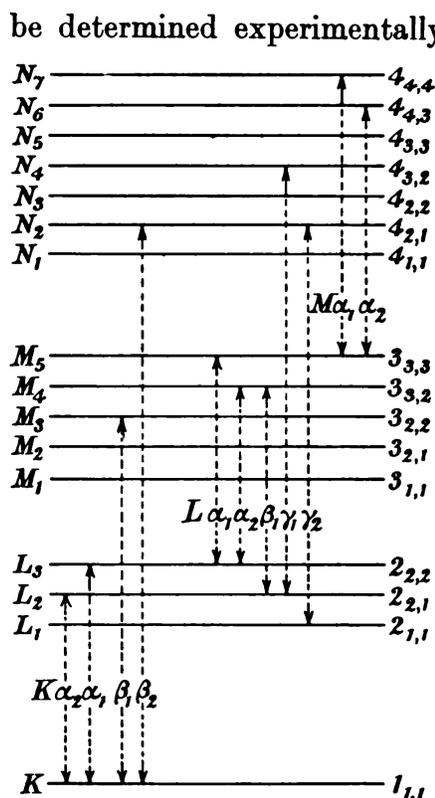
Fig. 74

The energy associated with an atomic level is usually expressed in electron-volts (p. 72). Similarly a homogeneous radiation is often specified by its quantum energy, also expressed in the same unit. Since 1 "volt" $= 1 \cdot 591 \times 10^{-12}$ erg, the frequency ν of a one volt radiation is $1 \cdot 591 \times 10^{-12}/6 \cdot 55 \times 10^{-27}$ or $0 \cdot 243 \times 10^{15}$ per sec. Its wave length c/ν is $12 \cdot 34 \times 10^{-5}$ cm. Similarly the familiar yellow sodium line may be described as $2 \cdot 1$ volt radiation.

93. Secondary corpuscular radiation. In addition to the scattered and homogeneous secondary radiations which are themselves X-radiations, a beam of X-rays falling on a substance also gives rise to a very easily absorbable radiation which can be deflected by a magnetic field, and can thus be shewn to consist of negatively charged electrons. The velocity of these electrons can be measured by the application of equation (37). These corpuscular rays are all absorbed within a few centi-

TABLE VI

X-ray emission spectra and absorption edges

The measurements are mainly due to Siegbahn [9]

Element	K series $\times 10^8$ cm.			L series $\times 10^8$ cm.		
	K_{α_1}	K_{β_1}	Absorption limit	L_{α_1}	L_{γ_1}	L_3 absorption limit
11. Na	11·88	11·59	—	—	—	—
24. Cr	2·285	2·081	2·066	—	—	—
26. Fe	1·932	1·753	1·739	—	—	—
27. Co	1·785	1·617	1·604	—	—	—
28. Ni	1·654	1·497	1·484	—	—	—
29. Cu	1·537	1·389	1·377	13·31	—	—
30. Zn	1·432	1·293	1·280	12·23	—	—
42. Mo	0·7078	0·6310	0·6185	5·395	—	4·904
47. Ag	0·5583	0·4960	0·4845	4·146	3·515	3·691
50. Sn	0·4896	0·4343	0·4239	3·592	2·995	3·149
74. W	0·2086	0·1842	0·1782	1·473	1·096	1·213
78. Pt	0·1822	0·1637	0·1577	1·310	0·956	1·071
92. U	0·1264	0·1119	0·1066	0·909	0·614	0·721

TABLE VII

Absorption of X-Rays.

Wave length $\lambda \times 10^8$	Mass absorption coefficient τ/ρ					
	O	Al	Cu	Mo	Ag	Pb
0·1	—	0·164	0·323	—	1·13	3·78
0·2	0·183	0·269	1·53	4·02	5·75	4·62
0·3	0·240	0·531	4·47	12·7	18·0	13·9
0·4	0·338	1·05	10·1	26·7	38·4	32·7
0·5	0·498	1·91	18·8	48·6	11·0	59·3
0·6	0·746	3·18	31·6	80·7	18·7	91
0·7	1·10	5·00	49·2	18·8	25·6	133
0·8	1·55	7·50	—	27·2	—	—
0·9	2·12	10·3	97	37·5	57	140
1·0	2·87	13·8	133	51	75	77

metres of gas, and hence the ionization they produce is very intense.

Taking the theory of X-rays already propounded, the electric force in the primary pulse will be at right angles to its direction of propagation. The electrons will, therefore, have an acceleration in this direction, which if their attachment to the atom is sufficiently weak will cause them to be projected in this direction, that is at right angles to the primary beam. This lateral projection is extremely well shewn in photographs taken by C. T. R. Wilson's cloud chamber method and shewn in Figs. 18 and 59 (Plate I). The primary beam, which is invisible, passes across the gas from left to right. The tracks of the electrons ejected by the rays are revealed by the condensation of water
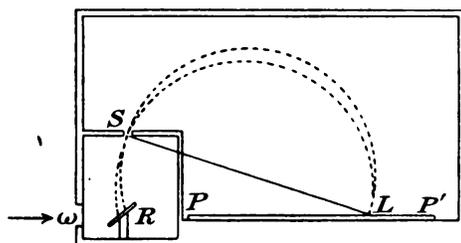
Fig. 75

upon them. It will be seen that each of these tracks begins nearly normal to the line of the beam.

This secondary corpuscular radiation bears the same relation to the incident X-radiation that the photo-electrons bear to light, and it is now customary to refer to them also as photo-electrons. Owing to their much higher speed, however, the distribution of velocities among them can be determined more directly and with greater certainty than for the ultra-violet photo-electrons. The experiments were first carried out by de Broglie[15], and have since been extended by Robinson[16] and others.

The method employed is indicated in Fig. 75, which represents the apparatus used by Robinson. The incident beam of X-rays entering the chamber by an aluminium window ω falls on the radiator at R. The secondary corpuscular rays emerge from R in all directions and some pass through a narrow slit S

immediately above the radiator. The photographic plate PP' is placed film upwards to receive these radiations. The whole box is evacuated to a high vacuum, and is placed in a uniform magnetic field, the lines of which are perpendicular to the plane of the paper. Each of the particles thus describes a circular path of radius $\rho = \dfrac{mv}{He}$. It is easy to shew that if the radiator is not too large all particles of the same velocity passing through the slit will be brought to a line focus on the photographic plate, the plane of which passes through the radiator. The electrons describe a semicircle in passing from S to L, and their velocity is therefore given by $\frac{1}{2}SL = \dfrac{mv}{eH}$. The field H is supplied by a pair of large Helmholtz coils, and is accurately calculable from the current flowing in the coils.

If the radiator is illuminated with homogeneous X-radiation the plate is found after development to be crossed by a number of sharp lines, shewing the presence of groups of electrons of identical velocity. The theory of X-ray spectra already described provides a convincing explanation of these groups of electrons and their existence provides additional support for the theory.

Suppose the frequency of the incident radiation to be ν, where ν is greater than ν_K, the K absorption frequency. The K electron will absorb a whole quantum $h\nu$ of the radiation but of this an amount w_K (where w_K is the energy required to remove an electron from the K level) will be used in extracting the electron from the atom. Thus its energy on emerging from the atom will be $h\nu - w_K$. Similar effects will occur at each of the other absorption levels since the primary radiation may be absorbed in any of the levels in the atom. Thus for incident radiation of definite frequency ν the corpuscular radiation will contain groups of electrons the energies of which are $h\nu - w_K$, $h\nu - w_{L_1}$, and so on. Thus if we measure these energies experimentally from the observed magnetic deflections, the energy values for the different levels in the radiating atom can be determined. The values obtained in this way are in excellent agreement with those determined by the methods already described. The method has the advantage that it can be applied to determine the energy

associated with levels for which the critical absorption wave length is too great to be investigated by the absorption method, such for example as the K level for oxygen and the M and N levels for elements of medium and high atomic numbers.

The relations we have been discussing are very vividly illustrated by the "cloud" photograph reproduced in Fig. 18 (Plate I), and due to C. T. R. Wilson. A very faint beam of X-rays is directed against the thin copper plate which is to be seen in the centre of the photo. The beam is so weak that during the exposure only a single quantum has been absorbed by the copper. The track of the ejected photo-electron is seen emerging from the copper plate. An electron falling back into the vacant place in the K ring of the atom causes the emission of a quantum of copper K radiation. This after travelling outwards for a short distance is completely absorbed in a molecule of gas, and the resultant photo-electron forms the short track which is visible towards the lower left-hand corner.

94. Reflection, refraction and diffraction of X-rays. On the classical theory the refractive index μ of a substance for radiation of frequency ν is given by

$$\mu^2 = 1 + \frac{e^2}{\pi m} \sum_1^N \frac{n_s}{(\nu_s^2 - \nu^2)}, \quad \ldots \quad (93)$$

where n_s is the number of electrons per unit volume with a natural frequency ν_s, the summation extending to all the electrons present. The frequency of X-radiation is usually greater than the natural frequency of the electrons in the atom. The second term is, therefore, negative and the refractive index of any substance for X-rays is less than unity.

A pencil of X-rays falling on a polished glass surface is therefore passing into an optically less dense medium, and should be totally reflected if the angle which it makes with the surface is sufficiently small. This conclusion was verified by Compton, who found that at glancing angles of the order of 10' or less as much as 90 per cent. of the incident X-radiation was reflected from a well polished glass surface. The value of μ for the glass could be determined by measuring the critical angle. It was found to be $(1 - 8{\cdot}12 \times 10^{-6})$ for radiation of wave length $1{\cdot}54$ A.U., and

decreased with increasing wave length. The value calculated from the formula is $(1 - 8.14 \times 10^{-6})$.

By directing a very fine pencil of X-rays at the edge of a large angle prism Siegbahn has obtained excellent dispersion spectra. Using the radiation from a tube with an iron target, the four K lines of the iron spectrum were quite clearly separated.

The fact that total reflection occurs, at small glancing angles, has made it possible to determine the wave length of X-radiation by means of an ordinary optical reflection grating. Let A, B (Fig. 76) be two adjacent rulings of an optical grating, and AC

Fig. 76

an incident wave front. A diffracted ray will exist in the direction AD if $CB - AD = n\lambda$, where n is an integer. Calling the angle CBA ϕ and the angle DAB $\phi + \alpha$ we have
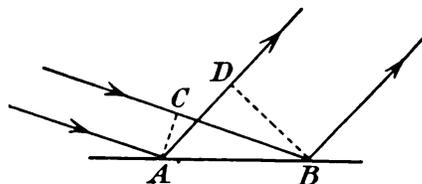
$$n\lambda = AB \{\cos \phi - \cos (\phi + \alpha)\} = d \left(\phi\alpha + \frac{\alpha^2}{2}\right),$$

if all the angles are small. Thus using a grating of only 500 lines per cm. and an angle of incidence of 10′, then for Mo_{K_α} radiation of wave length 0.70×10^{-8} cm. the value of α for the first order spectrum ($n = 1$) will be 3.5′, that is to say the angle between the directly reflected ray and the first diffracted ray will be 3.5′. This, though small, is quite measurable.

Experiments on these lines were carried out by Compton [17] and by Wadlund [18], and the method has subsequently been employed with increasing refinements in measuring the small angles concerned by Siegbahn and others. The radiation from the target X of an X-ray tube (Fig. 77) after passing through the slit S_1 is rendered approximately monochromatic by reflection at the crystal C, the crystal being set so as to pick out one of the strong emission lines of the target. It then passes through a second slit S_2 on to a speculum grating G about 5 mm. wide and having 500 lines to the centimetre, which it strikes at a glancing angle of a few minutes only. The directly reflected radiation, for which the angles of incidence and reflection are equal, makes an intense band at O on the photographic plate PP, and is accompanied by

diffracted rays corresponding both to positive and negative values of n. The angles can be determined from the geometry of the apparatus, and hence the wave length of the radiation.

In spite of the smallness of the angles, wave-length determinations can be made to an accuracy approaching 0·01 per cent., and to this order agree precisely with the determinations made by the crystal method. This coincidence affords very valuable
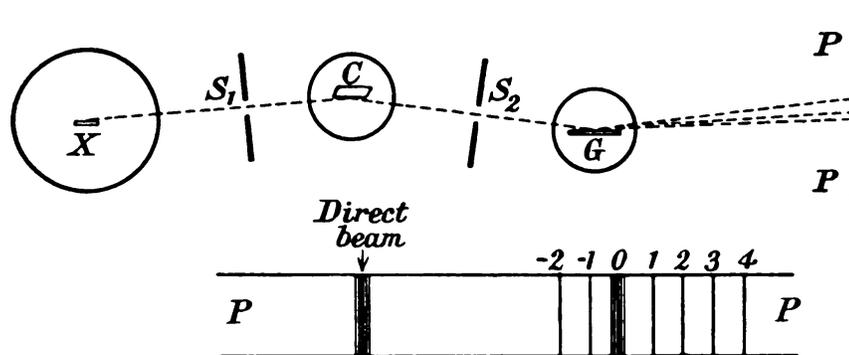
Fig. 77

confirmation of Bragg's theory of crystal reflection and, incidentally, provides a method of deducing the electronic charge e which is not markedly less accurate than that of Millikan. The value so obtained ($4·774 \times 10^{-8}$ e.s.u.) is in satisfactory agreement with Millikan's value. Apart from this, the method is proving useful in investigating the long wave length part of the X-ray spectrum, where, owing to the great absorbability of the radiation, it is difficult to get good crystal reflections.

95. Ionization by X-rays. The ionization produced by a beam of X-rays in its passage through a gas is the property generally employed to measure the intensity of the beam. X-rays, however, ionize, not directly, but by means of the corpuscular radiation excited in the gas. This is shewn very clearly by the photographs reproduced in Figs. 18 and 59. The ions formed along the tracks of the photo-electrons are clearly shewn, but there are no ions marking the path of the radiation itself. The corpuscular radiation is of two kinds. Photo-electrons are ejected when a whole quantum is absorbed by an atom; these form the long tracks shewn in Fig. 18. In addition recoil electrons are set in

motion when a quantum is scattered (§ 80). Since the scattered quant only transfers a small fraction of its energy to the recoil electron its velocity is small and its track usually very short. Some of these very short tracks can be seen along the centre line of Fig. 59. For radiation of long or medium wave length the absorption is much greater than the scattering so that most of the ionization is due to the photo-electrons. For very hard radiation, say 0·1 A.U., the reverse is the case, and the ionization is mainly due to recoil electrons.

In either case the number of ions produced is directly proportional to the energy absorbed in the gas from the radiation. It thus depends on the coefficient of absorption in the gas as well as on the energy of the radiation. Of two beams of X-rays of equal intensity the one with the greater wave length will produce the greater ionization, owing to its larger coefficient of absorption. The international unit of X-ray intensity, known as the *röntgen*, has been defined as the intensity of a beam which when passing through 1 c.c. of air at standard temperature and pressure enables it to transmit 1 e.s.u. of charge per second. The actual energy density corresponding to an intensity of 1 röntgen will be much less for radiation of long wave length than for short wave radiation. It is only when the beams are of the same quality that the ionization currents are a measure of the energy. Experiments seem to shew, however, that if the ionization chamber could be made so long that the beam of X-rays was completely absorbed in the chamber the total ionization produced by the beam would be independent of the quality. Unfortunately this is usually impracticable.

Gases containing elements of high atomic number, and hence of large absorptive power, are much more intensely ionized than air, and can be substituted for the latter in the ionization chamber when radiation of small intensity has to be measured. Methyl iodide is commonly employed for this purpose.

The measurement of the ionization produced in a gas by a beam of X-rays demands certain experimental precautions if the results are to be of any value. The number of photo-electrons produced in a gas is very small compared with the number emitted from a metallic surface under the same conditions. It

is very important therefore that the beam should pass through the gas in the ionization chamber without touching the electrodes. The windows through which the beam enters and leaves the chamber should be so far from the electrodes that the electrons emitted by them do not reach the gas between the electrodes. The form of chamber shewn in Fig. 6 is suitable for comparative measurements.

For absolute measurements it is necessary to surround the insulated electrode with a guard ring so that the field across the gas may be uniform, and the volume of gas from which the ions are collected well defined. To reduce errors arising from the radiation scattered in the gas which may fall on the electrodes and give rise to secondary emission, the electrodes are made of an element of low atomic number, usually aluminium, though paper covered with graphite is sometimes used. The distance between the beam and the electrodes must be sufficiently long to allow of the complete absorption of the photo-electrons in the gas itself. Two or three centimetres is usually sufficient. The voltage applied must be sufficient to ensure saturation.

Under these conditions very accurate measurements can be obtained both of weak and of intense beams.

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CHAPTER XI

THE α-RAYS

96. Properties and nature of the α-rays. The α-rays from radio-active substances are distinguishable from the other radiations by their absorbability, being completely stopped by less than 10 cm. of air or 1/10 mm. of aluminium. They can be detected by their action on a photographic plate, which is, however, very weak, by the ionization they produce in the gases through which they pass which is very intense, or by the fluorescence they produce on a fluorescent screen, the latter method being extremely convenient especially when the radiation is weak. On observing the fluorescence through a low power microscope it is found to consist of a succession of scintillations produced by the successive impact of the individual particles in the rays. It has been shewn that each particle produces a separate flash on the screen when it collides with it. The impact of a single α-particle can thus be observed.

The tracks of α-particles can readily be observed by means of a Wilson cloud chamber. Owing to the intense ionization produced the track of an α-particle appears as a thick white streak in the chamber. Such a track is shewn in Fig. 16 (Plate I).

By passing a beam of the rays down a long exhausted tube and applying electric and magnetic fields it can be shewn that the α-rays consist of particles carrying a positive charge. The velocity of the particles and the value of the ratio e/m can be deduced from the deflections in the usual ways. The value of e/m is the same for all the α-particles no matter what their source and is equal to 4823. The initial velocity depends on the radio-active substance from which they are ejected. These velocities range from $1\cdot45 \times 10^9$ to $2\cdot2 \times 10^9$ cm. per sec.

97. Nature of the α-particle. The ratio of charge to mass for a hydrogen atom when carrying a single electronic charge is 9649 e.m.u. per gm. The value for an α-particle is 4823 or half that of the hydrogen atom. If the charges were the same the particle would thus be twice the mass of the hydrogen atom, and hence probably a hydrogen molecule. It will be shewn later that the particle carries double the charge carried by an electron; its real mass is therefore four times that of a hydrogen atom, and thus corresponds very closely with that of the helium atom (atomic weight 4·0).

The proof of the identity of the particles with helium has been rendered complete by an experiment due to Rutherford. A very thin walled glass tube A (Fig. 78) was sealed into an outer tube B which was highly exhausted and connected to a small discharge tube C. To prove that there was no connection between A and B the former was filled with helium under pressure and left for some hours. No trace of the helium spectrum was obtained in the discharge tube C. The helium was carefully removed and radium emanation was passed into A, and allowed to stand. The glass walls of A were sufficiently thin to allow the α-particles from the emanation to pass into B where they were stopped by the outer walls. Under these circumstances the helium spectrum became visible in C in a few hours, and became brighter as the experiment was continued. As the α-rays were the only particles entering B during the experiment it is clear that the α-particles must be atoms of helium.
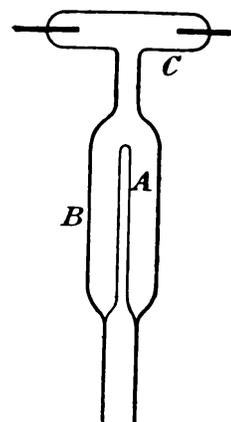
Fig. 78

98. The counting of α-particles. Owing to its high speed and comparatively large mass, a single α-particle possesses appreciable kinetic energy. The kinetic energy of the α-particle from radium C' for example is $1\cdot2 \times 10^{-5}$ erg or 7·7 million electron volts. It produces rather more than 200,000 pairs of ions during its absorption in air, and thus permits the passage across the ionization chamber of about 10^{-4} e.s.u. This is quite measurable with a sensitive electrometer.

An electrometer sufficiently sensitive to detect such a charge has necessarily a long period. For rapid counting it is desirable to amplify the effect. One method, employed by Rutherford as early as 1908, is to adjust the pressure in the ionization chamber until the field between the electrodes is sufficient to cause ionization by collision whenever a supply of ions is provided within the chamber. In this way the small primary ionization produced by the entrance of an α-particle is increased many fold by the secondary ionization produced by the collisions of the primary ions with the gas molecules in the chamber.
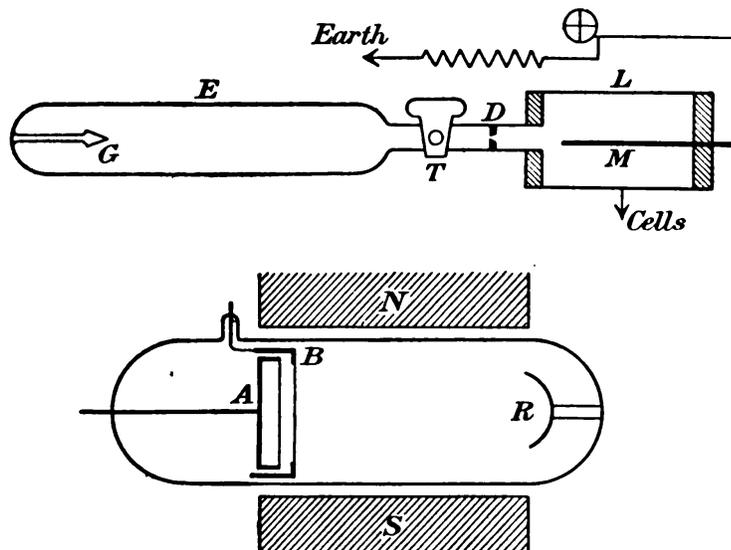
Fig. 79

This method was used by Rutherford and Geiger to determine the number of α-particles emitted per second per gram of radium, using the apparatus sketched in Fig. 79. The radio-active substance is deposited on the metal cone G, and a beam of α-particles passes, by way of a large bore tap, T, through a stop D, which subtends a known solid angle Ω at the source. They then enter the ionization chamber L, the inner electrode M of which is connected to an electrometer. The entrance of each α-particle into the chamber is marked by a kick of the electrometer needle. To prevent the accumulation of the charges on the needle the latter is earthed through a very high resistance, so that after each kick the charge leaks away to earth. If n is the number of

13-2

kicks recorded per second, the total number of α-particles emitted per second by the source is $4\pi n/\Omega$. A gram of radium, free from its dissociation products, emits $3\cdot72 \times 10^{10}$ α-particles per second.

If the α-particles are collected in a Faraday cylinder, the total charge conveyed by the particles can be determined. To avoid loss of charge through ionization currents, the chamber A (Fig. 79) is enclosed in a high vacuum. It is shielded from electrostatic disturbances by an earthed aluminium leaf B. Surfaces exposed to α-radiation give off large numbers of slow negative electrons, known as δ-rays. If these were allowed to escape from the Faraday cylinder, they would leave it with a spurious positive charge. The apparatus is placed between the poles of a strong magnet, NS, which, by coiling the δ-ray tracks into small spirals, prevents them from leaving their place of origin.

If the angle subtended by A at the source R is measured, the number of α-particles entering A is known. The charge on each particle can thus be deduced. Rutherford obtained the value $9\cdot3 \times 10^{-10}$ e.s.u.

The method of counting α-particles by the scintillations they produce on a fluorescent screen has been extensively used. The most suitable material is zinc sulphide in which has been incorporated about $0\cdot01$ per cent. of copper. The screen, covered with the powdered sulphide, is viewed with a low-power microscope of large aperture. The observations must be made in complete darkness, as the scintillations are very faint. Under good conditions a trained observer can count scintillations at the rate of about 20 per minute, and will record about 95 per cent. of the scintillations which actually occur.

Regener used the scintillation method to determine the number of α-particles emitted per second by a polonium source, and by measuring also the charge conveyed by these particles to a Faraday chamber, obtained a value for the charge on a single α-particle of $9\cdot58 \times 10^{-10}$ e.s.u. It will be seen that the values obtained both by Regener and by Rutherford are each very close to twice the electronic charge. The agreement of the two values was taken as evidence that every α-particle produces a scintillation when it strikes a fluorescent screen. On account of

the greater simplicity of the method the majority of the experiments on α-particles have been made by the scintillation method.

Recently, however, experiments on the scattering of α-particles made in connection with the investigation of atomic nuclei have necessitated the counting of many thousands of α-particles, a very tedious procedure by the scintillation method. At the same time the development of the thermionic valve amplifier has vastly increased the potentialities of the electrical method. We have seen that a single α-particle permits the passage of about 10^{-4} e.s.u. of charge. If this is applied to the grid of a thermionic valve, and if the capacity of the ionization chamber and grid is, say, 50 e.s.u., the resulting increase of grid potential will be of the order of 6×10^{-4} volts. A signal of this strength can be amplified in the usual way and can be made to furnish an output current capable of working an electromagnetic counter of the type used for recording telephone calls. Thus the entrance of a single α-particle into the ionization chamber can be made to record itself automatically on a dial.

Owing to its inertia a mechanical counter takes an appreciable fraction of a second to reset itself. α-particles entering the ionization chamber within, say, 1/20th of a second of each other would probably be recorded as one only. The recording can be speeded up by the use of a special type of valve relay known as a thyratron, in place of the mechanical relay. Alternatively the impulses from the amplifier can be passed through an oscillograph of very small free period. Each α-particle will then produce a deflection in the oscillograph which can be recorded on a moving photographic film. This method has the advantage that since the deflections are proportional to the output current, which in turn is proportional to the strength of the input signal, the deflections are proportional to the ionization produced by the ionizing particle itself in the ionization chamber. This is sometimes useful in determining the type of particle entering the chamber. The circuits used for automatic α-particle recording are mainly due to Wynn Williams[1], and the original papers must be consulted for the details. With recent improvements in the method it is possible to count 400 particles per second, with an accuracy of 1 per cent.

99. Passage of the α-particles through matter. If a narrow pencil of α-particles is formed in air by placing a small diaphragm in front of a thin layer of some radio-active material—so thin that the absorbing effect of the layer itself on the α-particles it emits is negligible—and the particles are viewed by a fluorescent screen, which is gradually withdrawn farther and farther from the source, it is found that the number of α-particles falling per second on the screen remains constant until a certain critical distance is reached. If this distance is exceeded, the number of scintillations falls off with such rapidity that they entirely disappear within the next few millimetres.

Similarly, if the screen is kept fixed close to the diaphragm and very thin sheets of aluminium, mica or other substance are placed successively in front of the diaphragm, the number of α-particles reaching the screen remains constant until some definite thickness of material has been placed in the path of the particles. This critical distance is called the *range* of the α-particle in the absorbing material.

The range of an α-particle depends on the particular radio-active substance from which it is emitted, all α-particles from the same substance having the same range. It also depends on the nature of the absorbing material. For the same material the range depends only on the mass of material traversed by the rays. Thus for a given gas the range is inversely proportional to the density of the gas. The range of an α-particle is usually specified as the distance the particle will penetrate through air at a pressure of 760 mm. and a temperature of 15° C. The range of the α-particles emitted by radium is 3·4 cm. and of those from radium C′ 6·9 cm. in air under standard conditions.

These results can be illustrated by experiments with a cloud chamber. If a speck of radio-active material is enclosed in the chamber, the tracks of the particles are clearly visible after exposure and can be photographed and measured. Fig. 80 (Plate III) shews the result obtained using a mixture of thorium C and thorium C′. The existence of two definite ranges and the practical equality of the lengths of track of particles of the same kind are very clearly brought out.

Since the number of α-particles in a beam remains constant up

to the end of the range, the absorption of the rays is not due to a gradual decrease in number, but to a gradual absorption of energy, which ultimately leaves the particles with insufficient energy to produce either scintillations or ionization. This conclusion can be verified by measuring the velocity of the particles after passing through various absorbing sheets of matter. The rays from a wire R coated with a very thin layer of radio-active material pass down a long air-tight glass tube T (Fig. 81) and are formed into a narrow pencil by the lead diaphragm D. This beam then continues between the poles of an electromagnet NS, and falls on a fluorescent screen F. From the geometry of the apparatus and a measurement of the shift produced in the fluorescent spot when the magnetic field is
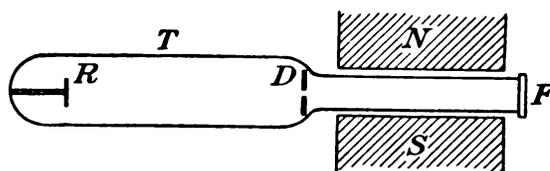
Fig. 81

applied, the radius of curvature of the rays in the magnetic field can be calculated, and using the equation $\rho = vm/He$ (37) v can be calculated since the ratio of e/m for the α-particles is known. It was found that the velocity of the rays after passing through a distance x of air could be expressed in the form

$$v^3 = a\,(R - x), \quad \ldots \quad \ldots \quad (94)$$

where R is the range of the particle in air. The cube of the velocity is thus directly proportional to the distance the particle has still to run. This conclusion has been further confirmed by Kapitza, who has measured the actual energy of the rays at different points along their course, by absorbing them in a silver disk, and measuring the heat developed by a sensitive radio-micrometer.

100. Ionization along the track of an α-particle. Much of the energy absorbed from the α-particle in its passage through matter is spent in producing ionization. The number of ions

produced per centimetre along the track of the particle depends on the velocity of the particle, and increases rapidly as the velocity diminishes. It rises to a sharp maximum as the particle reaches the end of its range, and then drops to zero as the particle comes to rest. If we assume that the number of ions produced is proportional to the energy absorbed from the α-particle, an assumption which is at any rate approximately correct, the intensity of the ionization I at any point will be proportional to $\dfrac{d}{dx}(\tfrac{1}{2}mv^2)$ or since the mass is constant

$$I \propto \frac{d(v^2)}{dx} \propto \frac{d}{dx}(R-x)^{\frac{2}{3}}$$

$$\propto (R-x)^{-\frac{1}{3}},$$

$$\therefore \quad I^3 = a'/(R-x), \quad \ldots \ldots \ldots \quad (95)$$

where a' is a constant.

It will be noticed that combining equations (94) and (95) we have

$$Iv = \text{constant}. \quad \ldots \ldots \quad (96)$$

The amount of ionization produced in an atom by an α-particle is thus proportional to the time which the particle takes to pass across an atom, a very interesting result.

The matter can be investigated experimentally by a method originally due to W. H. Bragg, and illustrated diagrammatically in Fig. 82. The source of the radiation is deposited in the form of a very thin film at R, and the emerging α-particles are limited to a narrow pencil by a lead stop C. The rays are received in a shallow ionization chamber AB, consisting of two parallel plates placed at a distance apart of 2 or 3 mm. The upper plate is connected to the electrometer, and the lower plate, which is made either of gauze or of very thin metal leaf so as to admit the passage of the α-rays is connected to a battery. The saturation current between the electrodes measures the mean intensity of ionization produced by the beam in the portion AB of its path. By altering the distance between AB and R the intensity at different parts of the path can be determined.

A more accurate and convenient design is shewn in Fig. 83. The source R is placed at one end of a tube, some 10 cm. in

length, the other end of which is closed with a stop C, covered with thin metal leaf. AB is a shallow ionization chamber. The tube is air-tight and can either be completely evacuated, or filled with gas at a known pressure. If the tube contains air at a pressure p mm., the effective distance that the particles have traversed before reaching the stop C is $RC \times p/760$ cm. and can thus be adjusted without moving the apparatus. The effect of the foils at C and B can be measured and allowed for.
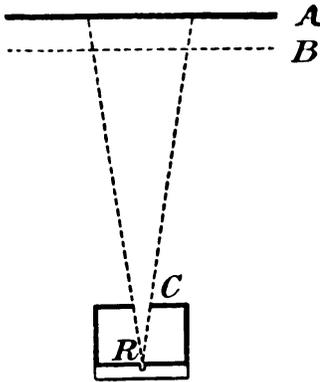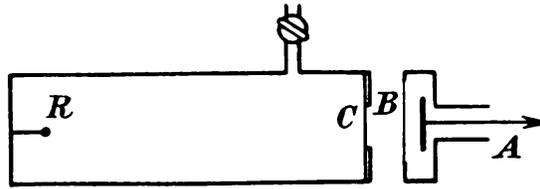
Fig. 82   Fig. 83

101. The straggling of the α-particles. The experimental curves for the homogeneous rays from polonium and from
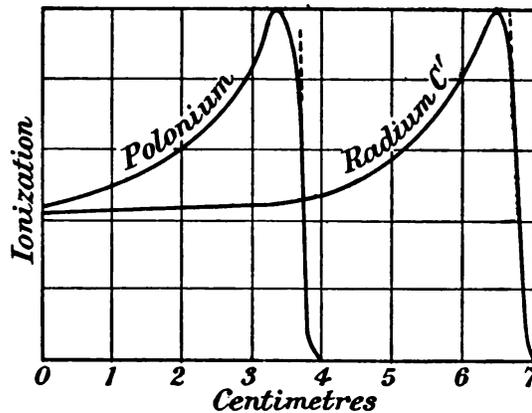
Fig. 84

radium C', are shewn in Fig. 84. Their general form agrees quite closely with the curve given by (95) except that the maximum is not so sharp, and the fall to zero not so precipitous as the

simple formula would lead us to expect. This is due to what may be called the straggling of the α-particles. The absorption of energy from the particle is due mainly to the ionization it produces. This will depend on the number of molecules it strikes along its path, and to the particular way in which it strikes them. Since the molecules in a gas are widely separated, some α-particles will strike rather more, others rather fewer than the average number, in passing through a centimetre of air, and thus the actual distance from the source at which their energy is completely expended will be somewhat different for different particles. This naturally causes a certain rounding off of the maximum in the experimental curves, which, of course, give the mean effect for a large number of particles.

Owing to straggling the range of an α-particle is not quite definite. To avoid this difficulty an *extrapolated range* is usually employed. This is obtained by producing to zero the straight descending portion of the curve indicated by the dotted line in Fig. 84.

The ionization curve for a short range α-particle is almost identical with the corresponding portion of the curve for a long range particle. Thus the curve for polonium (range 4 cm.) is practically identical with the last 4 cm. of the curve for the radium C′ particles (range 7 cm.). The range of a beam of homogeneous α-particles thus depends only on V, the velocity of projection. Putting $x = 0$ in (94) we have

$$V^3 = aR. \qquad . \quad . \quad . \quad . \quad (97)$$

This is Geiger's law, and while not quite exact, is sufficiently so for many purposes.

102.   The stopping power of substances. The range of the α-particles in any gas can be determined accurately by the method of Fig. 83. The stopping power of solid materials can be determined with the same apparatus, the absorbing foils being inserted between the stop C and the window B of the ionization chamber. Thus if the insertion of a given sheet of mica is found to reduce the range of the α-particles from radium C′ from 7 cm. to 5 cm., the sheet would be said to have a stopping power of 2 cm.

The ratio of the mass of a column of air of unit cross section to the mass per unit area of the substance which produces the same diminution in the speed of the α-particle is called the *stopping power* of the *substance*.

It was found better to express the stopping power in terms of the number of atoms traversed rather than in terms of the mass. The transformation can easily be made. Thus the stopping power of silver is 0·37; that is to say, in passing through a given mass of silver the velocity of the α-particle is only reduced by 0·37 of the decrease produced in passing through an equal mass of air. But for equal masses of air and silver the former contains 108/14·4 times the number of atoms, hence atom for atom silver stops $0·37 \times \dfrac{108}{14·4} = 2·8$ times as much as air. This is called *the stopping power of the atom*. Experiment has shewn that except in the case of very light elements *the stopping power per atom is proportional to the square root of the atomic weight*, the mean value of the stopping power over the root of the atomic weight being about 0·26.

The stopping power of an atom is independent of its state of chemical combination, being the same in compounds as in the free state. Thus the stopping power of a compound can be calculated from that of its constituents.

103. Long range α-particles. The α-particles emitted by a particular radio-active substance are projected with identical velocities, and the range of the particles emitted serves to identify the substance from which they come. In addition to the normal α-particles, however, some radio-active substances also emit occasional α-particles of range appreciably longer than the normal. The proportion of such particles is very small, and does not exceed one long range particle to 50,000 normal particles.

The ranges of these particles have been determined by Rutherford[2] and others using a modification of the apparatus of Fig. 83, the insulated plate being connected to the grid of the first valve of a valve amplifier. Sufficient absorbing material is used to cut off completely the normal α-particles. The experimental curve giving the relation between the distance from the source

and the number of α-particles counted per second for radium C′ was very complex (Fig. 85). It shewed the presence of one strong group of particles of range 9 cm. in air, together with at least eight other groups of less intensity with ranges varying from 7·8 cm. to 11·5 cm. Similar effects are obtained with other radio-active bodies.
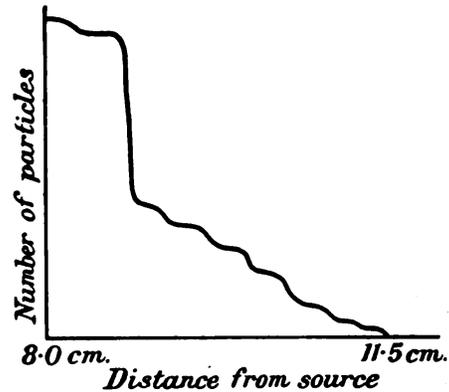
Fig. 85

The determination of the energy of emission of these long range α-particles is important in connection with the constitution of atomic nuclei. An approximate value could be deduced by Geiger's rule from the observed ranges. More accurate information, however, was much to be desired. Rutherford[3] has recently constructed a powerful electromagnet capable of bending the path of the α-rays into a semicircle, and thus made it possible to use the focusing method already described in § 93. The source of α-rays is placed at one end of a semicircular channel, cut in the magnetic poles in a plane at right angles to the magnetic field, and a small counting chamber is placed diametrically opposite to it, at the other end of the channel. The channel is completely exhausted of air, so that the particles lose no velocity in passing round the channel.

If ρ is the radius of the semicircular canal, a particle will only be able to traverse the canal, without hitting the sides and being lost from the beam, if the radius of curvature of its path in the magnetic field H is identical with that of the canal, that is if the particle has a velocity V equal to $H\rho E/m$, where E/m is the ratio of the charge to the mass of an α-particle. By gradually varying the magnetic field, successive groups of α-particles can be brought in turn into the counter. The corresponding value of H enables the velocity, and hence the kinetic energy of the particles to be determined, the accuracy being of the order of one in ten thousand. The results are contained in Table XI, p. 259. These are, of course, in addition to the normal groups of particles of range 6·9 cm.

104. The scattering of the α-particles. As is well shewn in Fig. 80 (Plate III), the track of the average α-particle is approximately a straight line from beginning to end. A few α-particles, however, suffer appreciable deflections. For example, the track shewn in Fig. 16 shews two such deflections, the first about two-thirds of the way along, and the second near the end of its track. The deflections are generally more numerous near the end of the track, where the velocity is small.

The scattering of α-particles can be investigated by allowing a narrow pencil of the rays to fall on a thin sheet of some material, and investigating the number of α-particles emerging at various angles to the incident pencil by means of a fluorescent screen. Thus Geiger found that using a thin sheet of gold leaf of stopping power 3·68 cm. about one particle in about 8000 suffered a deflection greater than 90° and re-emerged on the side on which it entered. The average deflection was of the order of 7°, and increased proportionally with the thickness of the scattering foil.

If we assume that the atomic radius is of the order of 10^{-8} cm. it is clear that an α-particle in traversing several centimetres of air must pass through some thousands of atoms of the gas. Only a minute proportion of such encounters, however, produce any appreciable deflection of the α-particle. It is difficult to avoid the conclusion that the greater part of the atomic volume is occupied only by electrons, which are too light to deflect the comparatively massive α-particle, and that the main mass of the atom is concentrated in a particle, or nucleus, much smaller than the atomic structure as a whole. The nuclear theory of the atom was first propounded by Rutherford in 1911, and has revolutionized our ideas of atomic structure.

105. Rutherford's theory of scattering. Let us assume that the mass of the atom is concentrated on a nucleus, the dimensions of which are negligible in comparison with the radius of the atom. We will assume that the positive charge in the atom also resides in this nucleus, and is equal numerically to *Ze*. Since the atom is neutral as a whole, there must be *Z* negative electrons outside the nucleus, arranged in some manner to be

discussed later. Z is thus the atomic number of the atom. The atomic system thus resembles in many respects a planetary system, the nucleus playing the part of the central sun. The α-particle, since it has lost its two planetary electrons, will consist of a nucleus only of atomic mass 4, and charge $2e$.

The electrons, on account of their small mass, cannot appreciably affect the motion of the α-particle. It also turns out that during a collision the colliding nuclei come within such a minute distance of each other that most of the deflection occurs while the α-particle is well within the innermost ring of electrons. The electrical screening of the nuclear charge by the planetary electrons is also negligible.

The α-particle and the nucleus, being both positively charged, repel each other with a force which at distances which are large compared with the radius of the nucleus, will vary inversely as the square of the distance. It is assumed that the observed deflections are due to this force. The problem is thus one of two gravitating bodies, except that the force involved is one of repulsion, not attraction. If the mass of the deflecting nucleus is large compared with that of the α-particle, so that the motion communicated to the nucleus is negligible, the path of the particle will be a hyperbola, with the nucleus at one focus.
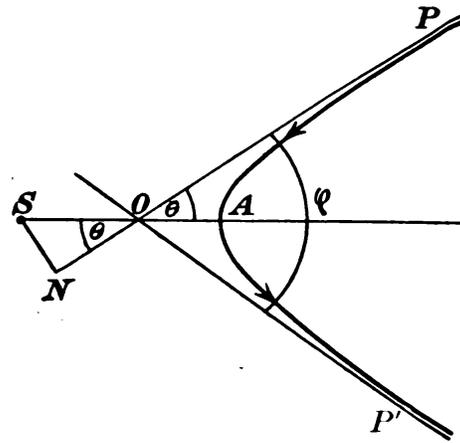
Fig. 86

Let S (Fig. 86) be the nucleus, supposed fixed, PO and OP' the initial and final directions of the α-particle, V its initial velocity, and v its velocity in passing through the apex A of its trajectory. Let p be the length of the perpendicular SN let fall from S on the initial direction of the α-particle.

By the principle of conservation of angular momentum

$$pV = SA \cdot v \quad . \quad . \quad . \quad . \quad (98)$$

and by the conservation of energy

$$\tfrac{1}{2}MV^2 = \tfrac{1}{2}Mv^2 + \frac{Ze \cdot E}{SA},$$

M being the mass and E the charge of the α-particle.

Hence
$$v^2 = V^2\left(1 - \frac{b}{SA}\right),$$

where
$$b = \frac{2Ze \cdot E}{MV^2} = \frac{Ze \cdot E}{T}, \quad . \quad . \quad . \quad (99)$$

where T is the initial kinetic energy of the α-particle. Combining this equation with (98) we have

$$p^2 = SA\,(SA - b). \quad . \quad . \quad . \quad (100)$$

If we write $S\hat{O}N = P\hat{O}A = \theta$, the eccentricity of the hyperbola is sec θ, and by the geometry of the conic, $SO = OA$ sec θ. Thus

$$SA = SO + OA = p \text{ cosec } \theta\,(1 + \cos\theta)$$
$$= p \cot \theta/2. \quad . \quad . \quad . \quad (101)$$

Substituting in (100) we have

$$b = 2p \cot \theta.$$

The resultant deflection ϕ of the α-particle is the angle POP' between the two asymptotes, or $\pi - 2\theta$, whence finally

$$\cot \frac{\phi}{2} = \frac{2p}{b}. \quad . \quad . \quad . \quad . \quad (102)$$

Thus to be deflected through an angle greater than ϕ, the initial direction of the α-particle must pass within a distance p of the nucleus, given by (102).

Let t be the thickness of the scattering foil, which we will suppose so small that the probability of the same α-particle suffering more than one deflection is negligibly small. Let n be the number of atoms per unit volume of the material of the foil. The number of atoms contained in a cylinder of length t, and base πp^2 is $\pi p^2 nt$. This measures the probability that the α-particle will pass within a distance p of a nucleus, and thus suffer a deflection greater than the corresponding value of ϕ. The probability ρ of a deflection exceeding ϕ is thus given by

$$\rho = \tfrac{1}{4}\pi nt\, b^2 \cot^2 \frac{\phi}{2}.$$

If we are dealing with a sufficiently large number of particles ρ is obviously also the fraction of the whole number which suffers displacements greater than ϕ.

Similarly the fraction $d\rho$ of particles whose deflections lie between ϕ and $\phi + d\phi$ is given by

$$d\rho = 2\pi pnt \, . \, dp$$

$$= \tfrac{1}{4}\pi nt b^2 \cot \frac{\phi}{2} \operatorname{cosec}^2 \frac{\phi}{2} . d\phi.$$

Hence the number q of α-particles which will reach a screen subtending a small solid angle ω at the scattering foil, in a direction making an angle ϕ with the direction of the incident α-rays can be shewn to be given by

$$q = \tfrac{1}{16} Qnt b^2 \omega \operatorname{cosec}^4 \tfrac{1}{2}\phi, \quad . \quad . \quad . \quad (103)$$

where Q is the number of incident α-particles.

106. Experimental verification of the theory of scattering.
A very elegant method of verifying the theory was devised by Chadwick[4]. The source of the α-particles was placed at A on the axis of a brass plate in which had been cut a narrow circular zone PP. The scattering substance (very thin leaves of copper, silver, or gold) covered this clear zone, while the observing screen was placed, also on the axis of the plate, at S. The apparatus

Fig. 87

can be visualized from the section in Fig. 87 by imagining the diagram to be rotated about the axis AS.
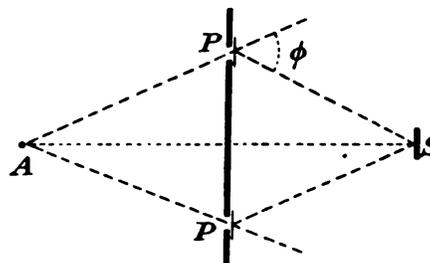
Thus all the particles which reach S must have been scattered through the same mean angle ϕ. The angle can be varied by varying the distance AS. The variation of scattering with the kinetic energy of the particles can be investigated by placing absorbing screens of known stopping power in front of the source A. The apparatus is enclosed in a highly evacuated box to eliminate absorption in the air.

Knowing the dimensions of the screen S, and of the other parts

of the apparatus it is easy to calculate, from (103), what fraction of the particles incident on the foil should be scattered to the screen. The predictions of the theory were fully borne out by the experimental results.

If the number Q of α-particles falling on the scattering annulus is found, the only unknown in equations (99) (103) is the factor Z, the number of charges on the scattering nucleus. Q can obviously be calculated if the number of particles per unit solid angle emitted by A is known. This can be measured by removing PP, and so allowing the incident beam to fall directly on the screen S. In this way Chadwick found for copper, silver and gold values of Z equal respectively to 29·3, 46·3 and 77·4. The atomic numbers of these elements are 29, 47, and 78. Moseley's suggestion that the charge on the nucleus of an element is equal to its atomic number is thus confirmed.

The closest distance of approach between an α-particle and a nucleus for a head-on collision is obviously given by b, or $Ze.E/T$. It is thus directly proportional to the atomic number of the scattering element, and inversely proportional to the energy of the incident particle. For oblique collisions it is given by (101). A swift α-particle will thus penetrate more closely to a nucleus than a slow one, and more closely to a nucleus of low, than to one of high atomic number. The closest distance of approach in Chadwick's experiment was of the order of 10^{-12} cm. for the copper foil. The accuracy with which the experimental results agreed with the theoretical predictions shows that at distances equal to or greater than 10^{-12} cm. the nucleus behaves as a point charge, and the law of force is that of the inverse square.

107. Scattering by light elements. Departure from the inverse square law. For elements of small atomic mass it is necessary to take into account the motion transmitted by the collision to the deflecting nucleus itself. The necessary modification in the theory has been made by Darwin[5]. The correction is of the order of $2 (M/m)^2$ where M is the mass of the α-particle and m that of the nucleus. It amounts to about 4 per cent. for aluminium, and is greater for elements of still lower atomic number.

Using the annular ring method just described, Bieler[6] found that for aluminium and magnesium the number of α-particles scattered at any given angle was less than that predicted by the theory, the effect being most marked for the faster particles and for large angles of scattering where the particles have approached more closely to the nucleus. The closest distance of approach of an a-particle from radium C' to an aluminium nucleus is of the order of 5×10^{-13} cm.

At distances of this order of magnitude the electrical force between the particles is, therefore, less than that calculated from the inverse square law. Bieler's experiments suggest that the force between the two particles may vary as $\dfrac{a}{r^2} - \dfrac{b}{r^5}$ where r is the distance. A relation of this type would arise if the aluminium nucleus became polarized in the field of the particle. The moment M of the electrical doublet induced in the nucleus will be proportional to the field of the α-particle, that is to $1/r^2$, while the attraction between the doublet and the α-particle will vary as M/r^3, that is as $1/r^5$. While this suggestion seems adequate to account for the scattering of α-particles by aluminium and magnesium, it fails to account for the results obtained in hydrogen and helium, and it is possible that the true explanation is to be found on other lines.

108. Scattering of α-particles in hydrogen and helium.

In the case of hydrogen we are dealing with the collision of an α-particle with a nucleus less massive than itself. The effect of the collision on the path of the α-particle is comparatively small; the maximum deflection is, for example, only 14°. On the other hand the hydrogen nucleus is projected forward by the impact with considerable velocity. Assuming the ordinary laws of elastic collision the velocity u with which a hydrogen particle of mass m will be projected by the impact of an α-particle of mass M and velocity V is given by

$$u = 2V \frac{M}{M + m} \cos \theta = \tfrac{8}{5} V \cos \theta, \quad . \quad . \quad (104)$$

where θ is the angle between the direction of the hydrogen atom and the initial direction of the α-particle. The velocity of pro-

jection of the hydrogen particles may thus exceed that of an α-particle, and they acquire the power to ionize the gas through which they pass, and to produce scintillations on a fluorescent screen. These *H*-particles may be observed by passing a beam of α-particles down a tube containing hydrogen and having a fluorescent screen at its further end. If absorbing sheets of known stopping power are interposed in front of the screen it is found that after sufficient material has been used to cut off all the α-rays, occasional scintillations are observable until the total stopping power of the absorbing sheets is approximately four times that required to stop the α-particles themselves. The nature of the particles producing these scintillations can be determined by measuring the ratio of the charge to the mass, in the usual way. The value obtained, 10^4 e.m.u. per gm., identifies them as hydrogen atoms carrying a single positive charge. They thus consist simply of hydrogen nuclei, or protons.

It is known that the range of a proton is practically the same as that of an α-particle of equal velocity. Hence, assuming Geiger's relation (97) the range R_p of the proton projected by an α-particle of range R_α should be given by

$$R_p = R_\alpha \left(\frac{8}{5}\right)^3 \cos^3 \theta.$$

The maximum range of the proton or *H*-particle as it is sometimes called should thus be $(1\cdot6)^3$ or $4\cdot1$ times that of the α-particle. This is in agreement with the observations just described.

Experimentally it is more convenient to study the distribution of these *H*-particles than to measure the comparatively small deflections of the α-particles themselves. Since the forces binding the hydrogen atoms in a chemical compound are negligible in comparison with those generated in a collision, the hydrogen may be used in the form of paraffin wax, and experiments on the distribution of the *H*-particles can be carried out by the method of Chadwick and Bieler. The theoretical distribution can be calculated from the general theory of scattering.

For very short range α-particles the proton distribution is that given by the theory. For more energetic particles, however, there is a large excess of *H*-particles making small angles with the direction of the incident α-rays(7). An analysis of the results

14-2

indicates that for head-on collisions the inverse square law breaks down when the distance between the colliding particles is less than 4×10^{-13} cm. For very oblique collisions the law ceases to hold at an even greater distance, about 8×10^{-13} cm. The distribution of the particles is inconsistent with any central law of force, and resembles the distribution which would be obtained if the H-particles were rebounding from an ellipsoid of semi-major and -minor axes of about 8×10^{-13} cm. and 4×10^{-13} cm. respectively, with its minor axis in the direction of motion. Observations of the band spectra of helium indicate that the helium nucleus, and hence the α-particle, has full spherical symmetry. It is possible, however, to suppose that the α-particle becomes distorted and flattened by the very intense forces called into play in close collision with a proton.

Very similar results are reached when the collisions of particles in helium are studied. Here the forces called into play are even greater, since the helium nucleus carries twice the charge of the proton, and the resulting apparent distortion appears to be even greater.

109. Atomic disintegration by α-particles.

It was discovered by Rutherford[8] in 1919 that if a beam of swift α-particles from radium C' was fired down a tube containing pure nitrogen, occasional scintillations could be observed up to distances corresponding to a range in air of 40 cm. This is far beyond the range (7 cm.) of the α-particles themselves, and even beyond the range (28 cm.) of the H-particles produced in hydrogen. An examination of the particles by the magnetic deflection method confirmed that they were protons or H-particles. Hydrogen, in the form of water, is difficult to eliminate completely in any experiment, but experiments made with oxygen, and with carbon dioxide in place of the nitrogen did not yield any long range particles, and it could safely be assumed that the particles observed in nitrogen were produced from the nitrogen atoms by the impact of the α-particles.

The type of collision which produces disintegration of the nucleus is of very rare occurrence, the number of H-particles being of the order of 1 for 10^4 α-particles. Nevertheless Blackett[9],

using an automatic form of cloud chamber, was able to photograph seven such collisions. One of these is reproduced in Fig. 88 (Plate II). It will be seen that only two tracks leave the fork, a faint one due to the proton ejected from the nucleus and a short dense track due to the new nucleus formed. Since there is no third track, the original α-particle must have been absorbed in the nitrogen nucleus from which the proton is ejected.

The new nucleus will thus have a mass of $14 + 4 - 1$ or 17. Since nitrogen has an atomic number, and hence a nuclear charge of 7, the new nucleus will have a nuclear charge of $7 + 2 - 1$ or 8. It is thus an isotope of oxygen of mass 17. The reaction may conveniently be expressed in the form

$$N_7{}^{14} + He_2{}^4 = H_1{}^1 + O_8{}^{17},$$
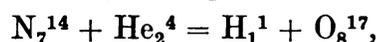
where the numbers above the letters indicate the atomic mass of the corresponding particle, and those below the atomic number.

Further research shewed that H-particles could similarly be obtained from other elements of low atomic weight. In general the elements of odd atomic mass give long range protons resembling those obtained from nitrogen. Elements of even atomic mass (with the exception of nitrogen) yield protons of much smaller range, and thus smaller kinetic energy. Elements of atomic number of the form $4n$, when n is an integer, as for example carbon and oxygen, are not disintegrated by α-particles. Measurement of the ranges of the particles concerned in the collision indicates that the kinetic energy of the particles after collision may be either greater or less than that of the colliding α-particle.

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CHAPTER XII

THE β- AND γ-RADIATIONS

110. Nature of the β-rays. The β-rays can be distinguished from the α-rays by their greater penetrating power, as they are able to produce measurable effects after passing through absorbing sheets of 100 times the thickness required to stop the α-particles. Their nature was first investigated by Becquerel who shewed that they consisted of charged particles by the following simple experiment. A small quantity of uranium oxide was placed in a small lead dish on the back of a photographic plate, the film side being downward. The whole was then placed between the poles of an electromagnet in a dark room. After some hours the plate was developed, and was found to be blackened immediately below the lead dish, the paths of the rays having been bent into circles by the action of the field.

A modification of the same experiment (Fig. 89) shewed that the rays were heterogeneous. The plate was placed film side upwards between the poles of the magnet and exposed to the rays for some time. On developing the plate a diffuse
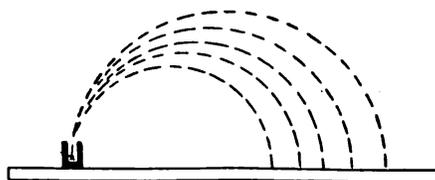
Fig. 89

patch was found shewing that some of the rays had been bent into smaller circles than others. By placing different thicknesses of aluminium foil on the plate it was found that the part of the patch nearest the source disappeared sooner than that further away. The more deviable rays were thus more absorbable than the others. Since

$$\rho = mv/He$$

these rays are the slower ones, assuming that the ratio of e/m is constant.

The similarity of the β-rays to cathode rays was further

established by Curie, who shewed that they carried a negative charge. In performing this experiment it is necessary to avoid the presence of air, as the latter becomes conducting under the action of the rays and the charge is thus unable to accumulate. In recent experiments this difficulty is overcome by working in a high vacuum. Curie however surrounded his plate by a solid dielectric instead. His apparatus is shewn in Fig. 90.
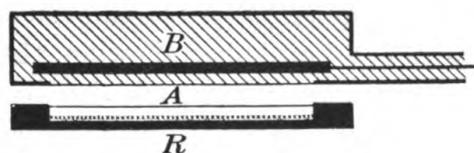
Fig. 90

The β-rays from the radio-active material in R penetrate the thin aluminium leaf A and the thin layer of wax, but are stopped by the lead plate B, giving up their charge to it. On performing the experiment it was found that the electrometer connected to B shewed a gradual but steadily increasing deflection when the source of radio-active substance was placed below A. The sign of the charge was negative.

111. Determination of e/m and v for the β-rays. Since the β-rays are rapidly moving negatively charged particles we can apply to them the methods of measuring the ratio of the mass to the charge, and the velocity, which were employed for the cathode rays. The first accurate experiments were made by Kaufmann[1]; they have been repeated by numerous observers.

The method adopted was the one where the electric and magnetic fields are parallel, and the two deflections thus at right angles to each other, the theory of which has already been considered (§ 50) in connection with the positive rays. The apparatus used is shewn in Fig. 91 (a).

The source of the rays was a small speck of radium compound placed at R, while the rays were limited to a narrow pencil by a slit A in a thick lead plate. Before reaching the hole A the rays passed between two metal plates, which could be adjusted by levelling screws to be perfectly parallel. The plates could

be raised to different potentials by means of wires which were fused through the walls of the containing glass vessel. The photographic plate P was mounted at the top of the chamber, and the whole was carefully exhausted to a very high vacuum. The whole vessel was placed between the poles of a strong electromagnet N, S.

On developing the plate the trace of the rays was a single continuous curved line (Fig. 91 (b)). If the rays had differed only in velocity this curve would by (50) have been a parabola. The line, however, was not parabolic, shewing that the value of e/m was not constant but varied with the velocity. The fact that the line was single and unbroken shewed that this important
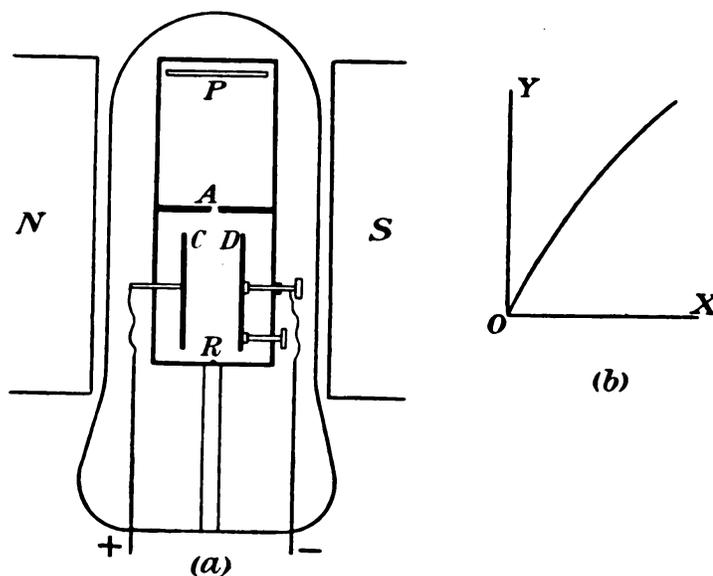
Fig. 91

ratio was a continuous function of the velocity of the rays. In other words for every value of the velocity there was a single, definite value for the ratio e/m which depended on the velocity alone.

The calculations necessary to evaluate the results are hardly so simple as those for Thomson's experiments on the positive particles. Allowance has to be made for the fact that the two fields are not coterminous. Very careful experiments and elaborate calculations were made to determine the end-corrections for the two fields.

Since the curve shewed no signs of breaks it was very improbable that the rays consisted of sets of different particles. It is equally improbable that the charge was gradually changing, since the great accumulation of evidence has shewn that the charge e is atomic. We are thus led to the conclusion that the mass of a β-particle is a function of the velocity with which it is moving. The value of e/m for the more slowly moving β-particles is identical with the value obtained for the cathode rays. The β-particles are thus simply swift electrons.

112. Electromagnetic mass. It can easily be shewn that a moving charge will act as if it possessed mass from the mere fact that it carries a charge. Consider a point charge moving with a velocity v. This will be equivalent to a current element coinciding with the path of the particle and equal to ev, where e is the charge and v the velocity. The magnetic field due to the moving charge at a distance r from it in a direction making an angle θ with the direction of motion will thus be $\dfrac{ev \sin \theta}{r^2}$.

The energy in a magnetic field of strength H is $\dfrac{\mu H^2}{8\pi}$ per unit volume. Hence if du is a small element of volume at the point considered the magnetic energy in that element of volume will be $\dfrac{\mu}{8\pi} \left(\dfrac{ev \sin \theta}{r^2}\right)^2 du$.

The whole magnetic energy in the space round the particle will be the integral of this from the surface of the particle to infinity. To evaluate this, with the electron as centre describe two spheres of radii r and $r + dr$ and draw two radii making angles θ and $\theta + d\theta$ with the direction of motion. If these are supposed to rotate about the direction of motion of the electron they will cut out from the spherical shell an annulus the volume of which is

$$2\pi r \sin \theta \cdot r d\theta \cdot dr.$$

But the magnetic field is obviously constant throughout the space so obtained and hence the energy in the annulus is

$$\frac{\mu}{8\pi} \left(\frac{e^2 v^2 \sin^2 \theta}{r^4}\right) 2\pi r^2 \sin \theta \, d\theta \, dr = \frac{\mu e^2 v^2 \sin^3 \theta \, d\theta \, dr}{4r^2}.$$

The energy in the spherical shell is thus

$$2 \int_0^{\frac{\pi}{2}} \frac{\mu e^2 v^2 \sin^3 \theta \, dr}{4r^2} \, d\theta = \frac{\mu e^2 v^2 \, dr}{2r^2} \int_0^{\frac{\pi}{2}} \sin^3 \theta \, d\theta$$

$$= \frac{1}{3} \frac{\mu e^2 v^2}{r^2} \, dr.$$

If the charge is carried by a small sphere of radius a the total magnetic energy in the space is $\int_a^\infty \frac{\mu}{3} \frac{e^2 v^2}{r^2} \, dr$

$$= \frac{\mu}{3} \frac{e^2 v^2}{a} \dots \dots \quad (105)$$

This energy must be given to the particle when it is set in motion. Comparing this expression with that for kinetic energy ($\frac{1}{2} m v^2$) we see that the charge behaves as if it had a mass of $\frac{2}{3} \frac{\mu e^2}{a}$ due to its charge e; this is called its *electromagnetic mass*. If we assume that the whole mass of an electron is electrical in origin the radius a of the electron can be deduced from this equation. The value so obtained, $1 \cdot 9 \times 10^{-13}$ cm., is of an order of magnitude not inconsistent with our knowledge of the dimensions of other fundamental particles.

113. Variation of the mass of an electron with velocity. Bucherer's experiments. It can be shewn on the electromagnetic theory that the above analysis is only true if the velocity of the particle is small compared with that of light (practically if it is less than one-tenth that of light). If the velocity of the particle approximates to that of light the distribution of the electric field round the moving charge is altered in such a way as to increase the electromagnetic energy of the field, and thus the electromagnetic mass of the particle.

Lorenz has shewn that if m_0 is the electromagnetic mass of a particle when moving with a velocity small compared with that of light (the rest-mass as it is called) its mass m_v when moving with a velocity v is given by

$$m_v = m_0 \left(1 - \beta^2 \right)^{-\frac{1}{2}}, \quad \dots \quad (106)$$

where β is the ratio of the velocity of the particle to that of light.

On the Principle of Relativity all mass, whether electrical in

its origin or not, should vary with velocity in accordance with (106). Since β-particles move with velocities approaching within about 2 per cent. of the velocity of light, they afford a very suitable means of testing the accuracy of the formula. An experimental test has been carried out by Bucherer[2] using a very ingenious method. The source of the β-radiation was a small speck of radium fluoride R placed at the centre of two parallel plates A and B (Fig. 92) which were very close together. The plates were maintained at a considerable difference of potential, and the apparatus was placed in a uniform magnetic field at right angles to the plane of the paper. The β-particles from the radium will obviously only be able to escape from between the plates if the electric and magnetic forces upon them
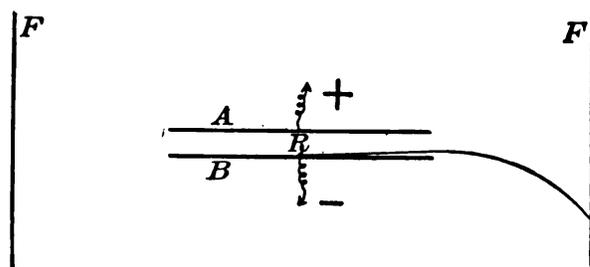
Fig. 92

are exactly equal and opposite. Otherwise the particles will be deflected by whichever of the two fields is the stronger, and will strike one or other of the plates. The particles are projected at all angles to the magnetic field. Those which emerge from between the plates at an angle θ with the magnetic field will have a velocity given by

$$Xe = Hev \sin \theta,$$
$$\therefore \quad v = \frac{X}{H \sin \theta}.$$

Thus for any given value of the angle θ the rays which succeed in escaping from between the plates have a definite and calculable velocity.

On emerging from the plates the electrons are acted upon only by the magnetic field, and their deviation is proportional to e/m where m is the mass corresponding to the velocity v. To measure the deviation the rays are allowed to

fall upon a photographic film F, F, which is bent into a cylinder coaxial with the plates. The field is reversed during the experiment and the distance between the two traces on the film gives twice the magnetic deviation corresponding to that direction, from which e/m can be calculated. Hence v and e/m are known for each point on the film.

The values of m_v/m_0 given by the Lorentz formula are contained in Table VIII. It will be noticed that the increase in mass is inappreciable until v is at least one-tenth the velocity of light. The discrepancy between the Lorentz formula and the experimental results of Bucherer was less than one per cent.

TABLE VIII

β	m_v/m_0
·01	1·000
·10	1·005
·30	1·048
·50	1·115
·60	1·250
·70	1·400
·80	1·667
·90	2·294
·95	3·203
·98	5·025

114. Passage of the β-rays through matter. Experiments on the absorption and scattering of β-rays are far more difficult than those on α-rays. The energy of a β-particle is only of the order of 400,000 volts, while that of the α-particle may be as much as seven million volts. This in the first place makes it difficult to detect single β-particles, and experiments of the type made on the scattering of α-particles are not feasible. We are thus compelled to work with pencils containing large numbers of β-particles. Further, β-particles, owing to their small kinetic energy, suffer many large collisions in their passage through matter and in consequence the straggling of the beam, which is appreciable even for α-rays, becomes so large that it is impossible to fix a range for the β-particle by experiments of the kind which are employed for α-rays. The actual length of track of a β-par-

ticle in a foil sufficiently thick to stop the β-rays completely will be many times greater than the thickness of the foil. Thus far less is known of the behaviour of β-particles in matter, than of α-particles.

Probably the most informative experiments on the subject are those made recently by White and Millington[3], using the focusing method described in § 93. The radiator R of Fig. 75 is replaced by a wire coated with radium B and C. These substances emit certain strong homogeneous groups of β-rays, each group being characterized by a definite velocity of emission. Thus when the apparatus is placed in a strong magnetic field several strongly marked sharp lines appear on the photographic plate.
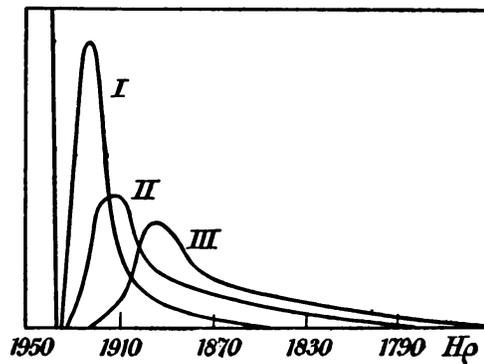
Fig. 93

If the source is covered with a thin sheet of mica each line is displaced towards the source, shewing that the particles have been retarded by passing through the absorbing screen, and at the same time the line is very much broadened, owing to the large straggling of the particles in the sheet. By placing the mica so that it covers only part of the source, both sets of lines can be recorded simultaneously on the same plate and the displacement can thus be accurately measured. Since the magnetic field is constant this displacement is, by (37), proportional to the change in velocity in passing through the sheet.

The relative intensity of the β-particles at a given point in the broadened line can be estimated by measuring the density of the photographic trace by a microphotometer. One set of such results is shewn in Fig. 93, the curves I–III referring to three

different thicknesses of mica. It will be seen that the actual re-tardation suffered by a β-particle in passing through a given sheet of matter varies within fairly wide limits, according to the number and kind of collisions it has chanced to make in its passage. If we take the highest point of each peak as a measure of the most probable retardation, it is found that the most prob-able retardation δ is roughly proportional to the thickness of the absorbing screen. The value of δ/σ, where σ is the thickness of the sheet expressed as its mass per unit area, is known as the stopping power of the material. It is found that the stopping power I of a given substance is roughly, but not accurately, inversely proportional to the cube of the velocity of the β-particles. Thus approximately

$$Iv^3 = \text{constant} \quad \text{or} \quad T_0{}^4 - T^4 = k\sigma, \quad . \quad . \quad (107)$$

where T_0 is the initial, and T the final kinetic energy of the particle after passing through a thickness σ.

The stopping power does not appear to vary much with the nature of the absorbing foil. It appears to be somewhat greater for elements of low atomic number.

115. The scattering of β-rays. Rutherford's theory of scattering should apply to β-particles as well as to α-particles, and it can be shewn that except for elements of low atomic num-ber the scattering is due almost entirely to the central nuclear charge, the effect of the extra nuclear electrons being negligible. Remembering that the charge on the β-particle is simply e, the scattering formula (§ 105) becomes

$$\rho = \frac{\pi n t Z^2 e^4}{4T^2} \cot^2 \frac{\phi}{2} \quad . \quad . \quad . \quad . \quad . \quad (108)$$

Since the kinetic energy T is much less than for α-particles the probability of large angle scattering is very high. Thus unless the scattering foil is extremely thin the observations are com-plicated by the fact that a single electron may be scattered several times in the thickness of the foil. This is known as multiple scattering, and leads to a formula of quite a different type.

On the other hand, when the foil is very thin, the fraction of

β-particles scattered out of the beam is so small that it cannot be measured with any great accuracy. Experiments by the author and others give results which are in general agreement with the theory.

116. Diffraction of electrons by crystals. We have seen (§ 83) that if a pencil of X-rays is directed obliquely at the surface of a crystal, reflection takes place for certain values of the glancing angle, the crystal acting as a diffraction grating for the radiation. Davisson and Germer[4] in 1922 shewed that exactly similar results can be obtained if a pencil of fast cathode rays is substituted for X-rays in the experiment. Thus a pencil of electrons can be diffracted by a crystal grating. The critical glancing angle depends on the velocity of the particles, the angle becoming smaller as the velocity increases. The beam of electrons thus behaves exactly in the same way as a beam of light, the "wave length" of the beam becoming smaller as the velocity increases. These results are obviously of very fundamental importance, and throw quite a new light on the nature of the electron.

The results of Davisson and Germer were confirmed by a somewhat different method by G. P. Thomson[5]. Thomson allowed a narrow pencil of fast cathode rays to fall normally on very thin metallic films, the emergent rays falling on a photographic plate placed some distance on the further side of the film. It was found that the central spot marking the position of the undeflected beam was surrounded by a series of well-marked diffraction haloes, exactly similar to those which would have been obtained with a beam of homogeneous X-rays, but of smaller diameter, shewing that the wave length concerned was rather shorter than that of X-rays (see Fig. 94, Plate IV). If a magnetic field is applied between the film and the plate the ring system is deflected as a whole, shewing that the rings are formed by electrons and not by any X- or γ-radiation which might conceivably be present in the tube.

X-ray measurements shew that a metal foil consists of a large number of irregularly orientated crystals of the metal, and Thomson's arrangement thus corresponds to the "powder"

method used in X-ray analysis (§ 85). Thus by measuring the radii of the rings the corresponding wave length λ can be deduced since the lattice spacing of the crystals is known from X-ray measurements. For cathode rays of velocity 10^{10} cm. per sec. the value of λ was $7\cdot8 \times 10^{-10}$ cm. corresponding to that of a hard γ-ray. He was able to shew that the wave length λ was related to the velocity u of the electron by a relation of the form

$$\lambda = \frac{h}{mu}, \quad \ldots \quad \ldots \quad \ldots \quad (109)$$

where m is the mass of the electron and h is Planck's constant.

Electron diffraction is now being extensively used as a means of studying surface conditions, as owing to their small penetrating power electrons are diffracted mainly in the surface layers.

117. The wave theory of matter. Before the publication of Davisson and Germer's final results de Broglie had already advanced the suggestion that an electron might be regarded as a group of waves, or "wave packet" as it is now called. The velocity of a group of waves is not necessarily that of the waves themselves: the two are, in fact, only identical in a nondispersive medium. Observation of a group of waves formed by dropping a pebble into a pond will shew that the group is travelling more slowly than the waves themselves. It can be seen that waves form at the back of the group, travel through it, and finally disappear as they reach the group front. It is, therefore, not necessary that the electrons should move with the velocity of light; any velocity can be obtained for them by assigning appropriate (though rather unusual) dispersive properties to the medium. De Broglie's theory has been developed by Schrödinger and others with great success. The quantum relationships emerge from it quite naturally, and it leads to formulae identical with those of Bohr for the structure of the hydrogen atom. The relation between the velocity and the wave length is of the form of (109) which has been verified by Thomson.

The theory is not confined to electrons but is taken to apply

to all small particles whether charged or uncharged, the wave length being given by (109) in all cases. Thus a hydrogen molecule at ordinary temperatures has, owing to its velocity of thermal agitation, a wave length of about 10^{-8} cm. and Stern and Esterman[6] have succeeded in demonstrating the diffraction of a stream of hydrogen molecules by a crystal surface. An α-particle from radium C′ of mass 6.60×10^{-24} gm. and velocity 1.92×10^9 cm. per sec. must be regarded as a wave packet of wave length almost exactly 5×10^{-13} cm. It is not without significance that the ordinary laws of scattering begin to break down at a distance from the nucleus of this order of magnitude.

It is probably impossible to form any mental image of an entity which has some of the properties of a particle and some of the properties of a wave. The matter can, however, be dealt with quite rigidly by mathematical reasoning, and wave mechanics has now a very large and rapidly growing literature of its own. It is entirely beyond the scope of this work, though we shall have occasion to refer to some of its conclusions.

118. Nature and properties of the γ-rays. The γ-rays are distinguished from the α-rays and β-rays by their much greater penetrating power. The γ-rays from radio-active substances can be detected through 30 cm. of iron. They are not deviated by a magnetic field and, therefore, carry no charge. Their behaviour corresponds with the assumption that they are electromagnetic disturbances of extremely short wave length, even shorter than that of the most penetrating X-rays from a hard tube. The γ-rays from radium C, for example, correspond to X-rays having an excitation voltage ranging from 600,000 to 2 million volts.

If in sufficient intensity they produce luminosity in a fluorescent screen, and affect a photographic plate. They also produce ionization in gases, and are generally detected by this action.

119. Determination of the wave length of γ-rays. Direct determinations of the wave lengths of some of the less penetrating γ-radiations have been made by Rutherford[7].

The method adopted was an interesting modification of that of the X-ray spectrometer already described. As the glancing angle decreases with the wave length it is very small for γ-rays, and hence could not be measured with any precision. To overcome the difficulty a crystal S of rock salt was mounted with cleavage planes parallel to the line RO (Fig. 95), the source of γ-radiation being placed at R and a photographic plate at O. The γ-rays strike the crystal at all angles but only those which fall upon it in such a way that the angle between them and the reflecting planes is the glancing angle for the particular wave length will be reflected. The rays are thus left as it were to pick out their own reflecting planes, and beams of reflected rays AB and $A'B'$ will emerge from the crystal and fall on the photographic plate.
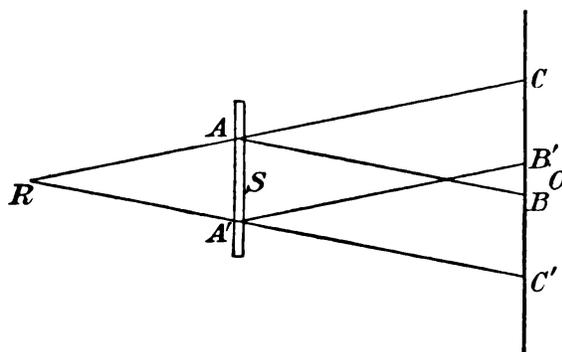
Fig. 95

Neglecting the absorption of the crystal, which will be very small, the energy transmitted plus the energy reflected must be equal to the energy in the primary beam. Hence a ray such as RA which is selectively reflected will suffer a much greater loss of energy in going through the crystal than rays which pass through without any loss by reflection. Thus in the direction RA produced the rays will be relatively enfeebled and the effect on the photographic plate will be small. The reflecting plane thus casts a shadow on the photographic plate at a point C in the direction RA produced. Similarly the plane A' casts its shadow at C'. It is evident that the angle CRC' subtended by the distance between two corresponding bright lines at the source R is equal to twice the glancing

angle for the rays. In this way by measuring the distance CC' on the plate and the distance of the plate from the source the angle of selective reflection for the rays used can be accurately determined.

The values of the glancing angle for the γ-rays from the mixture of radium B and radium C used for the experiment ranged from $44''$ to $4°$. The corresponding wave lengths ranged from 0.71×10^{-9} to 4×10^{-9} cm.

120. Production of γ-radiation. Just as the stoppage of a cathode particle produces an X-ray pulse of appropriate wave length, so we should expect that the stoppage of a high energy β-particle would produce a corresponding high energy γ-ray. This has been experimentally demonstrated. The number of β-particles emitted even by a powerfully radio-active substance is quite insignificant in comparison with the number of electrons in the cathode rays of an ordinary X-ray tube. As only a very small fraction of the energy of the β-rays is transformed into γ-radiation, the effect has been somewhat difficult to demonstrate. The method used is indicated in Fig. 96. The measuring apparatus was a simple gold leaf electroscope, E. For measurements on the γ-rays an electroscope of this type is generally preferred to the use of an electrometer with a separate ionization chamber.
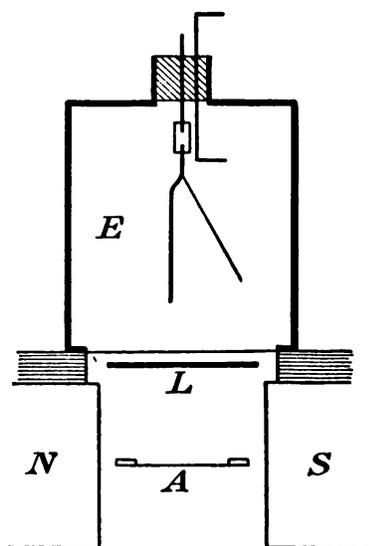
Fig. 96

The electroscope is usually constructed with lead walls 2 mm. in thickness, so as to cut off all secondary β-radiation from the surrounding air, table, walls, etc. This thickness causes little diminution in the intensity of the γ-rays themselves.

A source of β-rays (radium E) was chosen which while rich in β-rays was yet poor in γ-radiation. This was spread on a thin sheet of paper at A, the paper being used to reduce as

much as possible the γ-radiation which might be excited by the β-rays falling upon the support. The substance was placed between the poles N, S of an electromagnet. The lower face of the electroscope was closed by a thin sheet of aluminium leaf. When the β-rays were deflected away from the electroscope the current was due solely to the γ-rays from the radium E, and was therefore quite small.

If, however, a lead plate sufficiently thick to absorb all the β-rays was placed at L, immediately below the electroscope, and the field removed so that the β-rays fell upon L, the ionization in E at once increased. This could not be due to the β-rays themselves, as they were unable to penetrate the lead. If, however, the field was again applied so as to prevent the β-rays from reaching L the effect at once ceased. The increased ionization must therefore be due to γ-radiation set up in L by the impact of the β-rays upon it.

Experiments of a similar kind, but using α-rays instead of β-rays, have shewn that γ-radiation can also be excited by the stoppage of an α-particle.

The γ-radiation coming directly from radio-active substances, our main source of γ-radiation, are found to contain groups of homogeneous radiations of an absorbable type, and hence of a greater wave length. The coefficient of absorption in aluminium of the more penetrating of these groups is of the order of 0·17; that of the more absorbable about 14·0. From Tables VI and VII we see that these coefficients agree with those of the characteristic K and L radiations for elements of atomic number round about 84, that is of the radio-active elements themselves. These soft radiations are, therefore, the characteristic K and L radiations of the particular radio-active element emitting them, and are excited by the passage through the atom of the γ-radiation from its own nucleus. The observations are interesting as illustrating the continuity of the X-ray with the γ-ray spectrum. The characteristic X-ray spectrum of other elements can also be excited by γ-radiation.

121. The passage of γ-rays through matter. A narrow pencil of γ-radiation becomes enfeebled in its passage through

matter, the intensity I after passing through a thickness d of absorbing material being given for homogeneous radiation by $I = I_0 \epsilon^{-\mu d}$. The thickness d is usually expressed as mass per unit area, and μ is then the mass coefficient of absorption.

The coefficient μ may be regarded as being made up of three terms. In the first place the γ-ray may be absorbed as a whole in an atom, with the consequent ejection of a high speed photo-electron, or β-particle. The probability of the absorption of a quantum of radiation in an atomic level decreases very rapidly as the difference in energy between the photon and the level increases, so that except for elements of very high atomic number the photo-electric absorption is small, and for elements of low atomic number such as aluminium, negligibly small.

The second, and generally the more important, factor is the Compton scattering of the radiation. We have already seen that the scattering of a photon by a free electron results in the production of a recoil electron, and thus in the absorption of energy from the beam. The photon itself is also deflected or scattered out of the beam, so that energy is withdrawn from the beam in this way also, although it is not actually absorbed in the medium. The coefficient of absorption μ may thus be written in the form

$$\mu = \tau + \sigma_a + \sigma_s,$$

where τ is the coefficient of photo-electric absorption, σ_a the Compton absorption coefficient, and σ_s the coefficient of scattering.

The measurement of the scattering and absorption of γ-radiation is difficult for various reasons. In the first place all sources of γ-radiation give off complex radiations so that it is impossible to obtain a homogeneous beam. The best that can be done is gradually to decrease the mean wave length of the beam by filtering out its more absorbable constituents. Again, owing to the great penetration of the radiation, the diaphragms used to limit the beam must be several centimetres in thickness. The β-rays given off by conversion of the γ-radiation in this material can be prevented from reaching the measuring electroscope by placing each diaphragm in a strong magnetic field. The γ-rays,

however, scattered from the mass of material cannot be so removed, and since it is modified radiation it adds considerably to the uncertainties of the experiment.

The Compton change of wave length on scattering has been verified. Since the absolute change in wave length is independent of the wave length of the radiation, its effect is relatively much larger for γ-rays of wave length 10^{-9} to 10^{-10} cm. than it is in the longer wave length part of the spectrum. The distribution of scattered γ-rays round the radiator resembles that of scattered X-rays (§ 76), but the eccentricity is much more pronounced. The recoil electrons can be studied in a Wilson cloud chamber. Their energy is, of course, much greater than that of the recoil electrons from X-rays.

Klein and Nishina have obtained, on quantum mechanical considerations, a formula for $_\epsilon\sigma$, the total scattering per electron. They find that

$$_\epsilon\sigma = \frac{\pi e^4}{m^2 c^4} \, 2 \left\{ \frac{1+\alpha}{\alpha^2} \left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha} \log(1+2\alpha) \right] \right.$$
$$\left. + \frac{1}{2\alpha} \log(1+2\alpha) - \frac{1+3\alpha}{(1+2\alpha)^2} \right\}, \quad . \quad . \quad (110)$$

where $\alpha = h\nu/mc^2$, $h\nu$ being the energy of the γ-ray, and m the mass of the electron. The experimental evidence is not wholly inconsistent with this formula, but there are indications that, for very short wave length γ-radiation, some other effect possibly due to the nucleus of the atom may have to be considered.

122. Characteristic γ-ray spectra. Ellis's experiments. Although γ-rays can be produced by the impact of α- or β-rays on matter, our main source of γ-radiation is that emitted by the nuclei of radio-active elements during their disintegration. This emission is found to contain a number, often quite large, of homogeneous groups of waves, the wave lengths of which are characteristic of the particular element from which they are emitted.

Although it is possible, as we have seen, to determine the wave length of γ-radiation by crystal reflection, the method is incapable of great accuracy owing to the very small glancing angles

involved. The most accurate method is to measure the energy of the photoelectrons ejected when the γ-ray is absorbed in some suitable material. In the analogous case of X-rays we have seen that the absorption of radiation of frequency ν in an electron level of energy w_K gives rise to a photoelectron the kinetic energy E of which is given by $E = h\nu - w_K$. In the X-ray part of the spectrum the relation is used to determine the value of w, since the direct measurement of ν presents no difficulties. It is obvious, however, that if the electron energy levels are known from X-ray measurements, it is possible to use the relation to determine the frequency ν of the radiation employed.

The experimental arrangements[8] are essentially the same as those adopted for the X-ray measurements. The source of γ-
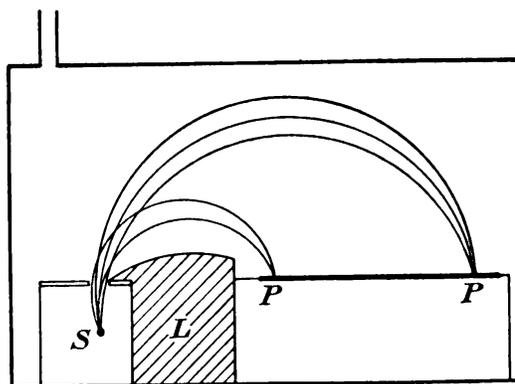
Fig. 97

radiation is usually a fine wire on which the appropriate radioactive substance is deposited. This is wrapped round with a sufficient thickness (about 3 mm.) of the absorbing material to cut off completely any β-radiation due to the source itself. The β-rays emerging are, therefore, all produced by the transformation of the γ-radiation in the absorbing material. The source, in its wrapping, is placed at S (Fig. 97) immediately below the slit. The whole apparatus is then highly evacuated to prevent scattering or absorption of the β-particles in their path to the photographic plate PP. L is a block of lead used to screen the photographic plate PP from the direct action of the γ-rays from S, which would tend to produce a general fogging of the plate.

Since the energies of the photoelectrons range between about 300,000 and 3,000,000 volts, strong magnetic fields are required

to produce the necessary deflection, and the apparatus is placed between the poles of a strong electromagnet. For absolute measurements the distribution of the magnetic field along the path of the particle must be determined, as it is usually not quite uniform. It is also necessary to take into account the variation of the mass of the β-particle with velocity. The radius of curvature ρ and the corresponding energy E of the particle are thus given by the equations

$$H\rho = \frac{m_0 c}{e} \frac{\beta}{\sqrt{1 - \beta^2}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (111)$$

$$E = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right), \quad \cdot \quad \cdot \quad \cdot \quad (112)$$

where m_0 is the rest mass of the electron, and β the ratio of the velocity of the particle to c, the velocity of light.

The applicability of the quantum relation to the γ-ray part of the spectrum was investigated in some preliminary experiments by Ellis, to whom most of our knowledge of this part of the subject is due. The β-ray spectra produced by the absorption of the γ-radiation from a single source (radium B + C) in a number of different elements of high atomic weight were measured. The spectra obtained were identical except that they were shifted more and more in the direction of lower energies, as the atomic number, and hence the energy of the absorbing level increased. If E is the energy of the β-particles forming some particular line in the spectrum and w the energy of the absorption level of the absorbing element, $E + w$ should be constant and equal to the energy of the corresponding γ-ray. This is found to be the case as is shewn in Table IX which is taken from one of Ellis's early papers.

TABLE IX

Absorbing element	Ba	W	Pt	Pb	U	
E	2·53	2·20	2·12	2·03	1·74	$\times 10^5$ volts
w	·37	·69	·78	·89	1·18	,,
$E + w$	2·90	2·89	2·90	2·92	2·92	,,

The accuracy of the method has been greatly increased by careful technique, and measurements of the frequency of radia-

tion are now made to an accuracy which is certainly better than one part in a thousand. It may be mentioned that conversion may also take place in the L or even the M levels of the absorbing material. The probability of these conversions is much smaller than for the K level, and the corresponding lines are usually faint.

The lines in the γ-ray spectrum of a given radio-active element shew the same type of interrelation which we found between the lines of the characteristic X-ray spectrum of an element, that is to say, there are numerous lines which can be related by an expression of the type $\nu_a = \nu_b - \nu_c$. It is reasonable to suppose that the characteristic γ-rays are emitted during transitions between various energy levels existing in the nucleus of the radio-active atom. We shall discuss this in more detail in a later chapter (§ 139).

123. The β-ray spectra. The β-radiation from a radio-active body comes partly from the nucleus. This nuclear β-radiation forms a continuous spectrum, lying between certain definite limits which are characteristic of the particular element
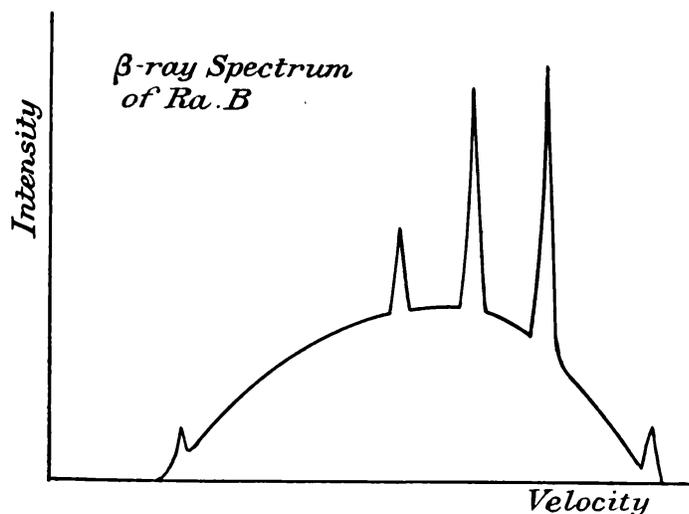
Fig. 98

from which it is emitted. The distribution of energy in the spectrum can be investigated by a modification of the focusing method. The photographic plate is replaced by a Faraday cylinder

with a narrow aperture, and different parts of the spectrum are focused in turn on this aperture by varying the magnetic field.

In addition to this general radiation, the spectrum also contains certain groups of rays of definite velocity. This characteristic β-ray spectrum can be photographed by Ellis's method (9), by omitting the absorbing sheet covering the source. A comparison of the spectrum so obtained with that produced by the conversion of the γ-rays in a metal of neighbouring atomic number shews that the characteristic groups of β-rays are due to the conversion of the γ-radiation in the extra-nuclear energy levels of the radio-active element itself. Since the energies of these levels are known, the energy and frequency of the corresponding γ-radiations can thus be determined. The lines in the natural β-ray spectrum are much sharper than those in the secondary spectra excited in other metals, so that the measurements can generally be carried out with greater precision, and the method is often employed for investigating the characteristic γ-ray spectrum.

The natural spectrum is also found to contain lines which are not shewn by the secondary spectra. These may be regarded as being due to γ-rays which are so strongly absorbed in the electronic structure of the radio-active atom, that they never emerge from it.

The continuous β-ray spectrum emitted by the nucleus itself is one of the outstanding problems of nuclear physics. Experiment shews that in a β-ray disintegration only one β-particle is emitted for each atom which disintegrates. Since some of these particles are comparatively slow, and others very swift, the atom emitting a slow β-particle should retain appreciably higher energy than that giving out a swift particle. Hence the nuclei formed in the two disintegrations should differ quite appreciably in energy content. Thus the atoms of radium C (which is formed from radium B with the emission of a β-particle) should differ among themselves in energy over a range corresponding to the range of energies in the continuous β-ray spectrum of radium B. There is no evidence, however, that the atoms of radium C are not all identical.

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CHAPTER XIII

NEUTRONS, POSITRONS, COSMIC RADIATION

124. The existence of a neutron. It was discovered by Bothe and Becker that some of the lighter elements, and in particular boron and beryllium, emit a highly penetrating radiation when bombarded by the α-particles from polonium. Polonium is used in these experiments because it emits no γ-radiation to complicate the observations. The radiation emitted from beryllium had a coefficient of absorption of 0·22 per cm. in lead, and applying the Klein-Nishina formula (110) it was found that its energy, assuming it to be γ-radiation, must be about 7×10^6 volts. This was higher than any previously known γ-radiation.

It was found by Curie-Joliot that if this radiation was allowed to fall on paraffin wax, or any other material containing hydrogen, protons were ejected with a maximum range of as much as 26 cm. in air, and consequently a maximum energy of the order of 5×10^6 volts. Since there can be no question of disintegration in the case of a hydrogen nucleus, the protons could only be regarded as having been set in motion by the Compton recoil from a direct collision with the γ-ray quant. The maximum energy which can be so transferred from a quant of energy $h\nu$ to a particle of mass M is given by $\dfrac{2h\nu}{2 + Mc^2/h\nu}$. We can thus estimate $h\nu$ for the beryllium radiation. It works out at 55×10^6 volts; a result quite inconsistent with that deduced from its coefficient of absorption.

Chadwick[1] investigated the effect of the radiation on other elements, both in the solid and in the gaseous form. The most complete information can, perhaps, be obtained by passing the radiation through a Wilson cloud chamber containing the gas under investigation. The projected nuclei produce intense ionization along their track, so that the length of the track can be measured and the corresponding energy of projection deduced.

It can also be confirmed from the absence of any second track that disintegration has not occurred. It was found that in nitrogen, for example, the projected nuclei had a range of about 3·3 mm. corresponding to an initial kinetic energy of $1·2 \times 10^6$ volts. Using the Compton relation the corresponding energy of the beryllium radiation becomes 90×10^6 volts. In fact, the greater the mass of the recoiling particle the greater the energy it was necessary to assume in the incident radiation.

The complete inconsistency of these observations when reduced on the theory that the beryllium radiation is of the nature of γ-radiation led Chadwick to put forward the suggestion that the radiation consists of material particles of mass comparable with that of an atom. To explain the very high penetration of the particles it was necessary and sufficient to assume that they carried no charge, and it was therefore proposed that they should be called *neutrons*.

Assuming the neutron hypothesis, the atomic nuclei are set in motion by direct collision with the high velocity neutral particle, and the problem is simply one of elastic impact between the two bodies. Let M and V be the mass and velocity of the neutron, A the mass of the atomic nucleus and u its velocity after impact. The maximum value of u, for a head-on collision, is given by

$$u = \frac{2M}{M+A} . V. \quad . \quad . \quad . \quad . \quad . \quad (113)$$

Thus, if u_p is the maximum velocity given to a proton, and u_n that to a nitrogen nucleus, both of which can be deduced from the observed ranges of the particles, we have

$$\frac{M+14}{M+1} = \frac{u_p}{u_n} = \frac{3·3 \times 10^9}{4·6 \times 10^8} \qquad M = 1·1.$$

The mass of the neutron is thus approximately equal to that of the proton. Applying the same argument to similar measurements made in argon and oxygen, it was found that the ranges observed could all be explained within the limits of experimental error on the assumption that the respective nuclei were set in motion by collision with a neutral particle of approximately unit atomic mass.

125. Origin of the neutrons. Neutrons, as we have seen, are produced by the α-ray bombardment of the nuclei of the lighter elements, and there is evidence that all the elements up to fluorine can be made to yield neutrons under suitable conditions with the exception of helium, carbon, nitrogen, and oxygen, and of course hydrogen. The process seems to be a nuclear disintegration in which the α-particle is captured by the nucleus, and a neutron is ejected. The atomic mass is thus increased by three units, and the atomic number by two. In the case of boron we assume that the nucleus concerned is that of mass 11, since the other isotope of mass 10 is known to disintegrate under α bombardment with the emission of protons. Writing n_0^1 for the neutron, the process may thus be represented in the form

$$B_5^{11} + He_2^4 \rightarrow N_7^{14} + n_0^1.$$
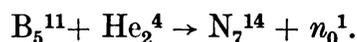
This relation provides us with the most accurate method yet available for estimating the mass of the neutron. Remembering that in these reactions matter and energy are interconvertible (§ 54) we may write the equation in the form

Mass of B^{11} + mass of He^4 + K.E. of He^4

$$= \text{mass of } N^{14} + \text{mass of } n^1 + \text{K.E. of } N^{14} + \text{K.E. of } n^1,$$

$$. \quad . \quad (114)$$

taking into account both the changes in mass and the kinetic energies of the various particles before and after impact. The masses of the different particles, with the exception of n^1, are all known, from Aston's measurements, and the K.E. of the α-particle from polonium is also known. The K.E. of the neutron can be deduced by (113) from the range of the protons which are emitted when the neutrons fall on a sheet of paraffin wax. Assuming the conservation of momentum the energy of recoil of the newly formed nitrogen nucleus can also be calculated. The different quantities in (114) must, of course, be expressed in the same units, and the atomic mass scale ($O = 16 \cdot 000$) is the most convenient. By Einstein's relation kinetic energy T is equivalent to mass T/c^2 gm., or $T/A_0 c^2$ atomic mass units, where A_0 is the mass in grams of an atom of unit atomic weight. In atomic mass units the actual figures are $B = 11 \cdot 00825$, $He = 4 \cdot 00106$, $N = 14 \cdot 0042$; while the kinetic energies of the α-particle, neutron

and nitrogen nucleus are respectively 0·00565, 0·0035, and 0·00061. Substituting these figures we find that the mass of the neutron is 1·0067. This is thus slightly less than that of the proton.

Chadwick(2) has more recently repeated these measurements and calculations, using the neutrons ejected by the bombardment of lithium by α-rays. The value obtained in this case was 1·0070 with a probable error not exceeding 0·0005.

The calculations have been given in detail as they illustrate a mode of argument which is being very extensively used in nuclear researches.

126. Passage of neutrons through matter. Owing to the absence of charge on the neutron, the particle is but little affected by the charges either of the electrons or of the nuclei of the atoms through which it passes, and can only transfer energy to either by what we may describe as a direct hit. On account of the very small radii of all the particles concerned this is a very infrequent event, and the neutrons are thus able to pass through very considerable thicknesses of matter before their energy is dissipated. From experiments made with a cloud chamber, Dee has estimated that a neutron in air makes an ionizing collision with an electron or a nucleus not more frequently than once in every three metres of its track. Its track is thus not visible in an expansion chamber, and its claim to be included in a work on ionizing radiations is a little tenuous.

The possibility of detecting neutrons by the ionization chamber is due to the fact that, as we have already noted, occasional collisions are made with atomic nuclei which give the latter sufficient energy to produce a considerable number of ions in the gas. Each collision is accompanied by a burst of ionization, and thus can be recorded by counting apparatus of the usual kind (p. 197). We may assume that the number of collisions in a given volume of gas is proportional to the number of neutrons passing through it, for neutrons of the same velocity. There is some evidence that the number of collisions increases as the velocity of the neutron becomes smaller. The number of collisions recorded with a given beam of neutrons passing through the ionization chamber differs

very little when different gases are introduced into the chamber. It is approximately the same in argon, oxygen, and nitrogen, and slightly smaller in hydrogen. The results are consistent with the assumption that the nuclei of nitrogen and oxygen present to the neutron a target of radius 4×10^{-13} cm.

127. Atomic disintegration by neutrons. The collisions between neutrons and atomic nuclei are most conveniently studied in an expansion chamber. The neutrons leave no visible track, but the recoiling nuclei give short dense tracks, owing to the intense ionization they produce. The majority of the collisions shew a single track only—that of the recoiling nucleus. In a small proportion of cases, however, two tracks leave the point of collision—one being the track of the nucleus, the other a fainter track due to some particle ejected from the nucleus. It is interesting to note that carbon and oxygen, elements which so far have not been disintegrated by α-ray bombardment, can be disintegrated by neutrons; the particle ejected being in each case an α-particle.

Nitrogen is also disintegrated by neutrons with the emission of an α-particle, the reaction being

$$N_7{}^{14} + n_0{}^1 \rightarrow B_5{}^{11} + He_2{}^4.$$
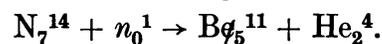
It will be noticed that this reaction is the exact reverse of that by which the neutron is itself produced from boron. We have here an example of a reversible nuclear reaction.

128. Nature of the neutron. The close approximation of the mass of the neutron to that of the proton invites the assumption that there is a close connection between the two. One obvious suggestion is that the neutron may be a close combination of a proton with an electron, the slight change in mass being ascribed to the "packing" effect. On the other hand, the discovery of a positive electron makes it possible that the proton is the complex particle, being formed by the addition of a positive electron to the neutron, which would then function as the fundamental particle. The possibility that both proton and neutron may be fundamental particles, although unwelcome, cannot be overlooked. At present there seems to be no experimental evidence on which the question can be decided.

129. Production of positive electrons. The positive electron was discovered by Anderson [3] in the course of experiments on the cosmic radiation (§ 131). This penetrating radiation produces high-speed electrons by its absorption in matter, and the tracks of these particles can be made visible in the usual way in a cloud chamber. Owing to the comparative rarity of these particles the probability of catching them in the chamber fortuitously is very small. Ingenious methods have been devised whereby a particle about to enter the cloud chamber can be made to set the expansion apparatus in motion, and thus, so to speak, to take its own photograph.

Owing to the high speed of the particles, deflections are rare and the track is usually straight and comparatively thinly studded with drops. On applying a transverse magnetic field to the chamber Anderson discovered that while the majority of the tracks were deflected in a direction which shewed that the particles producing them were negatively charged, a certain number were curved in the opposite direction. In order to eliminate the possibility that these might be tracks of negative electrons which were crossing the chamber in the opposite direction to that assumed (which would of course explain the opposite curvature) a sheet of aluminium was stretched across the centre of the expansion chamber to intercept the particles. A β-particle loses energy in passing through matter and consequently in a constant magnetic field the curvature of its track on emerging from the plate will be greater than it was before entering. It is thus possible to identify with certainty the direction in which the particle was travelling. It was found that all the particles were travelling in the same direction. The opposite curvatures could thus only be explained by assuming that the particles were oppositely charged.

The curvature of the tracks, the decrease in energy in passing through the absorbing plate, and the density of the droplets along the track shewed conclusively that the positively charged particles must be very similar in mass and in behaviour to the negative electrons which they accompanied. They must thus be positive electrons. It is convenient to call these newly observed particles *positrons*, and to keep the term electron for the familiar negatively charged particle.

130. Mode of origin of the positron. Blackett, who confirmed Anderson's original observations, pointed out that the Dirac theory of the electron indicated the possibility that a pair of electrons, of equal mass but opposite sign might be produced by the absorption in matter of a quantum of high energy radiation. The energy, mc^2, which must be condensed to form an electron of mass 9×10^{-28} gm. is $(9 \times 10^{-28}) \times (3 \times 10^{10})^2$ ergs, or almost exactly half a million volts. The result is independent of the sign of the charge, and the production of the pair of electrons will thus require 10^6 electron volts, assuming that the masses of the positron and electron are equal.

The calculation indicates the possibility that positive electrons may result from the absorption in matter of any γ-radiation of quantum energy exceeding a million volts. Radiation of this energy is rare, but thorium C'' gives out a strong γ-radiation of energy $2 \cdot 62 \times 10^6$ volts. Experiments with this radiation were made by Chadwick, Blackett, and Occhialini[4]. The active deposit of thorium was concentrated on a wire which was placed in a lead cylinder enclosed in a cloud chamber. A magnetic field of from 600 to 800 gauss was applied across the chamber, and the tracks were photographed in the usual way by means of two cameras with their axes inclined at a known angle.

The photographs shewed numerous tracks both of positive and negative curvature, about 12 per cent. of the tracks being those of positrons, the remainder of negative electrons. It must be remembered that in addition to the peculiar conversion of γ-ray energy which we have supposed results in the production of a pair of particles, we have also the normal photo-electric absorption of the γ-ray in the lead sheath which gives rise to photo-electrons only. It appears that for the thorium C'' radiation the photo-electric effect accounts for about 75 per cent. of the whole absorption.

On the Dirac theory a positron and an electron are produced simultaneously so that we should expect to observe a number of paired tracks starting from the same point but deviated in opposite directions by the magnetic field. One such pair is shewn in Fig. 99 (Plate IV). The right-hand track is that of the positron, and in this case the two particles have been emitted with
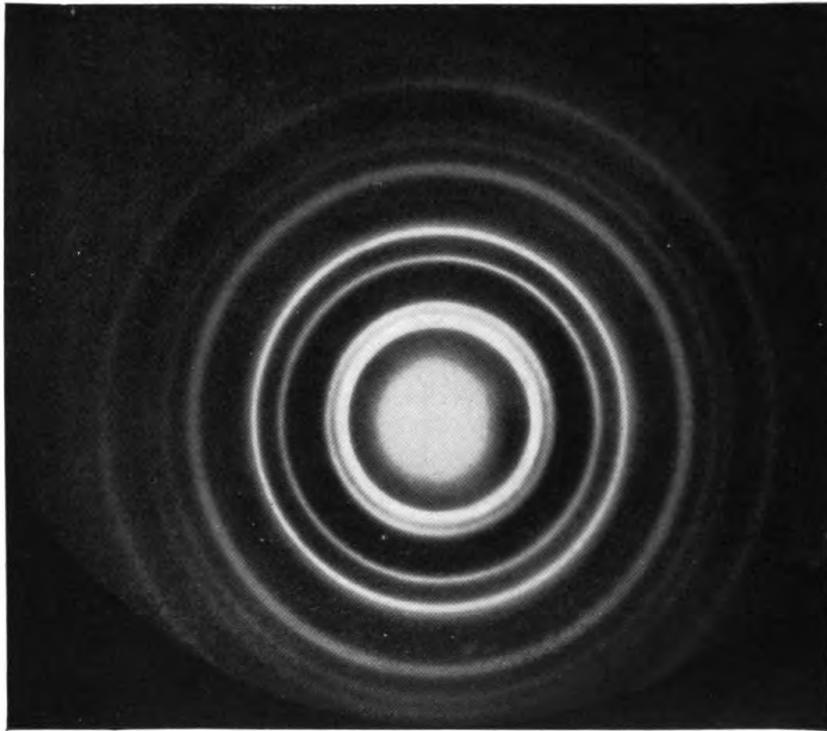
G. P. Thomson.

FIG. 94. DIFFRACTION OF ELECTRONS BY A METAL FILM.
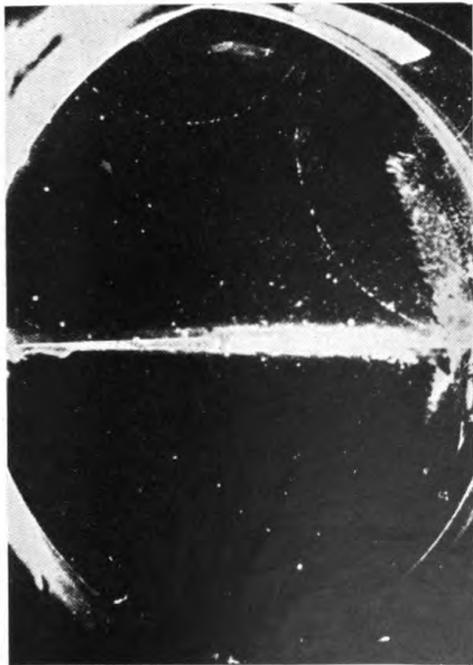
J. Chadwick, P. M. S. Blackett and G. Occhialini.

FIG. 99. TRACK OF A POSITRON.
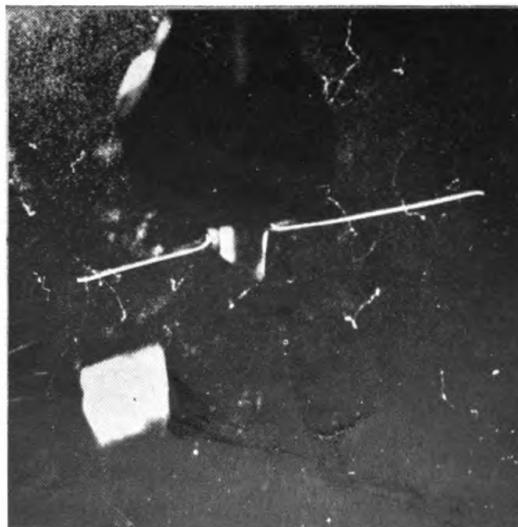
P. I. Dee and E. T. S. Walton.

FIG. 104. DISINTEGRATION OF LITHIUM.

approximately the same energy, as shewn by the equal curvatures. It is, however, not usually possible to observe these paired tracks, as the majority of the conversions take place well within the lead absorber, and owing to the large scattering of the particles in the lead, their tracks are generally widely separated before emergence.

The theory can be tested more satisfactorily by deducing the energies of the particles from the observed curvature of the tracks. The γ-radiation from the thorium deposit contains only one strong line of energy greater than one million volts, namely the line $2 \cdot 62 \times 10^6$ volts. The production of positrons may, therefore, safely be ascribed to this radiation. Since the creation of the pair of particles accounts for a million volts the combined initial kinetic energies of the two particles cannot exceed $1 \cdot 6 \times 10^6$ volts. This energy seems to be distributed at random between the two particles. Assuming that in some conversions the whole of the excess energy is carried away by the positron we see that the maximum kinetic energy of the latter cannot exceed $1 \cdot 6 \times 10^6$ volts. A careful measurement of the positron tracks indicated that the maximum energy of the particle was $1 \cdot 55 \times 10^6$ volts with a probable error of about 5 per cent. This agreement may be regarded as very satisfactory.

We have assumed in the calculation that the mass of the positron is equal to that of the electron. The substantial agreement between the theory and the experiment thus confirms this assumption.

On Dirac's theory the positron can have no permanent existence in matter of ordinary density. It should recombine with an electron to form a quantum of radiation with energy equal to the sum of the masses of the particles, that is one million volts. It cannot be said with certainty that this process has yet been observed.

Attempts to produce positrons by the absorption of β-particles and neutrons have yielded no results. Positrons are produced by the radiations emitted when beryllium fluoride is bombarded by α-rays, but the effect has been shewn to be due to a penetrating γ-radiation which is emitted during the process and not to the accompanying neutrons.

16-2

131. Cosmic radiation. Millikan has demonstrated the existence of radiation of great penetrating power, which apparently enters our atmosphere from extra-terrestrial sources. The experiments consisted in sinking self-recording electroscopes in the waters of snow-fed mountain lakes in California and Bolivia. The natural ionization (see § 4) in the air of the electroscope gradually became smaller as the depth of immersion increased until at great depths it became constant at the very low value of 1·1 ion per c.c. per sec. This is the smallest ionization yet recorded, though McClennan had obtained values as low as 4·8 in similar experiments in Lake Ontario.

The residual ionization at great depths may confidently be ascribed to very minute traces of radio-active material in, or on, the electroscope walls. The ionization which decreases with depth must be due to a penetrating radiation coming from above, which is gradually absorbed as greater and greater thicknesses of water are interposed between it and the electroscope. Experiments made on the top of Pike's Peak, and by balloon ascents, shewed that the intensity of this radiation increased as the surface of the earth's atmosphere was approached. The radiation is therefore not generated in the air but comes entirely from extra-terrestrial sources. The intensity of the radiation was shewn to be independent of the time of day or season, and was the same in the northern and the southern hemispheres. It is thus not associated with any particular direction in space but seems to come in uniformly from all directions. For this reason Millikan calls it *cosmic radiation.*

The absorption in water can be determined by measuring the intensity of the ionization at different depths in a lake. The absorption curve is not exponential, shewing that the radiation is not homogeneous. From an analysis of the absorption curve Millikan finds that there are various types of radiation present, their coefficients of absorption in water ranging from 0·35 to 0·018 per metre. The penetrating power thus far exceeds that of γ-radiation.

The nature of the radiation at the earth's surface can be studied most accurately by the cloud chamber method, already described in connection with the discovery of positrons. After

passing through the earth's atmosphere the radiation consists of a mixture of corpuscular and electromagnetic radiations all of very high energy, together with secondary β-particles, positrons, and secondary γ-radiation due to the conversion of the high energy radiations. The energy of some of the corpuscles is certainly not less than 10^9 volts. The corpuscular radiation is usually assumed to consist of electrons, but suggestions have also been made that it consists at least in part of positrons, or even of protons. At these high energies the relative difference between the masses of electrons and protons is small, and the point could probably only be decided by a determination of the charge.

A determination of the composition of the radiation at the earth's surface gives little information about the nature of the radiation as it enters our atmosphere. If we suppose it to be initially electromagnetic, the Compton scattering will give rise to recoil electrons, and the photo-electric absorption to photo-electrons, of energy not very different from that of the initial quant. The energy of the quant itself will be reduced by the scattering, so that the radiation after passing through the earth's atmosphere will be complex. Conversely if the initial radiation were corpuscular, its scattering and absorption in the atmosphere would give rise to electromagnetic radiation.

Radiation of energy 930×10^9 volts would be generated by the mutual annihilation of an electron and a proton, and this action has been suggested as a possible source of the cosmic radiation. On the other hand Millikan's observation, which has been amply confirmed by later work, that the intensity is independent both of the time of day and of latitude, shews that the radiation originates neither in our sun, nor in our galaxy, and it is a fair assumption that it does not originate in other galaxies. It seems rather difficult to imagine that the annihilation of protons is proceeding uniformly in intergalactic space. Blackett [5] suggests that the radiation was formed at an early stage in the history of the universe, when the laws of physics were different, and that it has been travelling ever since in a closed universe. It is to be hoped that further experiments may provide more decisive evidence on the subject than we possess at present.

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CHAPTER XIV

THE STRUCTURE OF THE NUCLEUS

132. Composition of the nucleus. The fact that the masses of all atoms approximate very closely to whole numbers when expressed on the scale $O = 16 \cdot 000$, very naturally leads to the conclusion that the atomic nucleus, in which practically the whole mass of the atom resides, is a composite structure, and is built up of an integral number of fundamental particles of unit mass. The slight divergences from the whole number rule are reasonably explained by the "packing" effect.

The mass of the atom is thus equal to the number of elementary unit particles which it contains. Its chemical and physical properties, however, are determined almost entirely by the resultant charge on the nucleus, which as we have seen is equal to its atomic number.

Experiments on nuclear disintegration shew that two particles each of approximately unit mass can be ejected from the nucleus under suitable conditions—the proton or hydrogen nucleus, which carries a unit positive charge, and the neutron which is uncharged. Until we have much more knowledge of the possible relation between these two particles it will probably be convenient to regard them both as units in the nuclear structure. Thus while ordinary hydrogen H^1 has for its nucleus a single proton, heavy hydrogen H^2 may be regarded as having a nucleus which is built up on one proton and one neutron. This suggestion is supported by recent experiments in which the bombardment of material containing heavy hydrogen in a discharge tube has been shewn to yield an ample supply of neutrons.

The nucleus of helium, the important α-particle, has a mass of 4 and nuclear charge 2. We may suppose that it contains two protons and two neutrons. Before the discovery of the neutron the α-particle was supposed to consist of four protons, to give

the necessary mass, together with two negative electrons, to reduce the nuclear charge to 2. As the helium nucleus is a very stable structure and has not been disintegrated it is impossible to discriminate experimentally between these two conjectures. The former seems to be usually adopted in the most recent discussions.

There is very strong evidence that the α-particle exists as such in the nuclei of elements of higher atomic number. These particles are ejected during radio-active disintegrations, and as we shall see later (§ 138) there is evidence that they play a very important part in the economy of the radio-active nuclei. It is also significant that elements of atomic mass $4n$ where n is an integer, and which can thus be regarded as being constructed of n α-particles, are not disintegrated by α-ray bombardment. The fact that they can be disintegrated by collision with neutrons, and that the collision results in the ejection of an α-particle points the same way. In the absence of direct evidence to the contrary it is usual to assume that a nucleus will contain as many α-particles as it is possible to construct from the protons and neutrons available.

Lithium with an atomic number 3 has two isotopes of masses 6 and 7. Li_3^6 could be formed by adding a neutron and a proton to the α-particle, Li_3^7 by adding a proton and two neutrons. It is interesting that the bombardment of Li^7 by protons results in the capture of the proton and the formation of two α-particles; while the capture by Li^6 of a diplon, or H^2 nucleus (which consists of a neutron and a proton) also results in the formation of two α-particles (§ 136).

Since the addition of a neutron to the nucleus increases its mass without changing its atomic number, the theory accounts —almost too liberally—for the existence of isotopes. With the exception of H^1 no atom is known which has a mass less than $2Z$, and for most atoms the mass is not greatly in excess of this value. We do not know what limits the proportions in which protons and neutrons can combine to form a stable nuclear structure.

These considerations should allow us to fix the composition of any given nucleus. A nucleus of mass A and atomic number Z would contain Z protons to supply the necessary charge, and

$A - Z$ neutrons to give the additional mass. There remains, however, one disturbing factor. Some radio-active substances disintegrate with the emission of high-speed electrons, or β-particles, which appear to come from the nucleus itself. The nuclei, at any rate of radio-active substances, must therefore contain electrons, the number of which is completely unknown. The quantum theory of band spectra indicates that these electrons cannot exist in the free state in the nucleus, but must be attached in pairs to some other particle in such a way that they neutralize each other's magnetic moment, or "spin" as it is called. The introduction of an electron into the nucleus would reduce its resultant positive charge by unity, so that, in order to keep the charge unaltered we should have to replace one of the neutrons by a proton. The exact composition of a given nucleus remains to this extent a matter of uncertainty.

133. The potential barrier. Gamow's theory. The nucleus behaves as a point charge at all distances greater than 10^{-12} cm. so that its radius must be less than this. We have already seen that an α-particle which comes too close to a nucleus may be captured within the nucleus, so that at some point the force of repulsion gives place to one of attraction. That this must be so is obvious also from the fact that the α-particles within the nucleus form an extremely stable system and must, therefore, be under the influence of strong forces tending to bind them within the nucleus. We have no conception at the moment as to the nature of these forces. We know, however, that generally a large amount of work has to be done upon an α-particle to extract it from the nucleus. The potential energy of an α-particle in the nucleus has, therefore, a large negative value.

At distances outside the nucleus which are large enough for the inverse square law to hold the potential energy of an α-particle, of charge $2e$, is $2Ze^2/r$, where Ze is the charge of the nucleus. At distances very close to the nucleus, scattering experiments indicate that the force becomes less than that given by the inverse square law, and the potential energy will rise rather less rapidly. Thus if we plot the potential energy U of an α-particle against its distance from the centre of the nucleus we

shall arrive at a curve somewhat of the form shown in **Fig. 100.**
The exact shape of the peak of the curve and of the descending
portions is not definitely known.
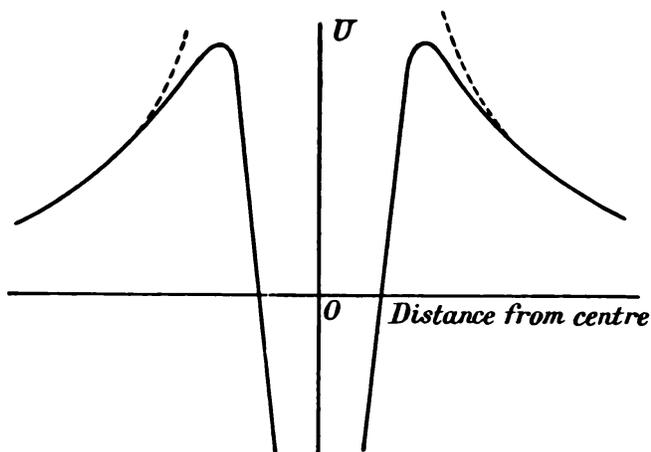
Fig. 100

We may regard the distance of the highest point of this
potential barrier from the centre as measuring the radius of the
nucleus. For the aluminium nucleus its value, as estimated from
the scattering experiments, is about 4×10^{-13} cm. The maximum
height of the barrier is similarly estimated at about $7 \cdot 5 \times 10^6$
electron-volts.

**134. Application of wave mechanics. Penetrability of
the nuclear barrier.** Since the wave length of an α-particle is
of the same order as the radius of a nucleus, nuclear problems
should be considered from the point of view of wave mechanics.
The mathematical discussion does not lend itself to elementary
treatment, and we shall assume such conclusions as we require
to explain the phenomena with which we have to deal without
attempting any proof. Mathematical treatises on the subject of
various grades of complexity are now available in considerable
variety.

On classical mechanics an α-particle in order to penetrate
within the nucleus must be projected towards it with kinetic
energy at least equal to the highest point of the potential barrier.
Conversely an α-particle leaving the nucleus must come over the

top of the potential barrier, and when it arrives at a distance from the nucleus must have at least the kinetic energy corresponding to its potential energy at the highest point.

Early observations by Rutherford had already thrown doubt on these conclusions. The scattering by uranium of the fast α-particles from thorium C′, of range 8·4 cm. is entirely normal, and we must conclude that these particles cannot rise above the lower slopes of the potential barrier of the uranium nucleus, where the inverse square law holds. On the other hand the α-particles given out by uranium itself have a range of only 2·4 cm., whereas if they had left the nucleus over the top of the potential barrier their energy after emerging must at least have been greater and their range longer than the α-particles from thorium C′.

On wave mechanics the wave packet representing the α-particle is regarded as being reflected at the potential barrier. Just as the wave theory of the reflection of light indicates the existence of a highly damped wave motion penetrating into the reflecting surface, so wave mechanics indicates that a wave, with a high coefficient of damping penetrates into the potential surface. If the barrier is thin, a portion of this wave may actually penetrate into the centre cavity representing the nucleus. The wave packet, representing an α-particle is, of course, indivisible, and the intensity of this wave is taken as giving the probability that an α-particle can penetrate the barrier at this point. The top of the barrier is thus definitely penetrable by α-particles of suitable energy. The probability rapidly diminishes to zero as we pass further down the slope.

A more important point, however, and one which has been experimentally verified, is the complete penetrability of the barrier at certain definite levels well below the peak. To put the matter extremely crudely, we may suppose that the α-particle in the nucleus will occupy such a position that it forms a stationary wave by reflection in the opposite walls of the descending funnel. These various resonance levels as they are called obviously constitute an energy level system for the nuclear α-particles. The energy levels normally occupied by the α-particles are levels of negative energy, that is to say work would have to

be done on the α-particle to place it at an infinite distance from the nucleus. In this case wave mechanics agrees with classical mechanics that there is no possibility of escape for the particle. If, however, the particle occupies one of the virtual energy levels of positive energy, wave mechanics indicates that there is a strong probability, perhaps a certainty, that it will penetrate the potential barrier at this level, and will thus arrive at a distant point with kinetic energy equal to its potential energy in the resonance level.

Conversely a particle projected towards the nucleus with initial energy equal to that of one of the resonance levels of the nucleus will be able to penetrate into the nucleus along the corresponding resonance level, and may thus be captured by the nucleus, although its energy may be far less than that required to carry it over the top.

135.   Disintegration of the elements by slow α-particles.
Very definite experimental evidence for these somewhat novel conclusions is provided by the researches of Chadwick, Pose, and others on the disintegration of the lighter elements by short range α-particles. We may take aluminium as a fairly typical example. Aluminium, as we have already seen, is disintegrated by the fast α-particles from radium C′, yielding protons with ranges up to 100 cm. in air. Since the energy of the radium C′ particle is 7·68 million volts we may assume that it enters the nucleus either over the top or through the upper part of the potential barrier. It was discovered, however, by Pose that aluminium could also be disintegrated by the α-particles from polonium the range of which is only 3·9 cm. These particles have quite insufficient energy to carry them up to the permeable part of the barrier.

A detailed analysis of the effect was made by Chadwick[1]. The polonium, deposited on a silver disc R (Fig. 101) was placed in a tube which could either be exhausted or filled with carbon dioxide at a varying known pressure. The end of the tube A was closed by aluminium leaf, the stopping power of which was equivalent to 2 mm. of air. Thus when the tube was exhausted the aluminium nuclei in the foil were being bombarded by α-

particles of all ranges between 3·9 and 3·7 cm. The mean range of the particles falling on the foil could be progressively reduced by admitting carbon dioxide into the tube. This gas is chosen for the purpose because its constituents do not themselves emit long
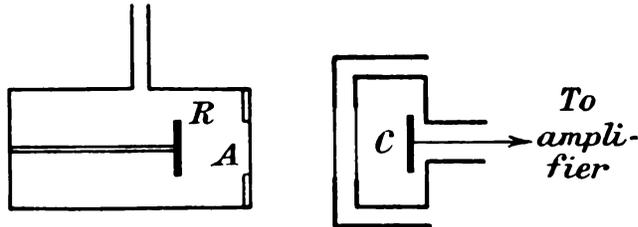
Fig. 101

range protons. Any protons emitted by the aluminium were collected in a small ionization chamber C, connected to a Wynn Williams counter. Their range could be determined in the usual way by interposing screens of known stopping power between A and C.

It was found that protons of maximum range 66 cm. were emitted when α-particles of maximum range 3·9 cm. fell on the aluminium. If the range was reduced to 3·7 cm. by admitting carbon dioxide at low pressure, the emission of protons ceased. The aluminium was no longer suffering disintegration. If, however, the range of the particles was still further reduced to 3·45 cm. protons were again emitted, the range this time being 61 cm. Thus while particles of range 3·9 cm. and 3·45 cm. produce disintegration, and thus must be able to enter the aluminium nucleus, particles of intermediate ranges are completely ineffective.

Further investigation with still slower particles revealed two further resonance levels for α-particles of maximum range 3·1 cm. and 2·7 cm. Aluminium has thus at least four resonance levels.

It was further found that the protons in each case con-

Fig. 102

sisted of two homogeneous groups (Fig. 102), one of much longer

range than the other. It is supposed that on entering the nucleus the α-particle of energy E_α may fall directly to the lowest energy level of energy $-E_n$. The energy thus rendered available, $E_\alpha + E_n$, is given to a proton which is thus ejected with kinetic energy $E_\alpha + E_n - E_p$ where E_p is the energy required to remove a proton from the nucleus. On the other hand the α-particle may come to rest, temporarily, in some higher energy level $-E_m$, in which case the proton ejected will have kinetic energy $E_\alpha + E_m - E_p$. The difference in energy of the two groups of protons is thus $E_n - E_m$. If a thick sheet of aluminium is used so that the α-particles have all velocities from 3·9 cm. down to zero, all eight groups of protons are emitted simultaneously.

TABLE X

Effective α-particle		Range of protons ejected cm.
Range cm.	Energy volts	
3·9	5·25 × 10⁶	66 and 34
3·45	4·86 × 10⁶	61 and 30·5
3·1	4·49 × 10⁶	55 and 26·5
2·7	4·0 × 10⁶	49 and 22
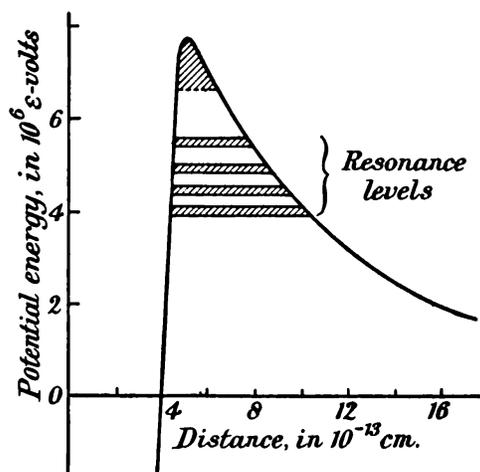
Fig. 103

The α-particle, however, must ultimately fall to the lower level, giving out in the process energy also equal to $E_n - E_m$.

We should expect this emission to take the form of γ-radiation. It is an interesting confirmation of the theory that γ-rays of precisely this energy have been detected by Webster when aluminium is bombarded by α-particles from polonium. Similar results have been obtained for other elements of low atomic number. Chadwick's results for aluminium are contained in Table X, and pictorially in Fig. 103.

136. Artificial disintegration of the elements. It was discovered by Cockcroft and Walton [2] that elements could be disintegrated by bombarding them with high-speed positive particles from a discharge tube. The positive particles were generated by passing a current through hydrogen in a discharge tube with a perforated cathode, and the positively charged hydrogen rays passing through the cathode were further accelerated by passing them through a long column, the ends of which were at a potential difference of the order of 300,000 volts. The accelerated particles emerged through a small window to fall on a target of lithium.

It was found that under bombardment the lithium gave off particles which could be detected by the scintillations they produced on a fluorescent screen, or by an ionization chamber. They were immediately identified as α-particles. By enclosing the target in a Wilson cloud chamber it was possible to photograph the tracks of the particles, and by reducing the intensity of the bombardment so that only one disintegration occurred during a single expansion, it was found (Fig. 104, Plate IV) that the particles were ejected in pairs travelling in opposite directions along the same straight line. The disintegration may thus be expressed in the form

$$\mathrm{Li_3^7 + H_1^1 \rightarrow 2He_2^4}.$$
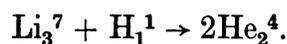
If we take into account the "packing" effect we find that this reaction takes place with the liberation of considerable energy. Substituting the actual mass numbers, as determined by Aston, we have

$$\mathrm{Li + H - 2He} = 7{\cdot}013 + 1{\cdot}0078 - 2 \times 4{\cdot}0010 = 0{\cdot}0188.$$

The energy liberated by the complete conversion of 7·013 gm. of lithium is thus 0·0188 × 9 × 10²⁰ ergs, or 1·68 × 10⁹ kilojoules. Since the mass A_0 of an atom of unit mass number is 1·66 × 10⁻²⁴ gm. the energy liberated in a single disintegration is

$$1·68 \times 10^{19} \times 1·66 \times 10^{-24} \text{ gm., } \quad \text{i.e. } 2·80 \times 10^{-5} \text{ ergs,}$$

or 17·6 × 10⁶ volts. In addition we have also the kinetic energy of the H particle which is 300,000 volts. Assuming that the whole of the available energy is carried away by the two helium nuclei produced, we see that each of these particles should have kinetic energy equal to 9 million volts. They should thus be α-particles of range about 9 cm. in air. The observed ranges of the particles (8·4 cm. in air) agreed excellently with this calculation.

It should perhaps be pointed out that since the fraction of the incident H particles which produce a disintegration is very small (about 1 in 10,000) the experiment as a whole does not leave us with a surplus of energy.

It has later been shewn by Rutherford (3) that the large voltages employed by Cockcroft and Walton are not essential for disintegration. Occasional disintegrations of the lithium atom are observed with H particles of energy as low as 30,000 volts. The yield of the process, however, increases rapidly as the energy of the incident H particles is increased.

Rutherford has recently employed the nuclei of "heavy" hydrogen (diplons or deutons) as the bombarding particles. The effect on lithium is identical with that of the ordinary H particles, that is, two helium atoms are produced. In this case it is probable that the lower isotope of lithium, Li_3^6, is the one which is affected, the equation being $Li_3^6 + H_1^2 = 2He_2^4$. If the diplons are used to bombard hydrogen itself atoms of a hydrogen isotope H_1^3 are produced.

The disintegration of the affected nucleus does not always occur immediately after the impact. If graphite is bombarded by H particles it continues to emit α-particles for some considerable time after the bombardment has ceased, the emission falling off exponentially with the time, with a half value period of about 10 minutes. The nucleus of the new element formed by

the bombardment thus behaves exactly like that of a radio-active element.

Among other elements boron is easily disintegrated, with the simultaneous emission of three α-particles. Beryllium and fluorine have also yielded disintegration particles in measurable numbers.

137. The wave theory of scattering. Mathematical investigation shows that, assuming the inverse square law of force, the law of scattering on the wave-mechanical treatment of the problem is identical with that deduced by Rutherford, except
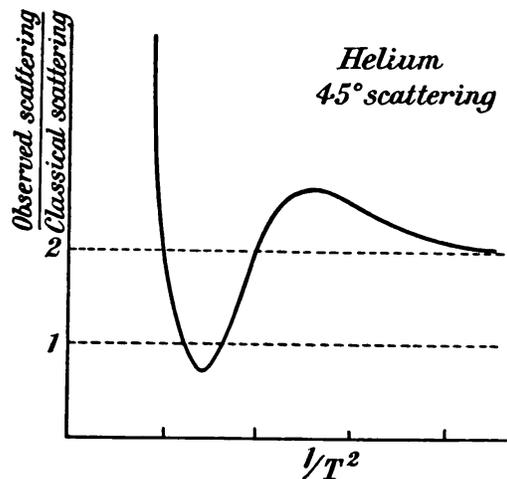
Fig. 105

in one case: the scattering of α-particles in helium. Here the projected helium nuclei are identical in nature with the scattered α-particles, and the possibility of interference between the beam of scattered α-particles and the beam of projected nuclei has to be taken into account. Thus something of the nature of interference bands are formed and at certain angles the number of scattered particles falls to zero. It can be shewn that the number of particles scattered at 45° to the beam should be twice the number given by the classical theory.

This prediction was investigated by Chadwick[4], who compared directly the scattering at an angle of 45° in helium with that in argon which is known to be normal. His results are shewn in Fig. 105 where the ratio of the number of scattered particles observed to the number to be expected on the classical

C I   17

theory is plotted against the reciprocal of the energy of α-particles employed. It will be observed that the ratio asymptotes to a value of twice the classical value for the more slowly moving α-particles.

If we suppose that the more swiftly moving α-particles actually penetrate the helium nucleus, without being captured by it, wave mechanics also provides a possible explanation of the anomalous scattering shewn by the earlier portions of the curve. Near the top of the potential barrier there is a finite probability of penetration, that is to say a certain fraction of the incident α-particles will penetrate the barrier, the remainder being reflected from its outer slope. We may suppose that the particles penetrating are themselves reflected internally in the nucleus, and thus form a second reflected beam. Interference may then take place between the two reflected beams. Calculations along these lines have been made, and lead to equations which are not too much out of harmony with the experimental results.

It may be possible to explain the anomalous scattering which occurs in other light elements in a similar way.

138. Origin of the long range α-particles. We have seen that a radio-active substance normally emits α-particles of perfectly definite and constant range. The cause of the instability which results in radio-active disintegration is not clear. We may suppose, however, that the effect is that $n - 1$ of the n α-particles in the nucleus are enabled to fall to an energy level of greater negative energy than that which they had previously occupied, and that the energy thus set free is transferred to the remaining α-particle, and raises it to a virtual energy level of positive energy, whence it escapes from the nucleus by the process of "resonance" already described. Thus all the α-particles from the same substance emerge with the same energy since they have all emerged at the same level.

A few radio-active substances, however, as we have seen (§ 103) give out, in addition to the normal particles, definite groups of particles of much longer range. It is found that the substances giving long range particles have two definite characteristics; they are formed as the result of a radio-active change in which a

β-particle is expelled, and they have themselves an extremely short life. Thus radium C', which is the only one we will consider in detail, is formed from radium C with the emission of a swift β-particle, and has a half value period which is estimated at $1\cdot5 \times 10^{-8}$ sec.

We may suppose then that the disturbance which results in the expulsion of the β-particle from radium C leaves the newly formed radium C' nucleus in an "excited" state, that is to say with one or more of its α-particles in energy levels of greater energy than that which they would occupy in the normal radium C' nucleus. The time for which a particle can remain in a meta-stable state of this kind, though usually very small, is not zero. Since the transformation of a radio-active substance follows an exponential law, there will be a small but finite chance that the nucleus will disintegrate before the "excited" particle has fallen to the normal level. If this occurs the particle will be ejected with a kinetic energy which is greater than that of the normal particle by the difference between the energy of the particle in the "excited" and in the normal energy level.

TABLE XI

Long Range α-particles from Radium C'.

Energy of the α-particle in volts $\times 10^{-6}$	Energy excess of of excited level above normal level in volts $\times 10^{-5}$	No. of α-particles per million dis-integrations
7·683	0	10^6
8·280	6·08	0·43
8·941	9·112	0·45
9·069	14·12	22
9·315	16·63	0·38
9·492	18·44	1·35
9·660	20·15	0·35
9·781	21·38	1·06
9·908	22·68	0·36
10·077	24·39	1·67
10·149	25·13	0·38
10·329	26·97	1·12
10·509	28·80	0·23

The fact that the long range particles form definite homo-geneous groups thus affords strong evidence for the existence of a system of energy levels for the α-particles in the nucleus, and the energies of these levels are given by the difference between the energy of the corresponding long range particle and that of the normal particles. The experimental results for radium C′ are given in Table XI(5). The energies have been determined by the magnetic deflection method (§ 103).

In calculating column 2 allowance has been made for the energy of recoil of the nucleus. On the theory propounded these num-bers give the energy level system of the radium C′ nucleus, as measured from the ground level, or to put the matter another way, they correspond to the excitation potentials of the nucleus.

139.   Origin of the γ-ray spectrum. The last column of Table XI shews quite clearly that the emission of a long range α-particle is distinctly abnormal. The majority of the excited nuclei acquire their normal configuration before disintegrating, and must thus dispose of their surplus energy by some other process, presumably by radiation. The energies of the levels indicate that this radiation would be in the γ-ray part of the spectrum. We should, therefore, expect to be able to correlate the 65 lines observed by Ellis in the γ-rays given out during the transition from radium C to radium C′ with the energy levels in column 2 of the table.

The return of an α-particle from an excited to a normal level may take place in a single stage, or in a succession of stages. Thus a particle originally in the level of energy 22·68 might fall directly to the ground level emitting an α-ray of energy 22·68, or it might fall first into the level 6·08 emitting a ray of energy (22·68 − 6·08) or 16·60, all the numbers being expressed in a unit of 10^5 electron volts. The subsequent fall from the level 6·08 to the normal would give rise to a ray of energy 6·08 in the same units. Thus the energies of the γ-rays in the radium CC′ spectrum should be expressible either by the numbers in column 2 or by differences between these numbers.

An examination of the spectrum shews that a large number of the observed lines are in fact so expressible to an accuracy well

within 1 per cent., and the number of such coincidences is far too great to be fortuitous. The theory thus appears to have a strong experimental basis. To express the whole of the lines in the γ-ray spectrum, however, Rutherford[5] has found it necessary to postulate the existence of five energy levels which are not included in Table XI and from which no long range α-particles have so far been detected. With this addition all the known lines of the RaCC′ spectrum can be included in the scheme.

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CHAPTER XV

THE STRUCTURE OF THE ATOM

140. The extra-nuclear electrons. We have seen that the mass of the atom resides almost entirely in a nucleus, the radius of which is somewhat less than 10^{-12} cm. The nucleus carries a positive charge equal to its atomic number Z. Since the atom, as a whole, is electrically neutral, the nucleus must be associated with a number of electrons equal to the atomic number. The radius of the atom, as deduced from the kinetic theory of matter, is of the order of 10^{-8} cm. so that we must suppose that the motions of the extra-nuclear electrons are confined in a sphere of this order of magnitude. The electron itself may be regarded as a particle with a radius of the order of 10^{-13} cm. The atom is, therefore, an exceedingly open structure, which explains why it can be so easily penetrated by high speed particles of various kinds.

Earnshaw's theorem tells us that any arrangement of point charges is unstable, on classical theory, if the particles are at rest. Stability can, however, be obtained (as in the similar case of the solar system) if we suppose that the electrons are describing circular orbits around the nucleus, with appropriate velocities. The condition to be satisfied is clearly that the centrifugal force mv^2/r shall be equal to the attractive force $Ze.e/r^2$ between the nucleus and the electron. This gives an infinite number of possible orbits. On the other hand since the electrons would have an acceleration towards the nucleus they should, on classical theory, radiate energy continuously. Their velocity would thus continually diminish and the structure would ultimately collapse.

A solution of the difficulty is clearly to be found along the lines of the quantum theory. We have already seen that in those cases where we are able to follow the interchange of energy between electrons and radiation the electron does not radiate continuously, as demanded by the classical theory, but emits

either a whole quantum of monochromatic radiation or no energy at all. Assuming that these conditions hold within the atom the quantum theory indicates the possibility that electrons in certain preferred orbits may not give out radiation, in which case the stability of the nuclear atom could be assured.

The exact form in which the quantum theory should be applied was not immediately apparent. Planck's constant, h, has the dimensions of energy $\times$ time, or momentum $\times$ distance. The latter product is sometimes known as an "action." Bohr assumed that an orbit would be non-radiating or stationary if the electron in it had an amount of "action" equal to an integral multiple of h, which may thus be regarded as the natural unit of action. For an electron describing a circular orbit we have, therefore,

$$mv \cdot 2\pi r = nh, \quad \ldots \ldots \quad (115)$$

where r is the radius of the orbit, and n is an integer which is known as the quantum number of the orbit. This may be expressed in the more general form

$$2\pi m r^2 \omega = nh, \quad \ldots \ldots \quad (116)$$

where ω is the angular velocity of the electron.

A stationary orbit must satisfy this relation in addition to the requirements of ordinary mechanics. Thus only a select few of the orbits mechanically possible are possible electronic orbits.

141. Bohr's theory of the hydrogen atom spectrum. The fundamental truth of Bohr's assumptions was made evident by their success when applied to the case of the hydrogen atom. Since the hydrogen atom consists of a positive nucleus and a negative electron, each of which behaves as a point charge, the calculation of the stationary orbits can be made with certainty and exactness.

Let e, m be the charge and mass of the electron, Ze and M the charge and mass of the nucleus, and let r be the radius of the orbit in which the electron is moving with a velocity v. Equating the centrifugal force to the mutual attraction of the two charges we have as the mechanical condition of equilibrium

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}.$$

If τ is the time of revolution of the electron in its orbit $v = 2\pi r/\tau$, and, substituting this value of v in the previous equation,

$$\frac{4\pi^2 mr}{\tau^2} = \frac{Ze^2}{r^2}. \qquad \ldots \ldots \quad (117)$$

Applying now Bohr's second postulate the "stationary" orbits are to be distinguished by the relation

$$2\pi mr^2 \omega = nh,$$

or, since $\qquad\qquad \omega = \dfrac{2\pi}{\tau},$

$$\tau = \frac{4\pi^2 mr^2}{nh} \qquad \ldots \ldots \quad (118)$$

Substituting this value in (117) we have

$$r = \frac{n^2 h^2}{4\pi^2 m Z e^2}, \qquad \ldots \ldots \quad (119)$$

which gives the radii of the possible stationary orbits. All the quantities on the right-hand side of the equation are known. For the hydrogen atom, for which $Z = 1$, the radius of the smallest orbit, obtained by putting $n = 1$, is 0.52×10^{-8} cm. The radii are proportional to the squares of the natural numbers, and all the orbits except the first are outside the generally accepted value for the radius of the hydrogen atom.

The kinetic energy of the electron in its orbit is $\frac{1}{2}mv^2$ or $Ze^2/2r$. As the force between the electron and the nucleus is attractive the maximum potential energy will be when the electron is at an infinite distance from the nucleus. If W_∞ is this maximum value, the actual potential energy at a distance r from the nucleus is $W_\infty - e \cdot \dfrac{Ze}{r}$.

The total energy in the orbit is thus

$$\begin{aligned}
W_r &= \frac{Ze^2}{2r} + W_\infty - \frac{Ze^2}{r} \\
&= W_\infty - \frac{Ze^2}{2r} \\
&= W_\infty - \frac{2\pi^2 m Z^2 e^4}{n^2 h^2} \qquad \ldots \ldots \quad (120)
\end{aligned}$$

substituting for r from (119).

Now by the ordinary quantum relation if an electron falls

from an orbit of energy W_{r_1} to one of energy W_r the difference is emitted as a monochromatic radiation of frequency ν given by

$$\nu = \frac{W_{r_1} - W_r}{h}$$

$$= \frac{2\pi^2 m Z^2 e^4}{h^3}\left\{\frac{1}{n^2} - \frac{1}{n_1{}^2}\right\} \quad \cdots \quad (121)$$

substituting for W_{r_1} and W_r from (120). For hydrogen $Z = 1$. Thus the lines in the spectrum of the hydrogen atom should be obtainable by substituting different integral values for n and n_1 in this equation. n is the number of the orbit into which the electron falls, n_1 that of the orbit from which it starts.

We have assumed, in the analysis, that the mass of the electron is negligible in comparison with that of the nucleus. The necessary correction, which is easily made, gives for the hydrogen spectrum

$$\nu = 2\pi^2 \frac{Mm}{M+m}\frac{e^4 Z^2}{h^3}\left\{\frac{1}{n^2} - \frac{1}{n_1{}^2}\right\}. \quad \cdots \quad (122)$$

142. Numerical test of Bohr's theory. It is usual in spectroscopy to employ the wave number ν', where $\nu' = 1/\lambda = \nu/c$, in place of the frequency ν. Balmer discovered as early as 1885 that the wave numbers of all the lines in the normal hydrogen atom spectrum could be derived by substituting integral numbers for n, in the general relation

$$\nu' = R_H\left(\frac{1}{4} - \frac{1}{n_1{}^2}\right), \quad \cdots \quad (123)$$

although no explanation of the fact could be offered. R_H is a constant known as the Rydberg constant for hydrogen. Its value is $1\cdot09677 \times 10^5$ cm.$^{-1}$.

Putting $n = 2$ in (122) we see that the two relations are identical in form. The relation, however, is much more than formal. For hydrogen $Z = 1$, and consequently R_H should be given by $\dfrac{2\pi^2}{c}\dfrac{Mm}{M+m}\dfrac{e^4}{h^3}$; dividing by c to convert frequencies into wave numbers. All the quantities in this expression are known to an accuracy of the order of 1 in 1000, and there are no "disposable constants" to enable us to evade the full rigour of a numerical test. The numerical value of the expression is

$1 \cdot 0955 \times 10^5$. The agreement is thus perfect within the limits of experimental error.

It will be seen that in Bohr's theory a given line of the Balmer series is emitted when an electron falls into the orbit, for which $n = 2$, from one of the outer orbits. The H_α line, for example, is emitted by an electron passing from $n = 3$ to $n = 2$; or in X-ray nomenclature from the M to the L level. Ultimately, however, the electron must return to the innermost level of lowest energy, so that we should expect to find a series of lines given by

$\nu' = R_H \left(\dfrac{1}{1} - \dfrac{1}{n_1{}^2} \right)$, and calculation shews that this series would
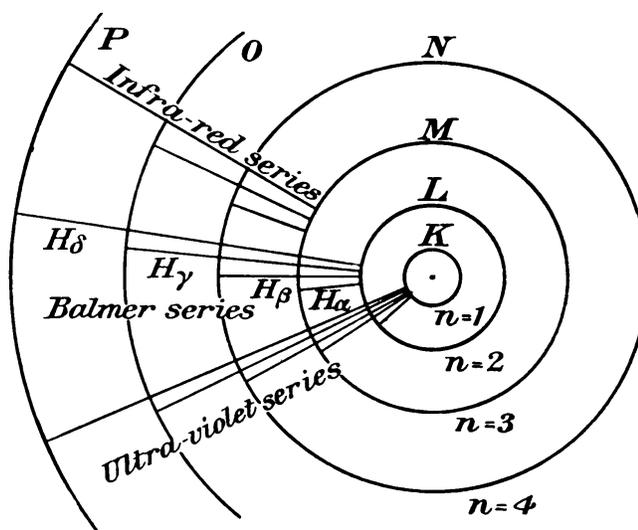
Fig. 106

be in the ultra-violet. They have been identified by Lyman. A series in the infra red for which $n = 3$ has been discovered by Paschen. The origin of the various series is indicated in Fig. 106.

It will be seen that a line is only emitted if the atom becomes ionized, or at least "excited." The electron on its return may fall from one quantum orbit to another, emitting a line at each transition, until finally it comes to rest in the most stable innermost orbit.

143. The spectrum of ionized helium. The hydrogen atom spectrum is the only normal spectrum for which accurate calculations can be made. As soon as we add a second electron

to the atom the problem becomes effectively that of three gravitating bodies, no accurate solution of which has yet been attained. If, however, a nucleus is stripped of all its extra-nuclear electrons in a very intense discharge, the return of the first electron to the nucleus will be a two body problem, and its spectrum should be given by equation (121). Millikan has succeeded in exciting and measuring the spectra of these stripped atoms for all the elements in the first series of the periodic table.

The most interesting case is that of helium. Both Pickering and Fowler discovered some years ago a spectrum, the various lines in which could be represented by the relation

$$\nu' = 4R\left(\frac{1}{n^2} - \frac{1}{n_1{}^2}\right), \quad \ldots \ldots \quad (124)$$

where R had very nearly, but not exactly, the value of Rydberg's constant for hydrogen. Putting $Z = 2$ in (121) we see that the Pickering-Fowler spectrum is exactly what we should expect, on Bohr's theory, from the return of a single electron to a stripped helium nucleus. The slight difference between the two Rydberg constants is due to the slight difference in the correcting term for the motion of the nucleus.

Slight as this difference is, the accuracy of spectroscopic observations is so great that it provides probably the most accurate method available for determining the ratio of the mass of an electron to that of a proton. Writing R_{He} for the value of Rydberg's constant in the Pickering-Fowler series and M_H and M_{He} for the masses of the hydrogen and helium nuclei we have from (122)

$$\frac{R_H}{R_{He}} = \frac{M_H}{M_H + m} \bigg/ \frac{M_{He}}{M_{He} + m} = \left(1 + \frac{M_H}{M_{He}}\,x\right)\bigg/(1 + x),$$

where $x = m/M_H$. But

$$R_H = 109677 \cdot 69 \pm 0 \cdot 06 \qquad M_H = 1 \cdot 0072,$$
$$R_{He} = 109722 \cdot 14 \pm 0 \cdot 04 \qquad M_{He} = 4 \cdot 0016,$$

whence

$$\frac{m}{M_H} = \frac{1}{1838}$$

with a probable error of not more than 1 in the last figure. The

ratio of the mass of the electron to that of the hydrogen *atom* is thus 1/1839.

The ratio e/M_H is, as we have seen earlier, the Faraday constant in electrolysis and is equal to 9649 e.m.u. per gm. Hence

$$\frac{e}{m} = \frac{e}{M_H} \cdot \frac{M_H}{m} = 1 \cdot 761 \times 10^7 \text{ e.m.u./gm.}$$

It is interesting to note that the most recent determinations of e/m by the deflection method are giving results in very good agreement with this value.

144. The origin of spectra. It is impossible to carry out the calculations which gave us the hydrogen spectrum, for atoms containing more than one electron. The effect produced on the motion of an electron by the other electrons in the system is too complicated to yield to mathematical analysis. It is clear, however, that the electrons will be arranged in definite quantum energy levels, although the appropriate energies cannot be calculated.

A given spectrum line will be emitted when an electron passes from one quantum level to another, and its frequency ν will be given by $h\nu = W_2 - W_1$, where $(W_2 - W_1)$ is the difference in energy of the two levels. If we write $W_1 = h\nu_1$ and $W_2 = h\nu_2$, we have

$$h\nu = h\nu_2 - h\nu_1, \quad \text{or} \quad \nu = \nu_2 - \nu_1.$$

The frequencies of the lines in a line spectrum are thus given by the differences between certain terms. This is a well-known law of spectroscopy, and had been discovered from a study of the numerical relations between the lines in line spectra, long before the Bohr theory gave it a theoretical significance.

The energies of these optical levels can be deduced from spectroscopic data, in the same way that the energies of the deeper levels can be measured by X-ray observations. In the visible spectrum the energies involved are of the order of a few volts, and the transitions are mainly those between virtual orbits and the outermost of the occupied orbits.

We can, however, also map these energy levels in an entirely different way. Since the atom can only exist in certain definite energy states, it can only absorb from a colliding electron the

exact amount of energy required to raise one of its outer electrons from its normal level to one or other of the higher virtual levels. The various radiation potentials (§ 35) thus correspond to the difference in energy of an electron in the ground state and in one or other of the virtual quantum levels. It should, therefore, be possible to determine these different levels from the observed radiation potentials. Values obtained this way agree well with those deduced spectroscopically, though the latter method is, of course, much the more accurate.

(Again, if the atom is excited at the minimum excitation potential, the electron is removed from the ground state to the one next above it. On returning to the ground state it can clearly only emit one spectral line.) On the other hand if it is raised to one of the higher states, it can return directly to the ground state, or by a series of transitions from one to another of the intervening energy levels. The full spectrum is clearly only developed when the electron is removed entirely outside the atom, that is to say when the atom becomes ionized. If v is the frequency term corresponding to the electron in its normal level, hv should be the energy required to ionize the atom. The ionization potentials deduced in this way are in excellent agreement with those determined directly by the methods described in § 34.

The various terms in the spectral series were deduced empirically in the first place, and were denoted by a rather complicated system of letters and numerals. It is, however, possible to correlate them with the system of quantum levels which will be described in succeeding sections. The detailed application of quantum principles to actual optical spectra is a large subject which is outside the purpose of this book.

145. X-ray spectra. The X-ray spectra differ from optical spectra in the fact that, owing to the much larger excitation potentials an electron is removed not from the periphery of the atom, but from the deeper levels, usually either the K or the L level. This vacancy is filled in the first place by an electron from a neighbouring ring. The transitions thus take place between levels deep in the atom, which are normally occupied by elec-

trons. In this case it is possible to make an approximate calculation of the energies of the levels, and of the frequency of the radiation emitted.

Let us suppose that to a first approximation we may regard the electrons constituting a given energy level as equivalent to a uniform distribution of negative electricity over a spherical surface. The p electrons interior to a particular orbit of radius a will act as if their charge were at the centre of the sphere, i.e. at the nucleus, and will thus reduce the effective nuclear charge from Z to $Z - p$. The electrons exterior to the given level will produce no resultant field upon any electron in it since the field inside a uniformly charged spherical surface is zero. The $q - 1$ electrons in the same level as the electron we are considering will (if their charge is supposed uniformly distributed) repel the given electron with a force $\frac{1}{2}(q - 1)e^2/a^2$. The attractive force on the electron is thus

$$(Z - p)e^2/a^2 - \tfrac{1}{2}(q - 1)e^2/a^2 = Fe^2/a^2, \quad . \quad . \quad (125)$$

where

$$F = Z - p - \tfrac{1}{2}(q - 1).$$

Thus applying our dynamical and quantum conditions we have

$$\frac{mv^2}{a} = F\frac{e^2}{a^2}; \quad mva = \frac{nh}{2\pi},$$

whence

$$a = \frac{n^2h^2}{4\pi^2 Fe^2 m} \cdot \quad . \quad . \quad . \quad . \quad . \quad (126)$$

To calculate the potential energy of the system we may suppose that all the orbits are magnified by a large factor N, so that the distances between the particles become infinite. Let the potential energy in this state be W_∞. As N is progressively reduced the orbits shrink until eventually they reach their normal size. At each stage the force on the given electron is $- Fe^2/r^2$, where r is the actual radius at any instant. The work done on the electron in bringing it to its normal orbit of radius a is thus $- \int_\infty^a \frac{Fe^2}{r^2}\, dr = - \frac{Fe^2}{a}$ and its potential energy is therefore

$$U = W_\infty - \frac{4\pi^2 e^4 F^2 m}{n^2 h^2}.$$

The kinetic energy $T = \frac{1}{2}mv^2 = \frac{2\pi^2 e^4 F^2 m}{n^2 h^2}$ and the total energy of the electron is thus $U + T$, or

$$W_\infty - \frac{2\pi^2 e^4 F^2 m}{n^2 h^2}.$$

The frequency of the line emitted when an electron falls from an orbit of energy W_i to one of W_f is thus $h\nu = W_i - W_f$ or

$$\nu = \frac{2\pi^2 e^4 m}{h^3} F_f{}^2 \left\{ \frac{1}{n_f{}^2} - \frac{F_i{}^2}{F_f{}^2} \frac{1}{n_i{}^2} \right\} = R F_f{}^2 \left\{ \frac{1}{n_f{}^2} - \frac{F_i{}^2}{F_f{}^2} \frac{1}{n_i{}^2} \right\}, \quad . \quad (127)$$

writing R for $\dfrac{2\pi^2 e^4 m}{h^3}$.

For a given line in the X-ray spectrum, which represents a transition between the same pair of quantum levels, we can write

$$K^2 = R \left(\frac{1}{n_f{}^2} - \frac{F_i{}^2}{F_f{}^2} \frac{1}{n_i{}^2} \right) \qquad F_f = Z - \{ p + \tfrac{1}{2}(q - 1) \} = Z - k,$$

where K and k are independent of the atomic number, and are constants for the same line. Hence the frequency of a given X-ray line in the spectrum of an element of atomic number Z is given by

$$\nu^{\frac{1}{2}} = K(Z - k), \quad . \quad . \quad . \quad . \quad . \quad (128)$$

which is Moseley's relation (91). It will be seen that in accordance with Moseley's results k depends only on the final orbit, and is the same for all lines of the same series.

For the K series we have $p = 0$, and $q = 2$, since experiment shews that there are only two electrons in the K level (§ 153) and none within it. Thus $k = 1$ in good agreement with Moseley's observations. For the L series, where $p = 2$ and $q = 8$, $k = 5 \cdot 5$, which is somewhat less than the experimental value.

For elements of high atomic number we can to a first approximation put $F_i / F_f = 1$, since k is small compared with Z. Thus for the lines of the K_α series, corresponding to transitions from $n = 2$ to $n = 1$, we have approximately

$$\nu^{\frac{1}{2}} = R^{\frac{1}{2}} \left(\frac{1}{1} - \frac{1}{2^2} \right)^{\frac{1}{2}} (Z - 1)$$

$$= (Z - 1) \sqrt{\frac{3}{4} R}, \quad . \quad . \quad . \quad . \quad . \quad (129)$$

which was the form in which Moseley first gave his relation. For molybdenum ($Z = 42$), substituting for R from the spectroscopic value of Rydberg's constant, we find that the K_α radiation of molybdenum should have a wave length of $0 \cdot 70 \times 10^{-8}$ cm. The mean wave length of the K_α lines of molybdenum is actually $0 \cdot 71 \times 10^{-8}$.

146. Sommerfeld's theory. The subordinate quantum number. The circular orbits discussed by Bohr are not the only orbits which satisfy the mechanical conditions of the problem. As is well known in gravitational theory a particle moving round a central body to which it is attracted by a force varying inversely as the square of the distance may, under appropriate conditions, describe an elliptic orbit of any eccentricity. If we apply Bohr's relation (116) to elliptical motion, it can be shewn that for a given quantum number n the energy of the system on Newtonian mechanics is the same whether the electron describes a circular or an elliptical orbit. The elliptical orbits do not give rise to any new energy levels, and the theory outlined in the previous sections remains unaltered.

It is possible, however, as Sommerfeld shewed, to look at the matter in a somewhat different way. As a particle describes an ellipse its distance from the nucleus alternately decreases and increases. Its motion can thus be regarded as the sum of two motions, one a circular motion round the nucleus, and the other an oscillation along a radius. The former is known as the azimuthal, the latter as the radial motion. Sommerfeld suggested that each of these motions must separately satisfy the quantum relation laid down by Bohr. Thus the total quantum number n of the orbit has to be divided between these two possible motions, and the eccentricity of the ellipse is determined by the mode of division.

It is customary to represent the mode of division by giving first the total quantum number, and secondly the azimuthal quantum number of the orbit. The radial quantum number is the difference between these figures. Thus if we consider the possible orbits for which $n = 3$, we may represent them by the symbols 3_3, 3_2, 3_1, 3_0. The subscript number is known as the

subordinate quantum number. The 3_3' orbit has obviously a radial quantum number of 0. There is thus no radial movement and the orbit is the circular orbit already discussed. The 3_0 orbit conversely corresponds to motion only along the radius, and is impossible since the path would pass through the nucleus. The remaining orbits 3_2 and 3_1 represent ellipses of increasing radial movement and hence of increasing eccentricity. These orbits, together with those for $n = 2$, are shewn in Fig. 107.

The energy associated with an elliptic orbit would be identical with that of the circular orbit of the same quantum number if the mass of the electron were independent of its velocity. This, however, owing to the relativity correction is not the case.
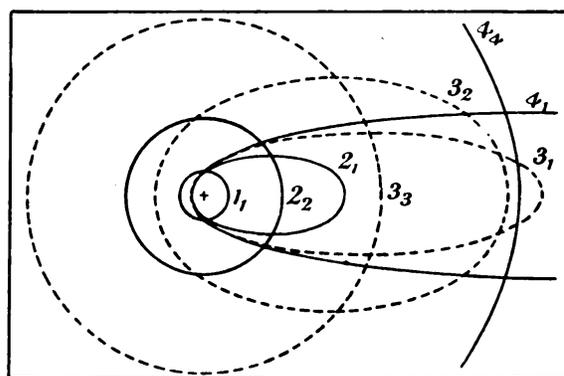
Fig. 107

The speed of an electron in a circular orbit is constant, but in an elliptic orbit its speed increases as it approaches its perihelion. Its mass is thus greater the nearer it approaches to the nucleus. Sommerfeld was able to shew that when this correction is taken into account there is a very small difference in energy between the circular and elliptical orbits, the latter having the slightly greater value.

The 2 quantum level (or L level to use the X-ray nomenclature) thus consists of two levels close together, and similarly the 3 quantum level is a close triplet of levels. This complexity in the levels gives rise to a corresponding complexity in the spectrum line emitted by the transition of an electron from one level to the other. The line H_α, the first line of the Balmer series, is found when examined under very high resolution to consist of

three lines very close together. It was in order to explain this fine structure of the Balmer lines (for which Bohr's original theory makes no provision) that Sommerfeld was led to put forward his theory. The three components of the H_α line are formed by the transitions $3_3 \rightarrow 2_2$, $3_2 \rightarrow 2_1$, and $3_1 \rightarrow 2_2$. (Experience shews that the only transitions which normally occur are those in which the subordinate quantum number changes by unity.)

The difference in energy between an n_n and an n_k level is given by $-RhZ^2\alpha^2/n^3k$, where $\alpha = 2\pi e^2/hc$ and is known as the fine structure constant. α is a non-dimensional constant, and has lately assumed some importance in connection with certain theories of the universe. Its value is $1/137$. The actual separation of the components of the Balmer series is so small that it is difficult to measure with accuracy, though the lines have been shewn to be triplets. The separation in the ionized helium spectrum, which is 16 times greater, has been accurately measured and is in excellent agreement with the theory.

147. The magnetic moment of an electron orbit. The Magneton.

An electron describing a closed path is equivalent to a current flowing round that path. Since the current is measured by the quantity of electricity crossing any cross section of the path per second, the current i equivalent to the electron is given by $e\nu$, where ν is the number of times the electron describes the path in one second. The electron orbit will thus have a magnetic moment μ given by ig, where i is the equivalent current and g the area of the orbit, that is

$$\mu = e\nu g.$$

If the electron is describing in the atom a circular orbit of radius r with velocity v, we have $\nu = \dfrac{v}{2\pi r}$ and $g = \pi r^2$, whence

$$\mu = \tfrac{1}{2}evr.$$

But by (115) $vr = \dfrac{nh}{2\pi m}$ where n is an integer, and thus the magnetic moment of the orbit

$$\mu = n \cdot \frac{1}{4\pi} \frac{e}{m} h. \quad \ldots \quad (130)$$

Since this is true of any orbit in the atom the magnetic moment of any atom must be an integral multiple of $\frac{1}{4\pi}\frac{e}{m}.h$. This quantity is thus a natural unit of magnetic moment, and is known as the Bohr *magneton*. Its value can be found by substituting for e/m in e.m.u. and h. It is equal to $9\cdot175 \times 10^{-21}$.

148. The inner quantum number. In developing the quantum theory of the atom we are exploring unknown territory. We are investigating how far the application of certain new and promising principles can introduce order into the complicated phenomena of atomic physics, and in particular into the field of spectroscopy. We must be guided, therefore, by the phenomena themselves, and the justification for our methods will be found in the degree of simplification which is introduced. If we further find that the scheme evolved to explain spectroscopic phenomena also throws fresh light on, say, the chemical properties of the atom we shall be satisfied that our efforts have been on right lines.

It is found that the spectra of elements of higher atomic number are more complex than that of hydrogen. Thus the Balmer series of hydrogen, with its fine structure, is represented in the alkali metals by three complete spectral series, the individual lines of which themselves shew fine structure. But we have already used the relativity effect to explain the fine structure of the Balmer lines. We must, therefore, introduce a still further quantum effect to account for that of the alkali metals.

If we write (116) in the form $m\omega^k r^2 = n.h/2\pi$ we can regard $h/2\pi$ as a natural unit of moment of momentum and the appropriate quantum number then gives the moment of momentum associated with a given orbit in these units. Thus an n_k orbit has k units of orbital moment of momentum associated with it. The fine structure of the lines in the alkali metal spectra indicates that each of these orbits is really a doublet, the two terms of which differ by unity, when measured in units of $h/2\pi$.

For reasons which we cannot go into here, the azimuthal quantum number k, which we have been employing hitherto, has recently been replaced by a subordinate quantum number l,

where $l = k - 1$; and may have any positive integral value up to $n - 1$, including the value zero. The fact that an orbit for which the moment of momentum, l, is zero would carry the electron through the nucleus presents no difficulties on wave mechanics, and the change is necessitated by various phenomena. The single orbit which is represented for the hydrogen atom by n_l is for more complex atoms represented by a pair of orbits with moment of momentum $l \pm \frac{1}{2}$. To indicate this Sommerfeld introduced a new quantum number j, known as the *inner quantum number*, where $j = l \pm \frac{1}{2}$.

To account for the additional term in the moment of momentum of the orbit, Uhlenbeck suggested that the electron which we have so far treated merely as an electrical charge was, in fact, spinning about an axis, like a top. A charged sphere spinning about an axis is equivalent to an electric current, and will thus have a magnetic moment in the direction of the axis of rotation. It will also have a moment of momentum about this axis. If we assume that the magnetic moment of the electron amounts to one magneton, its moment of momentum will be $\frac{1}{2} (h/2\pi)$ or $\frac{1}{2}$ in our quantum unit. Its *spin number* as it is called is $\frac{1}{2}$.

The electron must align itself with its axis perpendicular to the plane of the orbit, but it may spin in either direction about the axis. Thus the moment of momentum due to its spin is either added to, or subtracted from, that due to its motion round the orbit according as its direction of spin is parallel or anti-parallel with its direction of rotation around the nucleus. The total moment of momentum of the orbit is thus either $l + \frac{1}{2}$ or $l - \frac{1}{2}$.

As the spinning electron has a magnetic moment M, and its motion in its orbit round the nucleus produces a magnetic field H, the two possible quantum states will differ in energy. In the first case the magnetic axis of the electron lies along the lines of the magnetic field. In the second it is anti-parallel to them (i.e. with its north pole pointing south). Thus in the latter case it has magnetic potential energy equal to $2MH$, and the energy of the anti-parallel arrangement exeeds that of the parallel by $2MH$. The frequencies of the lines emitted when an electron falls into the orbit in the one or the other arrangement will

differ by a corresponding amount. The most familiar example is provided by the two well-known D lines of sodium.

The inner quantum number j is essentially a positive quantity. Thus if $l = 0$, the only possible value of j is $+\frac{1}{2}$.

149. Quantization in space. The magnetic quantum number. So far we have been considering the electron orbit as free from all external fields of force. In practice the nucleus of the atom and the motions of the other electrons in the atom produce a resultant magnetic field. There is thus a unique direction marked out in the atom, the direction of the resultant field, and the space in which the orbit lies is, to this extent, anisotropic.

A rigorous application of quantum mechanics demands that where a unique axis exists the motion relative to this unique direction shall also be quantized.

Thus an orbit for which the total moment of momentum is $jh/2\pi$ must lie in such a plane that the component of the moment of momentum in the direction of the resultant field can be represented by $mh/2\pi$, where m differs from j by an integer only. m is known as the *magnetic*, or sometimes as the *equatorial quantum number*.

The maximum value of m occurs when the plane of the orbit is perpendicular to the field and the component is then equal either to $\pm j$, according to the direction of rotation of the electron in its orbit. The possible values of m are thus given by

$$m = -j, \quad -j+1, \quad \ldots j-1, \quad j. \quad . \quad . \quad (131)$$

The angle ϕ between the axis of the orbit and the resultant field is given by $\cos \phi = m/j$. If $l = 0$, so that $j = \frac{1}{2}$, the only possible values of m are $\pm j$; that is the plane of the orbit is perpendicular to the magnetic field, but the electron may describe the orbit in either direction. We shall see in the next section that there is direct experimental evidence for this rather surprising deduction.

Since the orbit has a magnetic moment and is in a resultant magnetic field, its magnetic potential energy will depend on the angle between the axis of the orbit and the direction of the field. The total energy associated with a given orbit thus depends on its inclination, that is, on the value of m.

150. Orientation of the atom. The experiments of Gerlach and Stern. The conclusions arrived at as to the orientation of the electron orbits in a magnetic field have been brilliantly verified by some ingenious experiments of Gerlach and Stern. Silver was boiled in a high vacuum in an electric furnace F (Fig. 108) furnished with a single narrow aperture A. From this aperture the atoms of silver streamed out with the velocity of thermal agitation appropriate to the temperature of the furnace. Since the space into which they passed was highly evacuated, the atoms travelled in straight lines, and were formed into a very narrow pencil by means of a second slit B. This pencil then passed
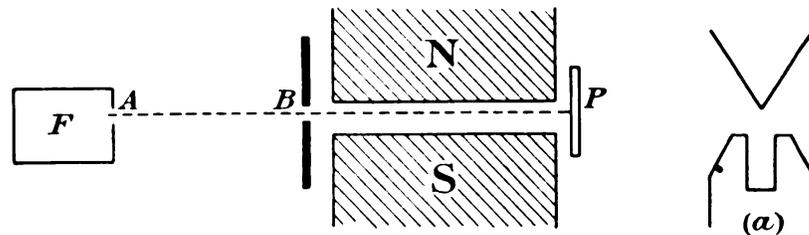
Fig. 108

between the poles N, S of a magnet arranged so as to give a magnetic field which varied as rapidly as possible in the direction of the field, i.e. from N to S. The pole pieces are shewn in section at (a). After leaving this field the atoms impinged upon a cold glass plate P where, it was found, they left a trace which was just perceptible, and which could be intensified if necessary by chemical methods. The position at which the atoms struck the plate could thus be ascertained.

If M_v is the resolved part of the magnetic moment of the atom in the direction of the field H there will be a force acting on it equal to $M_v \dfrac{\partial H}{\partial y}$. This will produce a deflection y in the direction H, since a magnet always moves from weak to strong parts of the field, equal to $\frac{1}{2}\dfrac{M_v}{A}\cdot\dfrac{\partial H}{\partial y}\dfrac{l^2}{v^2}$, where l is the length of path of the atoms in the magnetic field. The velocity v can be calculated from the temperature of the furnace, and the mass A of the atom is known. By measuring $\dfrac{\partial H}{\partial y}$ and l, M_v can be calculated, from the deflection y.

If the electron orbits had a random orientation the resolved part of the magnetic moment would have all values from zero to M, where M is the magnetic moment of the atom. As we shall see later the electron orbits in silver and also in copper and gold form a closed system in which the magnetic moments of the electrons balance out, with one additional electron which occupies an orbit of subordinate quantum number 0. The magnetic moment of the atom is due to this electron. For silver, copper and gold, Stern and Gerlach found that the trace on the glass plate consisted of two definite lines, one on each side of the undeflected position, the only values found for the magnetic moment being thus $\pm M$. None of the atoms was undeflected in the field. The atoms must, therefore, be completely orientated during the whole of their passage through the field, with the magnetic axis pointing in either the positive or negative direction of the field. That is to say the orbit is perpendicular to the field, though the electron may revolve in either direction around it. This is in exact accord with the predictions of § 149 for an orbit for which $l = 0$. By measuring the various quantities involved the value of the magnetic moment of the atoms of the three metals employed was found to be 9×10^{-21}, in excellent agreement with the calculated value of the magneton.

151. The Zeeman effect. If a source of light emitting a line spectrum is placed between the poles of a strong electromagnet, each line is split up into a number of components. In the simplest case the single line is split into two components equidistant from the position of the undisturbed line when viewed along the direction of the magnetic field. If viewed at right angles to this direction, there is also a line in the undisturbed position, and the single line becomes a triplet. The phenomenon is known as the Zeeman effect. The effect of a magnetic field on the electronic orbit can be determined by a well-known theorem due to Larmor. He has shewn that the form of the orbit and the velocity with which it is described may be regarded as unaltered by the magnetic field if we refer all our quantities to a system of co-ordinates which rotates around the

direction of the magnetic field with an angular velocity ω given by

$$\omega = \tfrac{1}{2}\frac{e}{\mu}\cdot\frac{H}{c}, \quad \ldots \ldots \quad (131)$$

where H is the magnetic field and μ the mass of the electron.

This velocity can be shewn to be small compared with the velocity of the electron in its orbit. The orbit may thus be regarded as of constant shape and size but precessing slowly around the direction of the magnetic field. It can further be shewn that, if the precession is slow, the quantum conditions will be unaffected, and an n quantum orbit will remain an n quantum orbit in spite of the new precessional motion. This is known as the principle of *adiabatic invariance*. The kinetic energy of the electron in its orbit will, however, in general, be slightly altered. Let us consider, for the sake of simplicity, a single electron describing a one quantum orbit about the nucleus. The plane of this orbit must be (§ 148) perpendicular to the lines of the field. Now the velocity of the electron is unchanged with respect to the *moving* axes of reference. If the axes move in the direction in which the electron is rotating in its orbit its actual velocity referred to fixed axes is obviously increased. If the two rotations are opposed, it is diminished. Hence the energy of the electron in the orbit is either increased or decreased according to its direction of rotation by some amount ∂T.

It can be shewn that

$$\partial T = m\frac{\omega}{2\pi}h,$$

where m is the magnetic quantum number (§ 149).

Thus for a transition in which the magnetic quantum number changes by unity, the effect of the magnetic field is to alter the frequency by an amount $\partial\nu$, given by

$$h\cdot\partial\nu = \frac{\omega}{2\pi}h; \quad \partial\nu = \frac{eH}{4\pi\mu c}\cdot \quad \ldots \quad (132)$$

The undisplaced line is given by transitions in which m remains unaltered.

A similar decomposition of the spectral lines is produced by a strong electric field. This is known as the Stark effect.

152. Pauli's exclusion principle. Pauli has suggested that it is impossible for a given quantum state to be occupied simultaneously by more than one electron. Thus all the electrons in the atom must be assigned a different set of quantum numbers. This is known as the exclusion principle.

We have seen that four quantum numbers are necessary and sufficient to specify completely the quantum state of an electron in the atom. Those most generally employed at present are n, l, j and m, and the state is usually written $n_{l, j, m}$. (In earlier work $k = l + 1$ is employed instead of l, and j and m are converted into integers by the addition of $\frac{1}{2}$. The earlier system is used in the diagram of X-ray levels (Fig. 74).) The total number of quantum states corresponding to a given shell of total quantum number n can be deduced from the relations already discussed.

For a shell of total quantum number n, there are n possible values of l, ranging from 0 to $n - 1$, and for each value of l we have two values of j, namely $j = l + \frac{1}{2}$; $j = l - \frac{1}{2}$. Substituting in (131) we find the following values for m:

$$j = l - \tfrac{1}{2} : m = -l + \tfrac{1}{2}, \quad -l + \tfrac{3}{2}, \ldots, \quad l - \tfrac{3}{2}, \quad l - \tfrac{1}{2} \quad \text{total } 2l$$
$$j = l + \tfrac{1}{2} : m = -l - \tfrac{1}{2}, \quad -l + \tfrac{1}{2}, \ldots, \quad l - \tfrac{1}{2}, \quad l + \tfrac{1}{2} \quad \text{total } 2l + 2$$
$$\text{i.e. in all} \quad \overline{4l + 2}$$

Thus the total number of electrons which can be contained in a set of levels of subordinate quantum number l is $2 (2l + 1)$.

For the K shell, for which n is 1, l must have the value 0 and only two electrons can be present. For the L shell we have $n = 2$, while l may have the values 0 and 1. Corresponding to $l = 0$ we have again 2 electrons, and to the value $l = 1$, 6, making 8 in all. Thus 8 electrons are required to complete the L shell. Similarly the M shell requires 18 electrons and the N shell 32 electrons for its completion. Of these 2 are in 4_0 orbits, 6 in 4_1 orbits, 10 in 4_2 orbits, and 14 in 4_3 orbits. Assuming Pauli's exclusion principle we can thus calculate precisely the number and distribution of the electrons in any completed shell.

It may be noted that the exclusion principle does not apply to particles carrying an even number of charges. Thus there is no limit to the number of α-particles which can occupy the same quantum level. Thus presumably all the α-particles in

the nucleus are normally in the ground level, and the different energy states, discussed in § 138, possibly represent differences in energy caused by the transference of different numbers of α-particles from one level to another.

153. Electron grouping and the periodic classification of the elements. The total number of extra-nuclear electrons in the atom is equal to the atomic number. The K ring thus becomes saturated for an element of atomic number 2, that is helium, and the L ring for an atomic number $2 + 8$, that is neon. Both helium and neon belong to the group of inert gases, and we can very reasonably associate their inertness with their electronic structure.

A complete energy level is a symmetrical structure which exerts very little force outside its own system, and is, therefore, unlikely to attract or attach a further electron. It is also a stable system, and will not readily part with one of its components. This is verified by the comparatively high ionization potentials of the inert gases. The atom will be neither electro-negative nor electro-positive and will thus not form polar compounds, while its very weak residual field will debar it from forming non-polar attachments.

Let us consider what will happen if we add another proton to the neon nucleus, thus increasing its atomic number to 11 (sodium). The extra positive charge requires an additional extra-nuclear electron in the atomic structure. Both the K and the L levels are, however, complete. The extra electron must therefore be attached in one of the M levels, and presumably in the lowest, or 3_0 level. This is an elliptic orbit of high eccentricity which at its furthest point carries the electron well beyond the close tangle of the K, L orbits. These screen it, to a very large extent, from the attraction of the nucleus, so that it is very easily detached from the atom. The atom thus is strongly electro-positive, and since it can only lose one electron (the remainder being firmly bound in the K and L levels) will obviously be mono-valent. We should thus expect an alkali metal to succeed each inert gas in the list of elements, as indeed we find to be the case.

Increasing the nuclear charge by another unit, i.e. passing

from sodium to magnesium, causes the addition of a second electron, also in the 3_0 level. Conditions are still very similar except that the atom can lose two electrons, giving it a positive valency of two, but since the nucleus has now an extra charge the force retaining the extra electrons in their orbits is somewhat stronger than for sodium, and the element is not so strongly electropositive. Thus the alkali metal is followed by a member of the alkali earth group.

Suppose, on the other hand, we reduce the nuclear charge from 10 to 9. The atom must now normally give up one of the electrons from its L level. The L level, however, will tend to become saturated if the occasion offers, giving up an atom with a resultant negative charge of unity. The element, fluorine, should thus be strongly electronegative, and of unit valency. Thus each inert gas should be preceded by a member of the halogens. Our model thus accounts for the most strongly marked recurrent feature of the periodic classification.

The M level has been shewn to require 18 electrons for its saturation, but the third inert gas has an atomic number 18, or $2 + 8 + 8$. We must suppose that the filling of the eight 3_0 and 3_1 levels produces an electron system with the symmetry, and hence much of the stability of the L system. At any rate it is certain that the next electron is bound, not in a 3_2 level, but in a 4_0 orbit. It can be shewn that the energy of binding in this orbit is greater than that in a 3_2 orbit, for a nuclear charge of 19, and this also applies to the next element calcium (20).

Since we are unable to calculate the energy levels for elements of high atomic number, we cannot construct our electronic scheme from first principles. We can, however, reconstruct it from spectroscopic data. The Zeeman effect and the Stark effect are often useful in identifying the particular quantum numbers to be assigned to a given electron. Table XII contains part of such a reconstruction due to Stoner. It is gratifying to note that an almost exactly similar table was drawn up by Main-Smith entirely on chemical grounds.

The general outlines of the periodic classification and their interpretation in terms of electron levels will be clear from the table. The first short period is caused by the regular filling up

TABLE XII

	K 1_0	L $2_0, 2_1$	M $3_0, 3_1, 3_2$	N $4_0, 4_1, 4_2, 4_3$	O $5_0, 5_1, 5_2$	P $6_0, 6_1$	
1. H	1						
2. He	2						
3. Li	2	1					
4. Be	2	2					
5. B	2	2, 1					
6. C	2	2, 2					1st short series
7. N	2	2, 3					
8. O	2	2, 4					
9. F	2	2, 5					
10. Ne	2	2, 6					
11. Na ...	2	2, 6	1				2nd short series
18. A	2	2, 6	2, 6				
19. K	2	2, 6	2, 6	1			
20. Ca	2	2, 6	2, 6	2			
21. Sc	2	2, 6	2, 6, 1	2			
22. Ti	2	2, 6	2, 6, 2	2			
23. V	2	2, 6	2, 6, 3	2			
24. Cr	2	2, 6	2, 6. 5	1			
25. Mn	2	2, 6	2, 6, 5	2			1st long series
26. Fe	2	2, 6	2, 6, 6	2			
27. Co	2	2, 6	2, 6, 7	2			
28. Ni	2	2, 6	2, 6, 8	2			
29. Cu	2	2, 6	2, 6, 10	1			
30. Zn	2	2, 6	2, 6, 10	2			
31. Ga ...	2	2, 6	2, 6, 10	2, 1			
36. Kr ...	2	2, 6	2, 6, 10	2, 6			2nd long series
54. X	2	2, 6	2, 6, 10	2, 6, 10	2, 6		
... 79. Au ...	2	2, 6	2, 6, 10	2, 6, 10, 14	2, 6, 10	1	Series containing rare earth metals
86. Rn	2	2, 6	2, 6, 10	2, 6, 10, 14	2, 6, 10	2, 6	

of the various L orbits, and the second short period which closely resembles it, by the orderly filling of the 3_0 and 3_1 orbits. The completion of these levels gives a structure resembling the L level, and the corresponding element is an inert gas argon. The next electrons are added in the 4_0 level, giving potassium and calcium. The structure of these elements, however, differs from that of sodium in the fact that there are still 10 vacant quantum states in the M level. With scandium the process of filling these states begins, and we have a succession of elements with somewhat similar properties and mostly with two electrons in the 4_0 state. They are thus all electropositive, many of them having a characteristic valency of 2, although, owing to the possibility of losing an electron from the incomplete 3_2 level, they also exhibit higher valencies. It will be noticed that the element of atomic number 28 is not an inert gas, as two of its electrons are found in 4_0 levels, instead of completing the M level.

Krypton, again, has the argon structure, with eight electrons in the N level. The development follows the lines of the first long series, and gives rise to a second long series. With Xenon we have the additional complication that not only are the O levels incomplete but there are 14 vacant states in the underlying N levels. The filling of these gaps gives rise to the series which includes the rare earth metals. It will be seen that the table accounts not only for the regularities but also for the irregularities of the periodic classification of the elements.

154. The electron theory of metals. The electrical conductivity of metals is most readily explained by assuming that the metal contains a large number of free electrons, capable of moving about in it under the influence of an electrical field. These electrons are presumably detached from the outer levels of the metallic atoms, which are, of course, all electropositive and thus tend to lose electrons. The positive metallic ions, so formed, are rigidly bound in a crystal lattice and take no part in the electrical transference.

In the absence of evidence to the contrary it was natural to assume that the electrons behaved like molecules of a gas, sharing in the energy of thermal agitation of the surrounding

atoms, and having an energy distribution given by Maxwell's distribution law. On these assumptions formulae were derived for the thermionic emission, for the electrical and thermal conductivities, and for the various thermo-electric effects, which agreed reasonably well with experimental observations.

If we assume that the electronic atmosphere behaves as a perfect gas, the current in a uniform conductor of cross sectional area A is by (5) $i = AnekX$, where n is the number of free electrons in unit volume, and k is their mobility. By (12) we have $k = \dfrac{1}{2}\dfrac{e}{m}\dfrac{\lambda}{v}$ where λ is the mean free path of the electron and v its root mean square velocity. Assuming the equipartition of energy we can write $\frac{1}{2}mv^2 = \alpha\theta$ where θ is the absolute temperature and α is Boltzmann's constant. Hence on substituting for k and eliminating m we have

$$i = A\,\frac{ne^2\lambda}{2mv}\,X = A\,\frac{ne^2\lambda v}{4\alpha\theta}\,X. \qquad . \quad . \quad . \quad (133)$$

If the field is uniform we have $X = \dfrac{V}{d}$, where d is the length of the conductor and V the applied E.M.F. Thus $i = \dfrac{A}{d}\,\dfrac{ne^2\lambda v}{4\alpha\theta}\,V$, which leads at once to Ohm's law. Comparing with the equation $i = \dfrac{A}{d}\,\sigma V$ where σ is the specific conductivity, we see that the specific conductivity is given by $\dfrac{ne^2\lambda v}{4\alpha\theta}$, and is constant for a given temperature. The only quantities in this expression which vary for different substances are λ and n. It does not seem probable that the variations in λ will be very great. The conductivity of a substance therefore should depend mainly upon n, the number of free electrons per unit volume.

Suppose that one part of a metallic conductor is heated. The electrons in the heated part have their velocities increased to correspond with the new value of the temperature. The electrons moving away from the heated part will therefore have a greater energy than those moving towards it. There will thus be a transference of energy from the hot to the cold part of the conductor, or in other words there will be conduction of heat through the

metal by the electrons. It is known that non-conductors of electricity are very poor conductors of heat. It seems probable therefore that the conduction by the electrons is very much greater than that due to the atoms of the substance.

Assuming that the atmosphere of electrons in the metal can be treated as a gas, the thermal conductivity κ of the electrons should be given by

$$\kappa = \frac{\pi}{8} n v \alpha \lambda \qquad \ldots \ldots \quad (134)$$

(see O. Meyer, *Kinetic Theory of Gases*), where n, v, α and λ have the same significance as in the equation for electrical conductivity. Neglecting any conductivity due to the atoms this will be the thermal conductivity of the metal. Thus the ratio of the thermal to the electrical conductivity is given by

$$\frac{\kappa}{\sigma} = \left(\frac{\pi}{8} n v \alpha \lambda \right) \bigg/ \left(\frac{n e^2 \lambda v}{4 \alpha \theta} \right) = \frac{\pi}{2} \left(\frac{\alpha}{e} \right)^2 \theta. \quad . \quad . \quad (135)$$

The ratio of the thermal to the electrical conductivity should at a given temperature therefore be independent of the nature of the conductor. This is the well-known law of Wiedemann and Franz. Again this ratio should be directly proportional to the absolute temperature, that is, its temperature coefficient should be $3 \cdot 67 \times 10^{-3}$ per degree Centigrade. Table XIII shews that, for most pure metals, these deductions from the electron theory are very approximately true.

The value of κ/σ as calculated from (135) is $3 \cdot 7 \times 10^{10}$. Considering the approximations made in the calculation the agreement is not unsatisfactory.

Difficulties, however, arose from another quarter, and of a serious kind. The atomic heat of most of the metals has the value 6, given by Dulong and Petit's law. The specific heat is, therefore, in good agreement with the supposition that it is due solely to the change in heat energy of the atoms. Experiments by Lindemann, in which a contribution from the free electrons was specially sought for, convinced him that their contribution was certainly not more than 1 per cent. of the total. On the other hand, to explain the specific conductivity of metals on the theory outlined above it is necessary to assume that n, the number of free electrons per c.c., is of the same order as the

number of atoms. They should, therefore, on classical theory, account for about one-half of the total heat energy of the metal.

The difficulty has been circumvented by Sommerfeld in the following manner. We have seen that energy of the order of a

TABLE XIII

Ratio of thermal to electrical conductivity

Material	κ/σ at 18° C.	Temperature coefficient
Copper	6.7×10^{10}	3.9×10^{-3}
Silver	6.9×10^{10}	3.7×10^{-3}
Gold	7.1×10^{10}	3.7×10^{-3}
Lead	7.2×10^{10}	4.0×10^{-3}
Tin	7.4×10^{10}	3.4×10^{-3}
Platinum	7.5×10^{10}	4.6×10^{-3}
Palladium	7.5×10^{10}	4.6×10^{-3}
Iron	8.0×10^{10}	4.3×10^{-3}

few volts is required to extract an electron from a metal. We may thus regard the surface of a metal as presenting a potential barrier of this magnitude against the escape of electrons. We may now further suppose that the motion of the electrons inside this barrier is quantized, so that there are a large number of quantum levels, or "phase states" to use the language of the new statistical theory, differing from each other by small but definite amounts of energy. By the exclusion principle there cannot be more than one electron in a given level at the same time. Thus all the electrons differ from each other in energy by small, but definite amounts.

If the number of electrons is small in comparison with the number of levels, so that most of the levels are unoccupied, the system can take up or give out energy freely. Thus an electron in a level of small energy can, by collision with a more energetic atom, take up sufficient energy to raise it to one of the slightly higher energy levels, or conversely it can give up a definite amount of energy and fall into a somewhat lower level. The lowest level in the system is, of course, the level in which the electron has zero energy. The average energy of an electron will

thus be very approximately equal to the average energy of the neighbouring atoms, i.e. about 0·023 volt at 0° C.

Let us suppose, however, that the number of electrons becomes comparable with the total number of possible states, so that most of the levels are occupied. The electrons, as we have seen, tend to have an average energy of about 0·02 volt, so that all the levels in this neighbourhood are rapidly filled. The remaining electrons cannot fall into levels of lower energy, since these are already filled, and must therefore rise into higher and higher levels. The more electrons there are, the higher the tide of occupied levels must rise, since the lower levels are all filled. Thus in the case of silver at 0° C. it has been calculated that the energies of the individual electrons range from 0 to 5·6 volts, instead of being distributed about a mean value of 0·023 volt. A system of this kind in which all the lower levels are occupied is said to be degenerate, and it can be shewn that, owing to their large number and small mass the electrons in any metal form a highly degenerate system.

Such a system is almost incapable of exchanging thermal energy with the surrounding atoms. An electron in a higher level cannot give up energy to an atom, because there is no unoccupied lower energy level to which it can pass. Thus if the temperature of the conductor is lowered the total energy in the electronic system remains practically unaltered, even if the temperature sinks to absolute zero. Similarly if the temperature is raised the electrons in the lower levels cannot absorb energy from the atoms unless they can absorb sufficient at one collision to raise them to one of the unoccupied highest levels. As this requires an amount of energy some 200 times greater than the average energy of an atom at 0° C. its occurrence is extremely infrequent, and when it does occur is liable to be nullified by an electron from a higher level falling into the now vacant state.

But the specific heat of the electronic system is the rate of increase of energy with temperature. The specific heat of a degenerate system is thus very small. Exact calculation shews that in the case of metals the contribution of the electron system to the total specific heat is, at ordinary temperatures, rather less than 1 per cent. It is thus too small to be detected.

The quantization of the electron introduces some modifications into the elementary theory described earlier. According to Sommerfeld the electrical conductivity σ is given by

$$\sigma = \frac{8\pi}{3} \frac{e^2\lambda}{h} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad (136)$$

and the thermal conductivity by

$$\kappa = \frac{8\pi^3}{9} \frac{\lambda\alpha^2\theta}{h} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad (137)$$

the symbols having the same meaning as before. Thus

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left(\frac{\alpha}{e}\right)^2 \theta. \quad . \quad . \quad . \quad . \quad . \quad (138)$$

The new theory thus gives the same temperature coefficient as the classical theory. The numerical value for the ratio k/σ works out at $7 \cdot 1 \times 10^{10}$, in excellent agreement with the experimental data.

155.   Thermionic emission. The theory can be applied to the problem of thermionic emission, which in an earlier chapter we treated by thermodynamical methods. Calculation shews that the electron system in a metal remains degenerate up to temperatures of the order of $15,000°$ C. Assuming that an electron will leave the surface if its kinetic energy perpendicular to the surface is greater than some constant W_a it can be shewn that the current density of emission should be given by

$$i = \frac{4\pi e m\alpha^2}{h^3} \theta^2 \epsilon^{-\frac{(W_a - W_i)}{\alpha\theta}}, \quad . \quad . \quad . \quad (139)$$

where W_i is the energy of the highest phase state which is normally occupied in the degenerate electron system. If we suppose that a fraction r of the electrons reaching the surface with the appropriate energy are reflected back into the metal

$$i = (1 - r)\frac{4\pi e m\alpha^2}{h^3} \theta^2 \epsilon^{-\frac{W_a - W_i}{\alpha\theta}} \quad . \quad . \quad . \quad (140)$$

The numerical value of $4\pi e m\alpha^2/h^3$ is about 120 when expressed in amperes per square cm. It may be noticed that it is independent of the nature of the metal. The most recent determinations of the emission constant A (§ 59) for clean surfaces of specially

purified tungsten, molybdenum and platinum is about 60. The reflection coefficient r is thus approximately $\frac{1}{2}$ for all these metals. The smaller values of A shewn by coated surfaces are due to a higher reflection coefficient.

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For the newer quantum wave mechanics

   FLINT. *Wave Mechanics,*

   MOTT. *Wave Mechanics*

are comparatively elementary.

   DIRAC. *Quantum Mechanics,*

   CONDON and MORSE. *Quantum Mechanics,*

   FRENKEL. *Wave Mechanics,* Vol. I, Elementary Theory

are more advanced texts.

CHAPTER XVI

RADIO-ACTIVE CHANGES

156. Disintegration of uranium. Uranium and its salts give off both α- and β-rays, together with some γ-rays of small intensity. Using a thick layer of the substance practically the whole of the effect on a photographic plate is due to the β-radiation, since owing to the great absorbability of the α-rays only those from a comparatively thin layer can reach the surface and at the best of times the photographic effect of an α-ray is small. In 1900 Sir Wm. Crookes shewed that it was possible by a single chemical operation to obtain uranium which was photographically inactive, the whole of the photographic activity being concentrated in a very small residue, free from uranium and consisting chemically of the small traces of the impurities present in the original salt. This residue to which he gave the name of uranium X could be obtained many hundred times as active weight for weight as uranium itself, while the major fraction which could be shewn by chemical tests to be uranium was photographically inactive. The method originally used was to precipitate the uranium with ammonium carbonate and to dissolve the precipitate in excess of the reagent. On filtering a trace of precipitate remained behind on the filter paper. This contained the uranium X. The same separation can also be carried out by other methods. So far the phenomena resemble very closely the separation of two ordinary chemical substances by the usual methods of analysis. However, if the two fractions are laid aside for two or three months it is found that the uranium has recovered the whole of its original activity while that of the uranium X has completely disappeared. The loss of activity of the uranium was therefore only temporary in character, while the increased activity of the separated uranium X was equally short lived.

It was further found that the total activity, as measured by the photographic effect, that is, by the β-rays, was constant at any time before or after the separation, the gain of activity of the uranium exactly corresponding to the loss of activity of the uranium X. The measurements are most conveniently made by the electrical method. The substance to be examined is spread in a thin layer over the lower plate B of the parallel plate ionization chamber (Fig. 109) which is used as the high potential plate and connected to a battery of cells. The upper plate A is connected to the electroscope or electrometer, and the saturation current is measured in the usual way. The
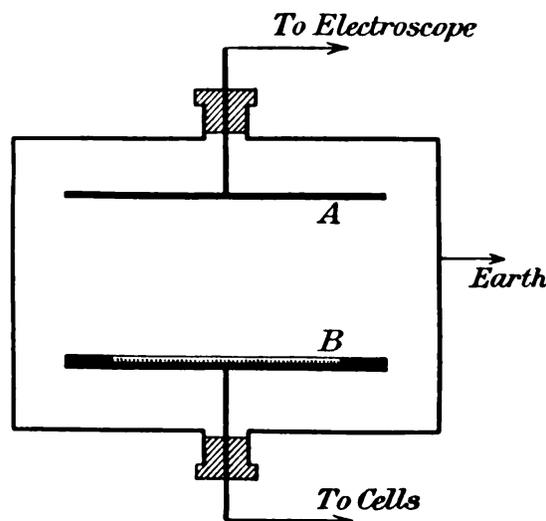
Fig. 109

saturation current is taken as proportional to the activity of the substance. In order to be comparable with the photographic effect which we have been describing and which as has been pointed out is due to the β-rays, the substance must be covered with 1/10 mm. of aluminium to cut off all the α-radiation.

Using two chambers of this type we can investigate more closely the change of activity with time in the two fractions. The results for uranium are shewn in Fig. 110. The two curves are complementary, the sum of the two ordinates at any point being the same.

By plotting the *logarithms* of the currents against the time it

is found that the decay curve of the uranium X follows an exponential law, that is, if I_t is the activity at a time t, then

$$\frac{I_t}{I_0} = \epsilon^{-\lambda t} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (141)$$

where I_0 is the activity at the moment when the measurements began, and λ is a constant, which is known as the *radio-active constant* for the particular substance, in this case uranium X.
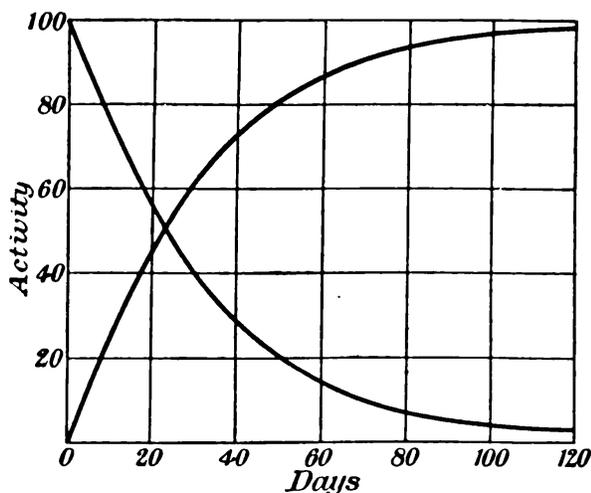
Fig. 110

Since the curves are complementary the recovery curve for the uranium can be expressed in the form

$$\frac{I_t}{I_0} = 1 - \epsilon^{-\lambda t}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (142)$$

where t is the time which has elapsed since the uranium was completely freed from uranium X, and λ *is the same constant as before.*

Differentiating the expression for the decay of uranium X we have

$$\frac{dI}{dt} = -\lambda I_0 \epsilon^{-\lambda t}.$$

But $I_0 \epsilon^{-\lambda t}$ is the quantity of the uranium X still present $= I$ say. Thus

$$\frac{dI}{dt} = -\lambda I. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (143)$$

In other words the rate of decay at any moment is simply proportional to the quantity of radio-active matter still present, a very important result.

The uranium which has been freed from UX is inactive as measured by its β-ray effect. If, however, we remove the aluminium screens from the two fractions in Fig. 109 we find that the ionization is now nearly all due to the uranium itself, the activity of the separated fraction being negligible in comparison with that of uranium itself. In other words uranium itself gives out α-rays but no β-rays while the uranium X gives out β-rays but no α-rays.

The rate of decay of activity of the UX has been shewn by many experiments to be quite independent of external conditions. It is the same whether the two fractions are kept separate or whether they are enclosed in the same tube; the same whether the product is exposed to the air or sealed in a thick walled lead box, so as to be freed as far as possible from all external influences. It is quite independent of temperature being the same at the temperature of liquid air as at a red heat. It does not depend on the processes used for the separation of the two substances and is therefore presumably independent of the state of combination of the substance. The growth of activity of the uranium salt is the same if it is changed into some other salt of the metal, or whether it is solid or in solution. It is in fact a constant of the element itself.

157. Theory of radio-active change. It is at first sight somewhat remarkable that the processes of recovery and decay should be so closely connected even when the two fractions are separated from each other in such a way as to preclude all possibility of interaction between them. The effects however have found a complete explanation on the following assumptions:

(1) That there is a constant production of the new radio-active substance (UX) by the radio-active body (uranium).

(2) That the new substance (UX) itself disintegrates according to an exponential law, with a constant equal to the radio-active constant λ for the change.

Suppose that from the given mass of uranium q_0 particles of uranium X are produced per second. The activity of the particles produced in a short interval of time dt will at their moment of production be equal to $Kq_0 dt$, where K is a constant measuring the effect produced on our electroscope by one particle of UX. The activity of these particles after a time τ will be given by

$$Kq_0 \epsilon^{-\lambda\tau} dt = dI. \quad . \quad . \quad . \quad . \quad (144)$$

Suppose we wish to know the total activity of the uranium at a time T after it has been completely freed from the product UX. Then the time which has elapsed since the formation of the particular particles we are dealing with is equal to $T - t$ where t represents their moment of formation. The effect due to these particles is thus $Kq_0 \epsilon^{-\lambda(T-t)} dt$ and the total activity at the time T is therefore given by

$$I_T = \int_0^T Kq_0 \epsilon^{-\lambda(T-t)} dt$$

$$= \frac{Kq_0}{\lambda}(1 - \epsilon^{-\lambda T}). \quad . \quad . \quad . \quad (145)$$

The maximum activity is reached when the process has been going on for a sufficient time to make $\epsilon^{-\lambda T}$ negligible, and is given by

$$I_0 = \frac{Kq_0}{\lambda}.$$

Substituting in (145) I_0 we have

$$\frac{I_T}{I_0} = 1 - \epsilon^{-\lambda T}$$

which agrees with the experimental results. It will be noted that λ is the constant measuring the rate of decay of the product.

The equilibrium state is obviously reached when the loss of activity due to decay of the product is equal to the rate of formation of the product from the original substance. Since the product is always decaying according to the exponential law, whether it is mixed with the parent substance or separated from it, it follows that uranium is constantly producing a new substance uranium X from itself at a definite constant rate. When equilibrium has been established it is evident that the

quantities of the two substances present will bear a constant ratio to each other.

The possibility of separating uranium X from uranium in various chemical ways shews that the two substances are chemically distinct. Moreover, the uranium not only gives uranium X but in the process emits α-particles which, as we have already seen, are charged atoms of helium. It is impossible to avoid the conclusion that the atom of uranium disintegrates spontaneously, giving off a charged helium atom and forming a new element uranium X which, although owing to its rapid decay it is always present in quantities too small to admit of direct chemical investigation, can be detected by the β-radiations which it emits. The product of the decay of uranium X has been identified as a new radio-active substance, Ionium, which in its turn has been proved to be the origin of the element radium.

158. Theory of successive transformations. The case we have so far considered has been a very simple one for two reasons. In the first case the amount of uranium breaking up during the time of our experiments is so infinitesimally small that we can without error regard the amount of uranium present during the experiment as constant. In the second place the substance formed by the disintegration of the uranium X is so feebly radio-active that its effect upon the electroscope is inappreciable. In general these simple conditions do not hold. Radium, for example, which has been prepared for more than a few days is found to contain at least five radio-active substances whose activity must be taken into account. The same principles which were successful in explaining the decay and recovery curves of uranium and its product can also be applied to the more complex cases with equal success. For convenience these principles have been stated in the form of six propositions by Rutherford, to / whom the theory is due.

(1) The activity shewn by radio-active substances is due to the disintegration of the atom.

(2) A definite fraction of the total number of atoms present become unstable in a given small interval of time.

(3) In most cases this instability and disintegration is accompanied by the emission of energy in the form of α-, β- and γ-rays, by α-rays alone or by β- and γ-rays alone. Occasionally it takes place without emission of ionizing radiations. If radiations are emitted it is assumed that the fraction of the atoms changed per second can be measured by the intensities of the radiations emitted.

(4) The expulsion of a single α-ray of atomic weight 4 gives rise to an atom differing in atomic weight by four units from the parent atom. The expulsion of β-particles, which have a mass insignificant compared with that of a hydrogen atom, produces no change in atomic weight, but only in the internal structure of the atom.

(5) At any time after disintegration has commenced there exist together in the substance

(a) the unchanged substance,

(b) the immediate product of its disintegration of the same or smaller atomic weight,

(c) any product or products formed from the disintegration of (b) if it is itself radio-active.

(6) Each of the products of radio-active change is a new element, and has different chemical properties from those of the parent atom. This is shewn by their different behaviour to various chemical reagents as in the case of uranium. It is still more clear in the case of radium in which the first decomposition product is a gas.

The general problem may be stated as follows: Suppose we have a series of elements A, B, C, D,... such that A changes into B, B into C, C into D, and so on. Given that the number of atoms of each present at a given moment in a substance is a, b, c, d,... respectively to find the number of each still present in the mixture after a time t has elapsed. The general problem is capable of solution, but it will be simpler and more instructive to confine our attention to one or two illustrative cases which are met with in actual practice.

By assumption (2) we have for each of the substances

$$dn/dt \propto n,$$

where n is the number of atoms of that substance actually present at the given moment. Thus

$$\frac{dn}{dt} = -\lambda n; \quad n = n_0 \epsilon^{-\lambda t}, \quad . \quad . \quad . \quad (146)$$

that is to say, each element by itself decays according to an exponential law. λ is known as the radio-active constant for the substance.

We shall see later that the decomposition of the atoms follows a probability law, and that λn is only the most probable value of the number disintegrating per second. When, however, as is usually the case, the total number of atoms is large, the actual value over a finite interval of time will not differ from its most probable value by an appreciable amount.

It must be noted that λn is also the rate of formation of the new substance B. We have already seen that λ is independent of the most extreme changes in external and chemical conditions. It is also independent of the age of the substance. Experiments have been made with radium emanation which loses half its activity in 3·85 days, over a period exceeding three months. The rate of decay throughout was strictly exponential, the constant λ being the same at the end of the experiment as at the beginning. It is thus the same for emanation which is freshly formed as for emanation three months old. In fact the break up of the atom depends solely on the law of probability and the nature of the atom.

Two other ways of defining the rate of decay of the radio-active substance are often used. The *half period value* is the time taken for the activity of the substance to fall to one-half its original value. This can be obtained from (146) by putting $n/n_0 = \frac{1}{2}$ and solving for t. Thus $-\lambda t = \log_\epsilon \frac{1}{2}$,

$$t = \frac{\log_\epsilon 2}{\lambda} = \frac{0·693}{\lambda}. \quad . \quad . \quad . \quad (147)$$

The *average life* of the radio-active atom can also be calculated. The number of atoms changing during a short interval dt at a time t since the separation of the substance $= \lambda n\, dt$. Also $n = n_0 \epsilon^{-\lambda t}$ and

thus $dn = \lambda n_0 \epsilon^{-\lambda t} dt$. These atoms have had a life of t seconds. The average life of all the atoms of the substance is therefore

$$\frac{1}{n_0} \int_0^\infty t \lambda n_0 \epsilon^{-\lambda t} dt$$

$$= \frac{1}{\lambda}. \quad . \quad . \quad . \quad . \quad . \quad (148)$$

159. Radio-active equilibrium. Suppose we commence with some substance such as uranium or radium the life of which is long compared with the time occupied by our experiments. The average life of uranium, for example, is about 7×10^9 years and that of radium about 2280 years. Over any ordinary period of time therefore the quantity of the original radio-active substance which we will call A remains constant, and hence fresh radio-active matter is produced from it at an approximately constant rate, which will be equal to $\lambda_1 a_0$ where a_0 is the number of atoms of A present, and λ_1 its radio-active constant. If B is the immediate disintegration product of A, B is being formed in the substance at this constant rate $\lambda_1 a_0$. But the rate at which B disintegrates is proportional to the amount of B actually present, and thus increases with the increase in the quantity of B. Hence a point will come when the rate of disintegration of B is equal to its rate of formation from A and the amount of B in the substance will then remain constant. The rate at which B increases is equal to the difference between its rate of formation from A and its rate of disintegration into C. Thus

$$db = \lambda_1 a_0 dt - \lambda_2 b dt \quad . \quad . \quad . \quad . \quad (149)$$

where b is the number of atoms of B present at the given instant. Similarly for the element C we have

$$dc = \lambda_2 b dt - \lambda_3 c dt.$$

It is evident that the amounts of $B, C, \ldots$ present in the mixture will become constant when

$$\lambda_1 a_0 = \lambda_2 b = \lambda_3 c = \ldots \quad . \quad . \quad . \quad . \quad (150)$$

Thus when radio-active equilibrium, as it is called, has been established the various radio-products will bear to each other

a constant ratio which is inversely proportional to their radio-active constants. Conversely, if on analysis two radio-active substances are always found occurring in nature in the same ratio, one of them must be a product, direct or indirect, of the other. Thus the fact that the proportion of radium to uranium in minerals is always constant is evidence that radium is a product of the disintegration of uranium.

A hydrostatic analogy may prove useful in understanding the process. Suppose we have a series of tanks P, Q, R,... emptying one into the other as shewn in Fig. 111. The rate at which water flows out of any tank will be proportional to the area of the aperture and to the height of the water in the tank at the moment under consideration. In other words, supposing the tanks to have the same area of cross section, the flow will be proportional to the quantity of water in the tank. The rate of efflux of the water thus follows the same law as the rate of decomposition of a radio-active substance.

Supposing now that the water in the tank P is kept at a constant level. This will correspond to the case we have just been considering. Water will rise in each tank until the rate of efflux, which is proportional to the quantity of water in the tank, is equal to the rate at which water pours into it from the tank above. When equilibrium is established the rate of flow will

Fig. 111

be constant throughout, and the height of the water in the different tanks will be inversely proportional to the size of their apertures. If the aperture is small the height of the water will be large, if on the other hand it is large a comparatively small height of water will produce the necessary efflux. Similarly when equilibrium is established substances of quick decay, for which the radio-active constant is large, will be present in relatively small proportions while those which decay slowly and for which the radio-active constant is small, will be present in large amounts. It is thus only the comparatively long-lived
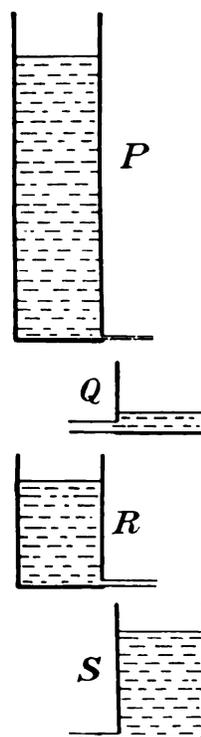
radio-active substances, such for example as radium itself, which we could expect to obtain in measurable quantities.

The case which we have just considered constitutes what may be described as permanent radio-active equilibrium, the amounts of each substance present remaining constant after equilibrium has once been reached. Let us suppose now that water is no longer poured into the first tank P, but that P has a small aperture so that the rate of efflux is small. This will correspond to the case of the decomposition of a radio-active substance of small but appreciable radio-active constant. The rate of flow of water through the system will obviously be governed by that of the tank with the smallest aperture, in this case by P. It is evident, therefore, that when equilibrium has been established the quantity of water in each tank will be proportional to the quantity remaining in P, since the rate of flow through the system is governed by this factor. A little consideration will shew that the relative amounts of water in the different tanks will be very nearly the same as if the level in P were maintained at the value which it has at the moment of observation by a continuous influx of water. It will actually be slightly larger. The two cases will approximate more nearly to each other the slower the rate of efflux from P.

We thus get a state which we may describe as that of *transient equilibrium*, the relative quantities of water in each tank remaining constant, but each of the quantities decreasing in absolute magnitude proportionately to the quantity in the first tank.

This case corresponds to that of a radio-active substance which gives rise by its disintegration to a series of radio-active substances, the half value period of which is short compared to its own. For example, radium emanation which has a half value period of 3·825 days gives rise to successive radio-active substances which have half value periods of 3·05, 26·8, and 19·7 minutes respectively. Thus, if radium emanation is placed in an enclosed space and left to decay, after equilibrium has been established, which takes place in about four or five hours, the quantity of any one of the products present is simply proportional to the quantity of the emanation remaining in the

vessel. This is a case of transient radio-active equilibrium. It can be shewn that in this case the quantity of each product actually present is about one per cent. greater than the value which it would finally attain if the quantity of emanation present were maintained at its actual value at that instant by an external source.

The problems arising can easily be solved if required by an application of the principles enunciated by Rutherford.

Taking the case we have just considered for an example, suppose that A, B, C,... are a series of such elements so that A changes into B, B into C, and so on. Then if the substance at the beginning consists only of the element A (for example only of radium emanation), and if a, b, c, ... are the number of atoms of each element present at a time t from the start, and λ_a, λ_b, λ_c,... are the corresponding radio-active constants, we have

$$a = a_0 \epsilon^{-\lambda_a t}$$

where a_0 is the number of atoms of A with which we commenced the experiment. Also by (149) we have

$$db = \lambda_a a\, dt - \lambda_b b\, dt,$$
$$dc = \lambda_b b\, dt - \lambda_c c\, dt,$$

and so on. Substituting for a, we have

$$\frac{db}{dt} = \lambda_a a_0 \epsilon^{-\lambda_a t} - \lambda_b b.$$

The solution of this equation is of the form

$$b = a_0 (k_1 \epsilon^{-\lambda_a t} + k_2 \epsilon^{-\lambda_b t}). \quad . \quad . \quad . \quad (151)$$

Now $b = 0$ when $t = \infty$, since all the substances eventually disintegrate completely; $\therefore k_1 = - k_2$. Differentiating the equation and applying the conditions that when $t = 0$, $a = a_0$ and $b = 0$, we find $k_1 = \dfrac{\lambda_a}{\lambda_b - \lambda_a}$; and thus finally

$$b = \frac{a_0 \lambda_a}{\lambda_b - \lambda_a} (\epsilon^{-\lambda_a t} - \epsilon^{-\lambda_b t}). \quad . \quad . \quad (152)$$

The method can obviously be continued to give the corresponding value of c, and so on. If λ_b is large compared with λ_a, then when t is comparatively large, $\epsilon^{-\lambda_b t}$ will be small

compared with $\epsilon^{-\lambda_a t}$ and the quantity of b present will thus be proportional to $a_0 \epsilon^{-\lambda_a t}$, that is, to the quantity of A remaining; the result we have already obtained from general considerations.

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CHAPTER XVII

RADIUM AND ITS PRODUCTS

160. The nature and properties of radium. The principles we have been considering will be made clearer, and the evidence for them more conspicuous, if we study in detail one series of radio-active changes. That of radium is the most suitable for the purpose, not merely on account of its intrinsic importance but also owing to various accidental causes which render the phenomena particularly clear.

Radium can be isolated from uranium ores, in which it exists as a product of the radio-active disintegration of the uranium. It is obtained by the processes used in the extraction of barium from the ores, to which element it bears a close chemical resemblance. It can be obtained free from barium by repeated fractional crystallization of the bromide, the radium salt being somewhat less soluble in water than the corresponding salt of barium, with which, however, it is isomorphic.

The proof of the elementary nature of radium is now complete. It is afforded in the first place by the spectrum, which is characteristic of the metal, and differs from those of all other elements. The lines in the radium spectrum have now been analysed into their component series, and are found to present the common characteristics of the metals of the alkali earths. Applying the usual laws of spectra the spectrum of radium is found to correspond to that of an alkaline earth metal of atomic weight about 225.

Radium has been obtained in sufficient quantities and of sufficient purity to enable its atomic weight to be obtained by direct chemical methods. The method employed is that of precipitating the radium chloride with silver nitrate, and weighing the silver chloride formed. In this way the atomic weight is found to be 226·0.

C I   20

The value of the atomic weight of radium is strong evidence for the disintegration theory of its formation. It is known that the conversion of uranium into radium is attended with the expulsion of three α-particles. Thus on the disintegration theory the atomic weight of radium should be less than that of uranium by the weight of three α-particles. The atomic weight of uranium is 238. That of radium should therefore be $238 - 3 \times 4 \cdot 0$, or 226, in satisfactory agreement with the chemical determinations.

Radium can be obtained in metallic form. It is a silver white metal, melting at about 700° C., and beginning to volatilize at a slightly higher temperature. It is attacked by air forming a nitride, and by water forming the hydroxide. It forms a series of salts similar in properties and appearance to those of barium. It thus possesses in every particular the characters of a metallic element of the alkaline earth group.

161. Radium emanation. The first product of the disintegration of radium is the heavy inert radio-active gas known as radium emanation. It is found that a sample of pure radium emits this gas at a constant, definite rate, the emission being attended by the expulsion of an α-particle. The phenomena of radio-active change are peculiarly striking in this instance, the parent substance being a metallic solid, while the disintegration product is an inert gas.

The emanation can be separated from the radium salt by dissolving the latter in water, and boiling the solution. The gas emitted, which contains hydrogen and oxygen, from the decomposition of the water by the radiations emitted, and carbon dioxide from the tap grease, is pumped off, and purified by suitable chemical means. The final purification is effected by condensing the emanation in a tube immersed in liquid air, and pumping off the more volatile gases present. Radium emanation is itself radio-active. It gives off α-particles changing into a substance, radium A, which being solid is deposited on the walls of the vessel containing the gas. Radium emanation, though formed from radium, is itself an element. This is shewn by its characteristic spectrum, which differs as much from that

of radium as from the spectra of all other elements. The spectrum can easily be obtained by passing a little of the emanation into a small discharge tube.

Since the emanation is formed from radium by the expulsion of an α-particle of mass 4 its atomic weight should be about 222, taking that of radium as 226. The matter was investigated directly by Ramsay and Gray, who succeeded in determining the density of the emanation using a quartz microbalance of special construction. Two bulbs of very unequal size but of equal mass are placed at the two ends of the beam of a small quartz balance enclosed in a small air-tight chamber. The weights are adjusted so that the beam is horizontal when the balance case is completely evacuated. If gas is now admitted to the space around the balance the buoyancy of the gas will reduce the effective mass of the larger bulb, and thus cause a deflection of the beam. The buoyancy of the gas can be calculated in terms of the deflection of the beam when the sensitivity of the balance is known, and from the buoyancy the density of the gas can be at once determined.

The mean result of several experiments shewed that the density of the emanation was 111·5 times that of hydrogen. This gives a molecular weight to the emanation of 223. The chemical properties of the gas resemble those of the argon group, and it is thus presumably monatomic. In this case its atomic weight is also 223. Considering that the total weight of the emanation available for the experiment was no more than 1/1000 of a milligram the agreement with the theoretical value is surprisingly good.

The emanation has been found to behave as a gas at ordinary temperatures. It obeys Boyle's law, it liquefies at $-65°$ C. at normal pressure, but exerts an appreciable vapour pressure down to a temperature of $-150°$ C. According to Ramsay and Gray its critical temperature and pressure are 104·5° C. and 63 atmospheres respectively. The density of the emanation at the temperature of liquid air, at which it is probably solid, is between 5 and 6.

Radium emanation is thus a definite chemical element

20-2

belonging to the group of inert gases. In recognition of this fact it has become usual to refer to it as *radon*.

162. Rate of decay of radon. As radium emanation is extensively used in experimental researches it is necessary to know its rate of decay with some accuracy. The simplest method is to allow the emanation in a closed tube to attain radio-active equilibrium with its immediate products radium A, B and C. These products are all short-lived, the most stable having a half period value of 26·8 minutes. A few hours thus
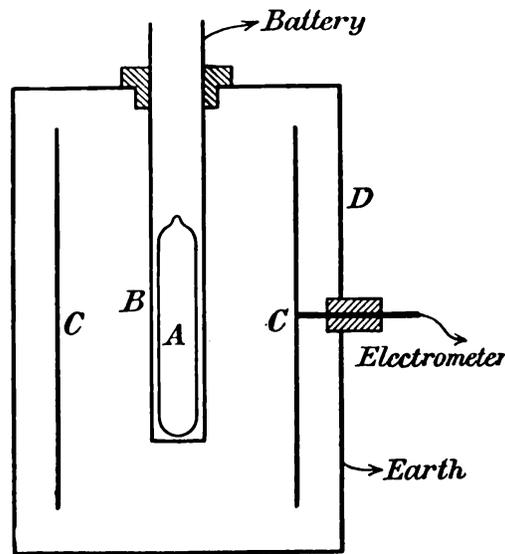
Fig. 112

suffices to set up transient equilibrium in the system. The rate of decay of any part of the activity is then, as we have already seen (§ 159), that of the most stable of the constituents, in this case the emanation. The advantage of this method is that it allows us to use the β- and γ-rays, which, as we shall see later, are actually emitted by its disintegration products, radium B and radium C, as a measure of the activity of the emanation itself. It further allows us to evade the complications due to the growth of these products in the emanation during the first few hours after separation.

The apparatus used by Curie is shewn in Fig. 112. The radon, enclosed in a sealed glass tube *A*, is placed inside the brass tube

B, which can be connected to a battery of cells and forms one plate of the ionization chamber. The insulated plate C takes the form of a cylinder concentric with B, and is connected in the usual way to an electrometer. The whole is surrounded by a metal chamber D which is earthed and serves to screen C from electrostatic disturbances. If D is made perfectly air-tight, changes in the current owing to fluctuations in the temperature and pressure of the atmosphere are avoided. The α-rays due to the radon itself are of course completely absorbed by the glass tube A and the metal tube B. The current is due to the β- and γ-rays from the radio-active decomposition products of the emanation. After a few hours these decay with the period of the emanation.

In this way the radio-active constant of radon was found to be 0·1801 (day)$^{-1}$ or 2·085 × 10^{-6} (sec.)$^{-1}$. Rutherford by a different method obtained a value 0·1802 (day)$^{-1}$. The latest determinations give a rather higher value for λ, namely 2·097 × 10^{-6}. This corresponds to a half value period of 3·825 days.

163. Measurement of the volume of radon in equilibrium with one gram of radium. The quantity of radon in radio-active equilibrium with one gram of radium is by the laws of radio-active change a constant. It is termed a *curie*. Since the curie is a somewhat large standard compared with the amounts of radon generally available for experimental purposes one-thousandth part of this is taken as a subsidiary standard and is known as the *millicurie*. The value of the curie can be estimated from the radio-active constants. It has been found by the method of § 98 that one gram of pure radium (free from its products) emits 3·7 × 10^{10} α-particles per second. As each atom of radium disintegrates into one atom of radon with the expulsion of one α-particle this is also the number of radon atoms formed per second. But the number present when equilibrium is reached is equal to q/λ where q is the rate of formation of the atoms, and λ the radio-active constant of the radon. The total number of atoms of radon in equilibrium with one gram of radium is thus

$$3·7 \times 10^{10}/2·097 \times 10^{-6} = 1·77 \times 10^{16}.$$

Since there are $2 \cdot 78 \times 10^{19}$ molecules in one c.c. of gas at normal temperature and pressure the volume occupied by one curie of radon under these conditions is

$$1 \cdot 77 \times 10^{16} / 2 \cdot 71 \times 10^{19} \text{ c.c.} = 0 \cdot 66 \text{ cubic mm.}$$

164.   The active deposit from radon. If a plate or wire of any kind is exposed to radon for a few hours and then withdrawn it is found to have become radio-active. This phenomenon was at first described as induced or excited activity. It is now known to be due to the deposition on the surface of the substance of a solid radio-active product due to the decomposition of the radon.

If the wire is allowed to remain in the radon sufficiently long to attain equilibrium the amount of the activity is independent of the position or material of the plate, and is strictly proportional to the amount of radon present. It is also directly proportional to the area of the surface exposed.

A curious property of the excited activity is that it can be concentrated on a very small area if the latter is charged negatively. Thus if a wire is passed into a metal chamber containing a radium compound, and charged to a high potential, the activity when the charge on the wire is negative is as much as 200 times its activity when positively charged. In this way practically the whole of this "excited" activity can be concentrated on the wire, which may be made to have an activity per unit area of over 10,000 times that of the surface of radium itself.

Since the activity is concentrated on the negative electrode the carriers of the activity must have a positive charge. Since the active deposit is formed from the emanation by the emission of a positive particle carrying two electronic charges we should have expected the residual atom to have been negatively charged. We know, however, that the impact of a positive particle on matter gives rise to a number of slow-moving electrons, or δ-rays as they have been called. It seems evident, therefore, that the escape of a positive ray from an atom must also be attended by an emission of negative electricity, probably

in the form of these slow-moving electrons. Since the residual atom has a positive charge it is evident that at least three such electrons must be expelled with each positive particle.

The velocity of the carriers in an electric field can be measured by methods analogous to those used to determine the mobilities of the ions. Their velocity in a field of one volt per cm. is about 1·4 cm. per sec. or very nearly that of the positive ion in a gas. There is some evidence for the assumption that they carry a single negative charge.

165. Recoil atoms. The α-particle is expelled from the radon atom with considerable velocity. The residual atom itself must thus be projected in the opposite direction with an initial velocity which is given by the consideration that the momentum of the system as a whole must be zero. Since the mass of the α-particle is 4, and that of the residual atom $(222 - 4)$, the velocity of the recoil atom will be 4/218 or about 1/55 of that of the corresponding α-particle. The range of the recoil atoms of radon is found to be about 0·12 mm. in air at atmospheric pressure. As we shall see later the phenomenon can be used to prepare an α-ray product in a state of purity.

166. Analysis of the active deposit of rapid change. A body which has been exposed to radon is found after removal from the emanation to give out all three kinds of radiations. The activity is comparatively short-lived and almost completely disappears within 24 hours. There is, however, always a small residual activity which if the body has been exposed for several days may reach as much as one-millionth of the initial activity, and the activity of this portion is found to increase steadily with time over the space of several years.

We may therefore for convenience divide the excited activity into two parts, (1) the active deposit of rapid change, (2) the active deposit of slow change. Since the activity of the latter is in general minute compared with that of the former, we may neglect the small residual effects due to it in our analysis of the short-lived deposit.

The active deposit can be obtained on a thin rod or wire by

charging the wire to a negative potential of some 200 volts and exposing in a vessel containing radon. If the activity is to be measured by the α-rays the rod may then be made the central electrode of a cylindrical ionization chamber, the saturation current being measured by an electrometer in the usual way. If β- or γ-rays are to be used to measure the activity the simple electroscope (Fig. 96) is convenient. If β-rays are to be employed the opening of the electroscope is covered with only sufficient thickness of aluminium foil to absorb all the α-rays. If only
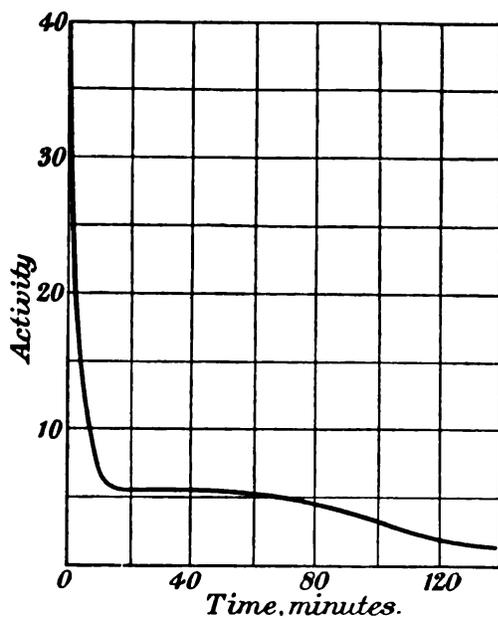
Fig. 113. Decay of excited activity; α-ray curve

γ-rays are to be dealt with the electroscope may be placed on a sheet of lead some half centimetre in thickness, which will cut off everything except the γ-rays.

The shape of the decay curves depends on whether the α- or the β-rays are used for the measurement, and also on the time of exposure of the wire to the radon. The active deposit consists therefore of a mixture of radio-active substances, all in the solid state, some emitting α-rays, and some β- and γ-rays only.

The decay curve obtained after a short exposure of the wire to the radon, and measured by the α-ray activity, is shewn in Fig. 113. It will be seen to be divisible into three parts.

The first stage shews a rapid decay falling to some 10 per cent. of its initial value in 15 minutes. This is followed by a period of some 20 minutes in which there is little variation in the activity. Then a gradual exponential decrease follows, the curve falling to half value in about 28 minutes.

Since the exposure was short the initial substance consisted almost entirely of the first decomposition product of the emanation which we will call radium A. An analysis of the first part of the decay curve shews that this substance emits α-particles and decays to half value in about three minutes,
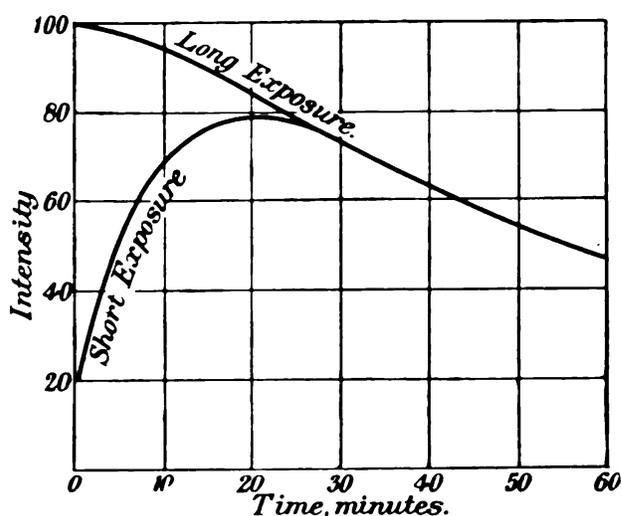
Fig. 114

giving rise to a product which emits α-rays and decays with a half value period of 28 minutes.

Further evidence on the nature of the changes can be obtained from a study of the β-ray curves. The β-ray curves for short and long exposures are shewn in the curves of Fig. 114. The curve for a short exposure of one minute shews that the β-ray activity is initially absent, and that therefore radium A emits only α-rays. If, however, the product emitting the β-rays was the immediate product of the decomposition of the radium A, the curve for the rise of activity of the β-ray product should be (neglecting the decay of the latter) complementary to the decay curve of radium A, that is, it should rise to half value in about three minutes. As a matter of fact the rise to half value

occupies rather more than ten minutes and a substitution of the numerical values in the formulae shews that this discrepancy cannot be explained by the small decay of the β-ray product in that interval of time. We are thus led to the conclusion that there is between the radium A and the β-ray product another radio-active substance which we will term radium B, which without itself emitting ionizing rays gives rise to the product radium C which does.

The period of the two products radium B and C can best be obtained from a study of the curves obtained for the β-ray activity with long exposure. In this case the three products will be in radio-active equilibrium, and the relative amount of the short-lived radium A will consequently be very small. Moreover as it has a short period it will rapidly cease to affect the shape of the decay curves. The whole of the radium A (except one per cent.) is, in fact, disintegrated within twenty minutes after removal from the emanation and the curve is then due solely to radium B and C.

Now it is found that this curve can be accurately expressed by an empirical formula of the form

$$I_t/I_0 = a\epsilon^{-\lambda_3 t} - (a - 1)\,\epsilon^{-\lambda_2 t} \quad . \quad . \quad . \quad (153)$$

where a is a numerical constant and λ_3 and λ_2 have the values $5 \cdot 86 \times 10^{-4}$ and $4 \cdot 31 \times 10^{-4}$ (sec.)$^{-1}$ respectively. It will be seen that the second of these gives a half value period of $26 \cdot 8$ minutes, the other a half value period of about $19 \cdot 8$ minutes.

Now we have already seen that the final rate of decay will be governed by the decay of the substance of longest period, irrespective of its position in the chain of decomposition. Hence we cannot immediately infer to which of the substances B or C the two constants refer.

Fortunately, however, it is possible to separate the two products. If the wire is heated to a temperature of some 600° C. surrounded by a cooled outer cylinder it is found that the activity can be separated into two parts, one part remaining on the wire while the other part is volatilized and condenses on the cool outer cylinder. The portion remaining

on the wire emits α-radiation and β-radiation, the activity in each case falling to half value in 19·5 minutes. The other portion is initially inactive but gradually begins to emit both α- and β-rays corresponding to those of the substance left behind on the wire. The shorter period therefore corresponds with the final product, radium C, which emits both α- and β-rays, while the longer period 26·8 minutes is that of the radium B which without emitting radiations is the direct parent of the radium C and the immediate product of the decomposition of radium A.

It has been found that the change from radium B to radium C is not entirely rayless. A quantity of slowly-moving β-particles comparable with the δ-rays are given off. These, however, have so little penetrating power that they are completely absorbed in the thickness of aluminium necessary to cut off the α-rays, and hence have no influence on the β-ray measurements. All the changes described as rayless are really of this nature.

Theoretical decay curves can be constructed from the equations in § 159, when the radio-active constants are known. They agree with those obtained experimentally to an accuracy of at least 1 per cent.

167. Separation of the products by the method of "recoil." Complex nature of radium C. Although the analysis of the radio-active product of short period was made in the manner explained above we have now a more powerful means of separating the various products of radio-active change. This can be done by making use of the "recoil" atoms already described. We have seen that the atom of radium A produced by the decomposition of radium emanation starts life with a velocity which will enable it to travel across several centimetres of gas at a sufficiently low pressure. The same considerations apply also to the atoms formed by the decomposition of radium A and indeed to any atoms whose formation is attended by the expulsion of an α-particle. Thus if we place the wire or plate carrying the induced activity in a vacuum at a short distance from another inactive plate, the atoms of radium B formed by the decomposition of radium A will in

many cases be shot across the intervening space, and collect on the inactive plate. In this way radium B of considerable purity can be obtained, since the atoms of radium C, which are formed from radium B with the emission of slowly moving β-particles only, have no appreciable velocity. The radium C thus remains on the active plate. The individual properties of the separate substances can thus be studied.

An application of this method to the case of radium C has led to interesting results. Most radio-active atoms disintegrate with the emission of either α-rays or β- and γ-rays but not both. Radium C, as we have noted, gives all three types. Pure radium C can be obtained from the radio-active deposit obtained from radon by dissolving it in acid, and suspending a nickel plate in the solution. The radium C is deposited on the plate, leaving the radium B in solution. It must be remembered that each radio-active product is an element with definite chemical properties, and differs from ordinary elements only in its instability. The various products can thus be separated by the usual methods of chemical analysis. If the nickel plate bearing the radium C is placed in vacuo near a negatively charged disk recoil atoms from the radium C collect on the disk, which thus becomes radio-active. It is found, however, that the properties of the radio-active substance thus collected are quite distinct from those of the normal product of the disintegration of radium C (which is known as radium D). Thus it has a half value period of 1·32 minutes as against 16 years for radium D. This new substance which has been called radium C″ gives out only β- and γ-rays of the same quality as those of radium C. Further, it does not give rise to radium D on disintegration.

We have here a case (the first one actually observed although others have now been recorded) in which a branch occurs in the radio-active chain. Radium C may disintegrate in two entirely different ways. Normally it emits a β-ray and gives rise ultimately to radium D. About 3 in 10,000 of the atoms, however, emit an α-particle and form an entirely different product radium C″, the disintegration product of which is not radio-active, and is probably an isotope of lead.

More exact analysis shews that the change from radium C to D is not direct. There is an intermediate substance, radium C', interposed. This has an exceedingly short life, about 1.5×10^{-8} sec., and gives rise to a swift α-particle. The series of changes we have been considering can thus be represented by the following chain:
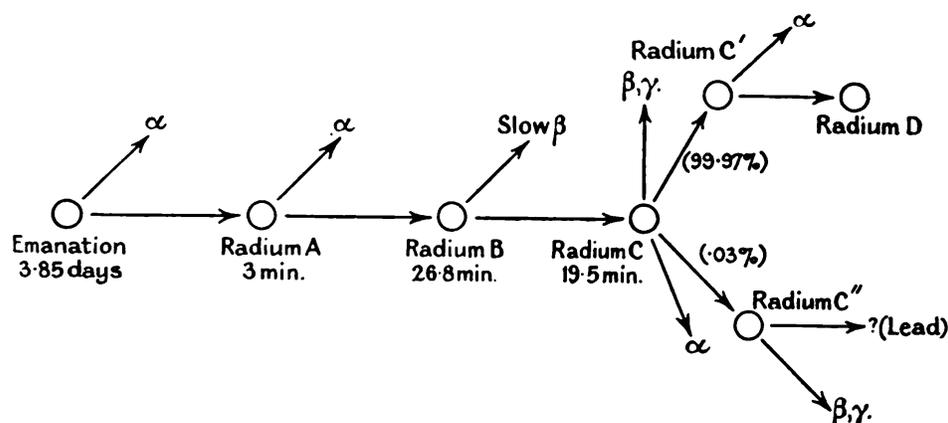
168. The radio-active product of slow change. As we have seen, radium C normally transforms into a product radium D. Radium D marks a period of comparative quiescence in the radio-active decay, its half value period being about 16.0 years. Owing to its long period it is present in minute but appreciable quantities in ores containing radium from which it can be separated by the chemical processes used for the separation of lead, to which metal indeed it bears so close a resemblance that no chemical test has yet been devised for distinguishing between them. Radium D gives out neither α- nor β-rays of the ordinary type. It has, however, been shewn to give off very slow β-rays (or δ-rays) of the type given off by radium B.

The succeeding product, radium E, gives off β- and γ-rays and has a period of 4.85 days. The relation between radium D and its immediate product is thus the same as that for uranium and uranium X, and the decay and recovery curves follow the same laws. Thus in freshly prepared radium D the β-ray activity rises according to equation (142) to a maximum which owing to the slow decay of radium D remains sensibly constant for a considerable time.

Radium F, the product of the decay of radium E, emits α-rays and decays to half value in 136 days. Its rate of decay and the range of its α-particles identify it with the substance polonium, the first radio-active substance actually isolated from pitchblende. The product of the disintegration of polonium is apparently not radio-active, no trace of any radiations being observed after the α-ray activity of the polonium has disappeared. The final product of the chain has with much probability been identified with lead.

The period of radium D is too long to be determined by direct measurements. It can, however, be deduced by indirect methods which form an interesting illustration of the principles we have been discussing. Suppose we commence with a definite quantity of radon, say, one millicurie. The number of atoms of radon present is then known from the determination of the curie already discussed (§ 163). Let it be N. The number of atoms breaking up per second at the beginning of the experiment is therefore $\lambda_1 N$, where λ_1 is the radio-active constant of radon. This will be the number of α-particles n_1, emitted per second, a quantity which we can determine by the method already described (§ 98).

The radon is then allowed to decay for a month or so at the end of which time it is practically all in the form of radium D. The number of atoms of radium D present is thus the same as the number of atoms of emanation with which we started, that is N, and the number breaking up per second is therefore $\lambda_2 N$ where λ_2 is the radio-active constant of radium D. Now radium D itself emits no α-particles. As, however, the period of radium D is long compared with that of its products E and F, the latter will be in radio-active equilibrium with it and hence the number of radium F particles breaking up per second will be the same as the number of radium D atoms disintegrating in the same time, that is $\lambda_2 N$. But this is the number n_2 of α-particles emitted per second by the mixture of radium D, E, and F in our tube, since D and E give no α-radiation. Hence

$$\frac{\lambda_2 N}{\lambda_1 N} = \frac{n_2}{n_1},$$

from which we can determine λ_2 since all the other quantities are known. The value of λ_2 is found to be $0\cdot043$ (year)$^{-1}$, corresponding to a half value period of 16 years.

170. **Relation between the radio-active constant and the energy of the α-particle.** Gamow has recently shewn that on the wave theory of matter the energy E of emission of an α-particle should be related to the radio-active constant λ of the element emitting it by an equation of the form

$$\log \lambda = a + b.E \quad . \quad . \quad . \quad . \quad (153)$$

where the constant a depends on the particular radio-active family to which the element belongs. A relation somewhat of this type was given on empirical grounds many years ago by Geiger and Nuttall. The relation is useful for determining approximately the radio-active constants in cases where direct determination is for some reason impossible. The constant for UII, for example, has been deduced in this way from the measured velocity of its α-rays.

170. **The radio-activity of thorium and actinium.** The element thorium is radio-active and gives rise to a chain of radio-active products in the same way as uranium gives rise to the radium chain. The disintegration process can be studied in detail by the methods already discussed, and involves no new principles. The results are sufficiently summarized in Table XV. For further details the books mentioned at the end of the chapter may be consulted.

Another element, actinium, isolated originally from pitchblende, also gives a radio-active chain of products. It is itself a product of uranium. It may be noted that very careful analysis has shewn that the disintegration of uranium is considerably more complex than we have described in the previous chapter. Uranium in fact contains two radio-active substances which can be differentiated by a slight difference in range of the α-particles which they emit. The disintegration of uranium I has been found to be complex, a small quantity of a new product,

uranium Y, being formed, in addition to the uranium X. There is thus a branching of the chain at uranium resembling that already described for radium C. This branch series has been shewn to give rise to the element actinium, one other radio-active substance (proto-actinium) of long, but as yet undetermined, period intervening.

171. Position of the radio-active elements in the Periodic Table. Since an α-particle has been shewn to be an atom of helium, the emission of an α-particle obviously produces a new atom with an atomic weight of four units less than that of the atom from which it was formed. On the other hand, the emission of a β-particle makes no sensible change in the atomic weight. Thus uranium I with an atomic weight of 238 loses an α-particle and changes into uranium X_1 which must thus have an atomic weight 234. The emission of a β-particle leaves the atomic weight unchanged so that 234 is also the atomic weight of both uranium X_2 and uranium II. Similarly, the atomic weight of ionium must be 230, that of radium 226, and that of radon 222. The two last results have, as we have seen, been verified by direct determination. The final product of the uranium and actinium series should thus have an atomic weight of 206 in each case, and that of the thorium series an atomic weight of 204. We have thus some 35 new elements to arrange in the nine spaces which occur in the periodic table between lead and uranium.

From a study of so much of the chemical behaviour of the radio-active elements as could be observed, Soddy suggested that the emission of an α-particle by a radio-active element produced a new element whose position in the table was two spaces to the left of that of the element from which it was formed. The emission of a β-particle moved the position of the new element one space to the right. Thus the emission of an α-particle by uranium I, which is placed in group VI of the periodic table, produces a new element uranium X_1 which should be placed in group IV of the table. Uranium X_2, formed from uranium X_1 by the emission of a β-particle only, would then occupy a position in group V, although its atomic weight is identical

with that of uranium X_1, and similarly uranium II, also of the same atomic weight, is placed in group VI in the same space in the table as the original uranium I, though differing from the latter in atomic weight by four units. The fact that uranium I

TABLE XIV

Uranium-Radium series

Substance and atomic number	Radio-active constant λ in (sec.)$^{-1}$	Half value period	Radiations emitted	Mean range of α-particles in air in cm.
92 Uranium I ...	$4 \cdot 9 \times 10^{-18}$	$4 \cdot 5 \times 10^9$ years	α	$2 \cdot 70$
90 Uranium X_1 ...	$3 \cdot 275 \times 10^{-7}$	$24 \cdot 5$ days	β (slow)	—
91 Uranium X_2	$1 \cdot 0 \times 10^{-2}$	$1 \cdot 15$ min.	β	—
92 Uranium II ...	2×10^{-14}	1×10^6 years	α	$3 \cdot 28$
90 Ionium ...	$2 \cdot 9 \times 10^{-13}$	$7 \cdot 6 \times 10^4$ years	α	$3 \cdot 194$
88 Radium ...	$1 \cdot 39 \times 10^{-11}$	1580 years	α	$3 \cdot 91$
86 Radon ...	$2 \cdot 097 \times 10^{-6}$	$3 \cdot 825$ days	α	$4 \cdot 014$
84 Radium A ...	$3 \cdot 78 \times 10^{-3}$	$3 \cdot 05$ min.	α	$4 \cdot 620$
82 Radium B ...	$4 \cdot 31 \times 10^{-4}$	$26 \cdot 8$ min.	β (slow)	—
83 Radium C* ...	$5 \cdot 86 \times 10^{-4}$	$19 \cdot 7$ min.	β	—
81 Radium C″	$8 \cdot 7 \times 10^{-3}$	$1 \cdot 32$ min.	β	—
84 Radium C′ ...	$4 \cdot 5 \times 10^7$	$1 \cdot 5 \times 10^{-8}$ sec.	α	$6 \cdot 870$
82 Radium D ...	$1 \cdot 37 \times 10^{-9}$	$16 \cdot 0$ years	β (slow)	—
83 Radium E ...	$1 \cdot 66 \times 10^{-6}$	$4 \cdot 85$ days	β (slow)	—
84 Radium F ... (Polonium)	$5 \cdot 88 \times 10^{-8}$	$136 \cdot 5$ days	α	$3 \cdot 805$
82 Lead ... (Uranium Lead)	—	—	—	—

* The production of radium C′ from radium C is attended by the expulsion of a β-particle only. The expulsion of an α-particle from radium C produces radium C″. As this α-particle gives rise to the branch series only, it is omitted from the table to avoid confusion.

C I   21

TABLE XV
Thorium and Actinium Series

Substance and atomic number	Radio-active constant λ in (sec.)$^{-1}$	Half value period	Radiations emitted	Mean range of α-particles in air in cm.
90 Thorium ...	$1\cdot3 \times 10^{-18}$	$1\cdot65 \times 10^{10}$ years	α	2·75
88 Mesothorium 1	$3\cdot26 \times 10^{-9}$	6·7 years	β (slow)	—
89 Mesothorium 2	$3\cdot14 \times 10^{-5}$	6·13 hours	β	—
90 Radiothorium	$1\cdot16 \times 10^{-8}$	1·90 years	α	3·81
88 Thorium X ...	$2\cdot20 \times 10^{-6}$	3·64 days	α	4·13
86 Thoron ...	$1\cdot27 \times 10^{-2}$	54·5 sec.	α	4·967
84 Thorium A ...	4·95	0·14 sec.	α	5·601
82 Thorium B ...	$1\cdot82 \times 10^{-5}$	10·6 hours	β (slow)	—
83 *Thorium C ...	$1\cdot90 \times 10^{-4}$	60·8 minutes	α β	4·729
84 Thorium C′	7×10^{10}	10^{-11} sec.	α	8·533
81 Thorium C″	3·61	3·20 sec.	β	—
82 Lead				
92 ?			(? α)	
90 Uranium Y ...	$5\cdot4 \times 10^{-6}$	1·5 days	β (slow)	—
91 Proto-actinium	$1\cdot9 \times 10^{-13}$	12,000 years	α	3·48
89 Actinium ...	$1\cdot08 \times 10^{-9}$	20 years	β	—
90 Radioactinium	$4\cdot24 \times 10^{-7}$	18·9 days	α β	4·43
88 Actinium X ...	$7\cdot14 \times 10^{-7}$	11·2 days	α	4·14
86 Actinon ...	$1\cdot77 \times 10^{-1}$	3·92 sec.	α	5·203
84 Actinium A ...	474	·0015 sec.	α	6·420
82 Actinium B ...	$3\cdot2 \times 10^{-4}$	36·0 min.	β (slow)	—
83 *Actinium C ...	$5\cdot35 \times 10^{-3}$	2·15 min.	α β	5·392
81 Actinium C″	—	—	β	—
84 Actinium C′	$2\cdot26 \times 10^{-3}$	4·71 min.	α	6·518
82 Lead				

* The C→C″ transformation is attended by the expulsion of an α-particle only; that from C→C′ by the expulsion of a β-particle.

and uranium II are inseparable by any chemical process gave weight to the assumptions.

It was considerations of this kind which lead Soddy to propound the theory of isotopes, which has been so brilliantly substantiated by Aston's experiments. As will be clear from Tables XIV and XV many of the radio-elements are isotopic, and differ only in the mass and stability of their nuclei. Thus all the emanations have the same atomic number, and fall into the same compartment of the periodic table. The significance of Soddy's rule is also obvious on our present nuclear theories. The emission of an α-particle reduces the nuclear charge, and hence the atomic number by two units, while the emission of a β-particle from the nucleus increases its positive charge and hence its atomic number by unity.

The appended table shews Soddy's classification for the whole of the elements in the uranium-radium series. To avoid confusion the actinium series and the thorium series have been omitted.

Table XVI

Classification of Radio-active Elements

At.Wt.	O	I	II	III	IV	V	VI	VII
206					Radio Lead			
210				RaC₂	RaD ———	—RaE—	—RaF	
214					RaB —	—RaC—	—RaC₁	
218							—RaA	
222	RaEm							
226			Ra					
230				Io				
234					UX₁ —	—UX₂—	→ U_II	
238							U_I	

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172. The end products of radio-active decay. It will be seen that the end product of each radio-active chain is an element of atomic number 82, that is, it is isotopic with lead. In the case of the uranium-radium series it is formed from uranium of atomic weight 238 with the emission of eight α-particles, and its mass should thus be 206. Similarly the atomic mass of the end product of the thorium chain should be 208, since thorium has an atomic mass of 232 and emits six α-particles during disintegration.

Uranium ores invariably contain small quantities of lead, and the ratio of the lead constant to that of uranium is approximately the same for all. This provides an indirect proof that the lead contained in the ore is a disintegration product of uranium, since it is highly improbable that the ores, which are widely distributed, should have all become contaminated to the same extent with lead from an extraneous source.

Lead has now been extracted from both uranium ores and thorium ores, and the atomic weights of the samples have been determined by purely chemical means. That from the uranium ores gives a value of 206·1; that from the thorium ores of about 208. The close agreement of these values with the predictions of the disintegration theory provides a very satisfactory confirmation of the theory.

Aston has examined the mass spectrum of lead separated from uranium ores, and finds that it gives a strong line of mass 206, a weaker line of mass 207, and a very faint line 208. In ordinary lead the line 208 is twice as strong as the line 207, so that the presence of the isotope 207 in the uranium lead cannot be due to infiltration of lead from some extraneous source. Aston makes the suggestion that it is the end product of the actinium chain. If so, all the elements in the actinium chain must have odd atomic weights, that of protoactinium being 231, since six α-particles are expelled during its transformation into lead.

Protoactinium cannot then be a product of the branching of the uranium chain as was originally suspected, but must be formed from still another isotope of uranium, probably of mass 235. The earlier stages in the actinium series are thus still uncertain. It is believed that UY which has been discovered in

uranium X forms part of the chain, but further evidence is much to be desired.

173. Production of helium from uranium. Geological age.

Since each α-particle is an atom of helium, helium must be in process of formation in all minerals containing uranium. The number of α-particles given out by one gram of uranium in equilibrium with all its products has been found to be $9 \cdot 7 \times 10^4$ per second. The number of atoms of helium formed per annum by one gram of uranium is thus

$$(9 \cdot 7 \times 10^4) \times 60 \times 60 \times 24 \times 365$$

or taking Avogadro's constant as $2 \cdot 7 \times 10^{19}$ molecules per c.c., about 11×10^{-5} cubic mm. The direct measurement of the rate at which helium is produced in uranium ores is in fair agreement with this estimate.

Thus if we can assume that the helium produced is all occluded by the mineral, the ratio of the helium to the uranium present affords us a method of estimating the age of the mineral. The results are found to be qualitatively consistent with the ages suggested by geological considerations, that is to say, the rocks of older formations give a higher ratio of helium to uranium than those ot more recent formation. Rayleigh, to whom most of our information is due, estimates the age of the oligocene rocks as eight million years, and the ages of the eocene, carboniferous, and archaean periods as respectively 31, 150 and 700 million years. Since there is always the possibility of a certain loss of helium from the rocks by diffusion into the air, these are obviously minimum estimates.

The ratio of lead to uranium may clearly also be used as a criterion of the age of the minerals. This will give a maximum estimate since loss of lead from the ore is improbable and on the other hand the presence of traces of ordinary lead in the original ore is always a possibility, although Aston's experiments (§ 172) seem to indicate that its amount is very small. The ages deduced from the lead contents are thus probably not far from the truth. In this way the age of the carboniferous rocks has been calculated as about 340 million years, and of the archaean rocks as about 1300 million years.

174.   The heating effect of radio-active bodies. Since the various radiations from radio-active substances are emitted with very high velocities it is evident that a radio-active substance is giving out energy at a very appreciable rate. If it is surrounded by sufficient material to absorb all the radiations this energy will manifest itself eventually in the form of heat. Thus radium is constantly producing heat and will maintain itself at an appreciably higher temperature than its surroundings. Owing to their relatively large mass the bulk of the energy is carried by the α-rays.

The heating effect of the α-rays can be calculated from their known velocities. Let n be the number of α-particles of velocity v emitted per second by each of the α-ray products present; n will be the same for each when equilibrium is established. The total energy of the α-rays is thus $\frac{1}{2}mn\Sigma v^2$ where m is the mass of an α-particle. To this we must add the energy of recoil of the various recoil atoms which as we have seen is m/M of that of the corresponding α-particle, where M is the mass of the recoil atom. Thus the total energy associated with the α-radiation is

$$\frac{1}{2}mn\ \Sigma\left(1+\frac{m}{M}\right)v^2.$$

For a gram of radium in equilibrium with its short period products this is equal to $1\cdot45 \times 10^6$ ergs per second, or about 125 gram calories per hour. If only the α-rays are absorbed in the apparatus this should be the rate of emission of heat by one gram of radium in equilibrium with its short lived products. If the radium has been prepared for several years so that an appreciable amount of polonium is present the heating effect of this must be added. If the apparatus, as is usually the case, absorbs an appreciable percentage of the β- and γ-rays the heating effect will be somewhat greater; if all the rays are absorbed it should be about 140 calories per hour, of which $6\cdot3$ calories are due to the β-rays and $9\cdot4$ calories to the γ-rays.

The heating effect of the α-rays can be measured most accurately by means of a differential resistance thermometer. The radio-active substance is contained in an aluminium tube, the walls of which are of sufficient thickness to stop all the α-

particles. Round the tube are wound two insulated coils of fine copper wire, which are connected in opposite arms of a Wheatstone bridge. The other arms of the bridge are formed by two similar coils also wound on a similar aluminium tube, and the whole system is enclosed in a thermostat. Any slight change in temperature of the surroundings as a whole will affect all four arms of the bridge equally. The change in resistance of the two coils round the source produced by the heat emitted by the radio-active substance will produce twice the effect on the bridge of a single coil, since the two are in opposite arms of the bridge.

The apparatus can be calibrated by passing a known current through a small heating coil of known resistance placed in the tube which is to contain the radio-active substance. In this way an emission of heat of the order of 0·005 cal. per hour can be detected. A small correction is required for the energy absorbed from the β- and γ-rays if any are emitted by the radio-active substance.

In this way Watson and Henderson were able to measure the emission of α-ray energy not only from radium in equilibrium with its products, but from each of the α-ray products separately. The experimental results were found to agree very closely with the values estimated from the known rate of emission and energy of the α-particles from the product.

They were able to verify that the rate of production of heat from a single product fell off exponentially with the time. Thus if H is the rate of emission of heat at the instant t, $H = H_0\epsilon^{-\lambda t}$, the coefficient λ of decay being identical with that of the substance deduced from ionization measurements. The heating effect of the β-rays from a β-ray product has been determined by Ellis in a similar manner, and agrees well with the value calculated from the known energies of emission of the β-particles.

The total heating effect of a curie of radon of volume 0·66 c.mm., when in equilibrium with its immediate products, is 113·6 cal. per hour. The total heat emitted by the radon during its complete disintegration into radium D is thus

$$\int_0^\infty H_0\epsilon^{-\lambda t}\, dt = H_0/\lambda,$$

where λ, the radio-active constant of radon, is $2 \cdot 085 \times 10^{-6}$ per sec., or $0 \cdot 0075$ per hour. This is equal to $1 \cdot 52 \times 10^4$ gram calories per curie, or $2 \cdot 2 \times 10^9$ gram calories per gm.

The formation of one gram of water is attended with the liberation of about $3 \cdot 8 \times 10^3$ calories of heat. It will be seen therefore that the heat liberated in any chemical reaction is infinitesimal compared with that produced by radio-active changes.

The source of this large amount of energy is probably to be found in the "packing" effect. The "packing" curve (Fig. 44) ascends slowly with increasing atomic number, after an atomic number of 30 has been reached. The transformation of an element of very high atomic number into elements of lower atomic number should thus be attended with loss of mass and hence with liberation of energy. The actual masses of the heavy elements have not yet been determined with sufficient accuracy to allow of a numerical test.

175. Radio-activity of ordinary matter. The air in an ionization chamber always shews a slight conductivity even in the absence of any recognized radio-active sources. A very considerable amount of labour has been spent in attempting to determine whether any of this ionization were due to a genuine radio-activity on the part of the ordinary materials forming the case of the chamber. The experiments are most conveniently carried out with a simple electroscope of the type shewn in Fig. 1.

The matter is complicated by the fact that radium, in minute traces, is widely disseminated. Many soils contain an appreciable quantity, and most river water is feebly radio-active owing to minute traces of radium salts. As radium emanation is a gas, traces of it are usually to be found in the air. Thus the air in the electroscope is subjected to γ-radiation from all these sources, in addition to the cosmic radiation discovered by Millikan. Attempts to shield the electroscope by heavy blocks of lead gave inconsistent results, probably owing to traces of radio-active material in the lead.

The most satisfactory experiments are those of Millikan

already described (§ 131). The mountain lakes of California and the Andes seem particularly free from radio-active impurities, and by sinking his electroscopes in their depths he was able to screen them from all outside radiations. Under these conditions the residual ionization was negligibly small; about 1 ion per c.c. per second. As a single α-particle will produce, on an average, about 30,000 ions per cm., the passage of a single α-particle through each cubic centimetre of the gas once every eight hours or so would be sufficient to account for the residual effects. The quantity of a known radio-active material necessary to produce such a trifling emission is so minute that its absence could never be certified. We must conclude that there is no evidence for any radio-activity among ordinary elements.

The survey of the subject has, however, led to the discovery of another radio-active substance, namely potassium, which is found to emit β-radiation of very much the same type as that from uranium accompanied by γ-rays of a peculiarly penetrating type. The activity of a surface of potassium salt is quite appreciable, being in general about one per cent. of that of a surface of a salt of uranium. Rubidium has also been found to possess a similar radio-activity. It is possible that in both cases the effect may be due to a particular isotope of the element, the nucleus of which is very slightly unstable. Since the disintegration gives rise to a β-particle only, the product of disintegration in the case of potassium should be an isotope of calcium, and in the case of rubidium, an isotope of strontium.

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TABLE XVII

Some Atomic Data

Electronic charge, e	$4 \cdot 770 \times 10^{-10}$ e.s.u.
	$1 \cdot 591 \times 10^{-20}$ e.m.u.
e/m for electron	$1 \cdot 761 \times 10^7$ e.m.u. per gm.
Mass of electron	$9 \cdot 035 \times 10^{-28}$ gm.
h, Planck's constant	$6 \cdot 547 \times 10^{-27}$ erg sec.
A_0, mass of an atom of unit atomic weight [$O = 16 \cdot 00$]	$1 \cdot 649 \times 10^{-24}$ gm.
M_p/m, ratio of mass of proton to mass of electron	1838
Avogadro's number	$6 \cdot 064 \times 10^{23}$ per mol.
Boltzmann's constant α or gas constant per molecule	$1 \cdot 371 \times 10^{-16}$ erg per degree
Faraday constant	9649 e.m.u. per gm. equiv.
1 electron-volt	$1 \cdot 591 \times 10^{-12}$ erg
Bohr magneton μ	$0 \cdot 917 \times 10^{-20}$ erg per gauss

The values in this table are mainly those advocated by Birge (*Phys. Rev. Supplement*, Vol. I, 1929). There is some uncertainty, amounting perhaps to $\frac{1}{2}$ per cent., in the value for e/m. For a discussion of these values see Bond, *Phys. Soc. Proc.* p. 374, 1932.

MISCELLANEOUS EXAMPLES

1. Assuming that the vertical potential gradient in the air near the ground is 100 volts per metre, and the vertical electric current density through the air is 3×10^{-16} amp. per sq. cm., how many ions of average mobility 1·5 cm./sec. per volt/cm. are there in each c.c. of air? [*Ans.* 1260 per c.c.]

2. The coefficient of diffusion of positive ions in oxygen is 0·025, and the mobility of the ions is 1·36 cm./sec. per volt/cm. Calculate the total charge carried by unit volume of oxygen at N.T.P. if all the molecules were ionized. [*Ans.* $1 \cdot 65 \times 10^{10}$ e.s.u./c.c.]

3. A volume of 500 c.c. of saturated air at 15° C. is expanded adiabatically so that its volume is increased by 30 per cent. What is the final temperature after expansion, and what mass of water will be deposited? [*Ans.* $-13 \cdot 7°$ C.; 0·0054 gm.]

4. A drop of oil of density 0·920 gm./c.c. falls freely under gravity in air of viscosity $0 \cdot 824 \times 10^{-4}$ c.g.s. with a uniform velocity of 0·0858 cm./sec. When a vertical electric field of 3180 volt/cm. is applied the drop moves at various speeds which differ from each other by small multiples of 0·00539 cm./sec. Calculate a value for the electronic charge. [*Ans.* $4 \cdot 88 \times 10^{-10}$ e.s.u.]

5. What is meant by an electron-volt? Calculate in electron-volts the energy (*a*) of a cathode particle moving with a velocity of 10^9 cm. per sec., (*b*) of an α-particle with a velocity of 10^9 cm. per sec., (*c*) of a quantum of sodium light of wave length $5 \cdot 89 \times 10^{-5}$ cm.
[*Ans.* (*a*) 283, (*b*) $2 \cdot 08 \times 10^6$, (*c*) 2·1]

6. According to Langmuir the energy necessary to dissociate into atoms one gram molecule of hydrogen molecules is 84,000 calories. Express this result in electron-volts per molecule. [*Ans.* 3·65]

7. The first radiation potential of mercury is 4·9 volts. Mercury when bombarded by electrons at this potential emits a single spectral line of wave length $2 \cdot 536 \times 10^{-5}$ cm. Discuss these observations.

8. A linear source of homogeneous β-particles is placed parallel to the lines of force in a uniform magnetic field. The β-particles are limited to a narrow pencil by passing through a narrow slit placed parallel to the source. Show that the pencil of β-particles will be brought to a linear focus and find its position.

9. In one of Thomson's early experiments on cathode rays, the cathode stream passed through coterminous electric and magnetic fields for a distance of 5 cm., entering the fields in a direction at right angles to the lines of force. The beam was undeflected when the fields were respectively 100 volt/cm. and 3·6 gauss. The magnetic field alone produced a deflection of 3° 40′. Calculate values for e/m, and the velocity of the particles.

[*Ans.* 0·99 × 10⁷ e.m.u./gm.; 2·78 × 10⁹ cm./sec.]

10. Positive rays are generated in a discharge tube working on 30,000 volts. What is the minimum deflection which the particles can experience in passing between a pair of plates 5 cm. in length and 1 cm. apart, charged to a P.D. of 200 volts, assuming that the charge on the particle remains constant throughout its course? What will be the deflection if the particle has a charge of $8e$ in the discharge tube and loses $7e$ between leaving the discharge tube and reaching the plates?   [*Ans.* 0·95₅°; 0·11₉°]

11. Taking the atomic mass of hydrogen as 1·00778 and that of helium as 4·00216, calculate the packing fractions for these two atoms. Calculate also (*a*) in calories, (*b*) in volts the energy liberated if 4 atoms of hydrogen were condensed to form an atom of helium. If the energy were liberated as monochromatic radiation calculate the wave length of the radiation.

[*Ans.* (*a*) 1·03 × 10⁻¹² cal.; (*b*) 2·70 × 10⁷ ε-volts; (*c*) 4·57 × 10⁻¹² cm.]

12. A pair of parallel zinc plates in air are connected to the 210 volt 50 cycle mains, and ions are formed at the surface of the lower plate by illuminating it with ultraviolet light. What is the greatest distance of separation at which the upper plate can receive a negative charge, assuming the mobility of the ions to be 1·5 cm./sec. per volt/cm.?   [*Ans.* 1·32 cm.]

13. How many quanta of radiation of wave length 5 × 10⁻⁵ cm. must fall per sec. on a blackened plate to produce a force of 1 dyne? If the mass of the plate is 1 gm. and its specific heat 0·1 at what rate would its temperature rise?

[*Ans.* 7·6 × 10²¹ quanta per sec.; 7·2 × 10³ °C. per sec.]

14. What is the minimum wave length in the spectrum of an X-ray tube working at 100,000 volts?   [*Ans.* 0·12 × 10⁻⁸ cm.]

15. Derive an expression for the Compton change of wave length on scattering. According to Sharp the Compton change amounts to 0·04825 × 10⁻⁸ cm. at an angle of 169° 45′ with the direction of the primary beam. Assuming that h/e is 1·372 × 10⁻¹⁷ estimate the value of e/m for the electron.   [*Ans.* 1·772 × 10⁷ e.m.u./gm.]

16. The K_a radiation from palladium is reflected in the first order from sylvine at glancing angles of 5° 23′ from the {100} planes, 7° 37′

from the {110} planes, and 9° 23′ from the {111} planes. To what order of cubic symmetry would you assign this crystal on this evidence?

[*Ans.* simple cubic]

17. The wave length of Mo. K_{a_1} radiation as measured by a reflection grating is 0.7083×10^{-8} cm. The glancing angle in the third order from the {100} planes of rock salt is 22° 10′. What value does this give for the lattice constant of rock salt? Assuming that the density of rock salt is 2·170 gm./c.c. and the atomic weights of sodium and chlorine are 23·00 and 35·46, what value do these measurements give for the electronic charge?

[*Ans.* 2.816×10^{-8} cm.; 4.79×10^{-10} e.s.u.]

18. If Q α-particles fall normally on a scattering foil of thickness t show that the number y of α-particles falling on unit area of a fluorescent screen placed at a distance r from the foil and in a direction making an angle ϕ with the incident particles is given by

$$y = \frac{Qntb^2 \operatorname{cosec}^4 (\phi/2)}{16r^2},$$

where n and b have the meaning assigned in § 105.

19. Assuming that the mass of an α-particle is 6.6×10^{-24} gm. and its velocity 1.92×10^9 cm./sec., calculate the intensity of illumination of a fluorescent screen on which α-particles fall at the rate of 1000 per sec. per sq. cm. The efficiency of the α-particles as a light source may be assumed to be 1 watt per candle. [*Ans.* 1.2×10^{-9} candles]

20. Calculate, on Bohr's theory, the velocity of an electron in the innermost orbit of the hydrogen atom. [*Ans.* 2.18×10^8 cm./sec.]

21. Calculate, on the wave mechanic theory, the wave length associated with (*a*) an electron moving with the speed of the electron in the K-ring of the hydrogen atom, (*b*) the particle from radium C′, (*c*) a molecule of hydrogen gas at 0° C. (its velocity $= 1.84 \times 10^4$ cm. per sec. at 0° C.).

[*Ans.* (*a*) 3.3×10^{-8} cm., (*b*) 5.17×10^{-13} cm., (*c*) 2.15×10^{-8} cm.]

22. Assuming that the nucleus of "heavy" hydrogen has a mass twice that of ordinary hydrogen, calculate the difference in wave numbers of the H line of ordinary hydrogen and the H line of "heavy" hydrogen. Assume the values for the Rydberg constant of hydrogen and the ratio of the masses of proton and electron given on page 267.

[*Ans.* 4.2 cm.$^{-1}$]

23. When boron is bombarded with protons generated at 100,000 volts the boron nucleus disintegrates into three α-particles. Calculate, in electron-volts, the energy liberated in each disintegration (the atomic masses of hydrogen, helium and boron are 1·0078, 4·00216 and 11·0110 respectively). [*Ans.* 11.7×10^6]

24. Calculate the energy set free by the mutual annihilation of an electron and a proton. If this energy is radiated as a single quantum, calculate its wave length.

[*Ans.* 1.495×10^{-3} erg; 1.31×10^{-13} cm.]

25. A radio-active element P has a half value period of 20 years, and the succeeding products Q, and R, half value periods of 19.5 and 11.4 days respectively. A quantity of P is left in a closed vessel for several months. Calculate the relative numbers of atoms of the three substances which will then be present.   [*Ans.* $1 : 0.0027 : 0.0016$]

26. Assuming that the atomic mass of radon is 222 and its radio-active constant is 2.1×10^{-6} per sec., calculate (*a*) the number of α-particles emitted per sec. by 1 gm. of radon when free from its disintegration products, (*b*) the volume of helium formed during the complete transformation of radon into radium D.

[*Ans.* 5.7×10^{15}; 304 c.c.]

27. 100 millicuries of radon are contained in a capillary glass tube 5 cm. long, with internal and external diameters of 2 mm. and 6 mm. respectively. Assuming that the thermal conductivity of glass is 0.001, and that the particles are stopped at the inner surface, what will be the difference in temperature between the inner and outer walls of the tube?   [*Ans.* $0.106°$ C.]

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