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THE STRUCTURE OF THE ATOM

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MODERN ELECTRICAL THEORY

SUPPLEMENTARY CHAPTERS

CHAPTER XVII

THE STRUCTURE OF THE ATOM

BY

NORMAN ROBERT CAMPBELL, Sc.D.

A MEMBER OF THE RESEARCH STAFF OF THE
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PREFACE[1]

THE apologies which were offered for Chapter XVI have no place here; most of Modern Electrical Theory centres round the structure of the atom. But the very importance of the subject has made this chapter the most difficult to write, as it is the longest. The variety of the sources whence evidence is adduced is so great and the theories invented to interpret that evidence so numerous that it has been almost impossible to follow the general scheme of this book, and to tell a connected story grouped round a few fundamental conceptions. I have done my best not to depart from a practice that seems to give satisfaction, but here my best is not very good. Again, even after the greatest care in selection has been exercised (with results that are sure not to meet with universal approval), the range of mere facts to be covered is so great that I have been only too often conscious that an adequate presentation of my subject requires more time for study and a greater width of information than I can bring to the task; I can only apologise beforehand for the many errors that I know must exist.

But there is one kind of error with which I am likely to be charged concerning which some explanation seems desirable. In this chapter, more than in any other, the difficulty arises what authors are to be mentioned by name. In general my principle is to mention names only where the reader is sure to meet with them in the original memoirs which it is the purpose of this book to enable him to study; work is associated with the name of a particular author only when that association represents general practice. But here there are several important ideas concerning the attribution of which there is no general agreement; and though nothing is further from my purpose than to take any part in barren wranglings concerning priority, it is difficult to avoid seeming to offer some opinion. The truth is that almost all the successful ideas in the modern theory of atomic structure have cropped up in

[1] The nature and purpose of these supplementary chapters is explained in the Preface to Ch. XV.

the endless speculations that have been made some time before they were finally established. In attributing any of these ideas to a particular worker I have followed the principle that, for the purposes of science, the author of an idea is he who first uses it to explain facts. Theories exist to explain facts, and an idea for which there is no experimental evidence is not part of a scientific theory. If this principle were abandoned, we should have to recognise Lucretius or Pythagoras, rather than Dalton, as the founder of modern atomic theory. What is important for science is not that matter "really" consists (whatever that may mean) of indivisible particles, but that by assuming that it does so consist we can explain the general laws of chemistry.

But the principle can be pressed too far, and by the following of it here sufficient prominence has not been given to the work of J. J. Thomson. Those who were studying physics 20 years ago will need no reminder, still less those who shared with me the privileges of pupils. But to the rising generation it may be well to point out that the magnificent structure that Rutherford and Bohr have raised rests on the foundations that he laid.

Once more I am indebted to my colleague, Mr J. W. Ryde, for unwearying care and invaluable advice in revision. And I have a less definite acknowledgement to make. When I was planning these chapters, I hoped that I should get others to write most of them. I was much too sanguine. Of eight physicists whom I approached only one returned anything but a blank negative. Prof. Andrade, his good nature overcoming his better judgement, consented to try to run in double-harness with me. He had written, and I had read, quite half of the chapter before he realised his error. Of course I have not consciously used any of his work; but if any reader should find in this volume any idea obviously too intelligent to be attributed to its nominal author, he will know the reason and assign the credit rightly.

N. R. C.

April, 1923.

CONTENTS

SOME CONSTANTS AND SYMBOLS

ϵ	electronic charge	$=4{\cdot}77\times10^{-10}$ c.g.s.e.s.	($\log\overline{10}{\cdot}6780$)
μ	mass of electron	$=8{\cdot}83\times10^{-28}$ gm.	($\log\overline{28}{\cdot}9460$)
c	velocity of light	$=3\times10^{10}$ cm./sec.	($\log\overline{10}{\cdot}4771$)
h	quantum constant	$=6{\cdot}56\times10^{-27}$ ergs	($\log\overline{27}{\cdot}8169$)
N	Rydberg's number	$=1{\cdot}097\times10^{5}$ cm.$^{-1}$	($\log 5{\cdot}0404$)
m_H	mass of H atom	$=1{\cdot}660\times10^{-24}$ gm.	($\log\overline{24}{\cdot}2200$)
R	gas constant for 1 gm. mol.	$=8{\cdot}31\times10^{7}$ dyne cm./degree	($\log 7{\cdot}9197$)
N_0	no. of mols. in 1 gm. mol.	$=6{\cdot}16\times10^{23}$	($\log 23{\cdot}7896$)

Å	Ångstrom unit $=10^{-8}$ cm.
Z	atomic number
A	atomic mass referred to O = 16
$\bar{A}$	mean atomic mass of isotopic group
γ, δ	screening constants
e, E	nuclear charge
λ	radioactive decay constant
ν	frequency of spectral line
n, n', k	total, radial, azimuthal quantum numbers
n_k	term (or orbit) of quantum numbers n, k
p, q	number of hydrogen nuclei and electrons in nucleus
R	range of α-rays (also gas constant above)
T	spectral term
W, W_r, w_r	energy of electronic orbit

ERRATA

Further to CHAP. XV

p. 8, the oxygen group should be included among the elements having typical series spectra.

p. 24. Table I. In first line for 6·17 read 8·41 and for 1·257 read 1·232.

CHAP. XVI

p. 27, l. 20, for c read $\sqrt{c^2 - v^2}$ (twice).

p. 113, l. 4 from bottom, for "manner" read "matter".

THE STRUCTURE OF THE ATOM

INTRODUCTION

1. **The earlier work.** The modern theory of the structure of the atom starts from the discovery of the electron. Before that discovery was made, there was no direct evidence that atoms had a structure at all; there was no experiment which could be explained only by the assumption that an atom is divisible into several parts. Such evidence appeared first when electrons were identified in the cathode rays. The experiments that proved that they were parts of atoms proved also that they were common parts, interchangeable between atoms of different kinds. The question naturally arose whether the different properties of the atoms of the various elements could be attributed to differences in the number and the arrangement of these parts, common to all.

But the atom could not consist of electrons only if the familiar laws of the electromagnetic field were true; and if they were not true, there was no evidence for the existence of electrons. Electrons are negatively charged; atoms are often electrically neutral; there must be some positively charged part of the atom. Further it was certain—again if those laws were true—that the positive part could not be a particle. No system of discrete and separate particles under their mutual electrostatic attractions and repulsions could be stable; such a system must either coalesce or disperse. If, on the other hand, it was supposed that the forces were not purely electrostatic, but partly electromagnetic and due to the relative motions of the particles, then it was certain that any system consisting of moving particles must radiate energy and lose energy; permanent unchanging atoms would be impossible. The only remaining alternative was that the positive charge was not concentrated on discrete particles, but distributed continuously over a space in which the electrons were imbedded. Simplicity led naturally to the investigation in the first instance of a uniform distribution of positive electricity throughout a sphere.

Such were the considerations that led Kelvin to the first electronic theory of atomic structure, which was advanced independently and greatly elaborated by J. J. Thomson. The theory is known now to be false; but no account of atomic theory would be complete without some mention of it. For up to a point it was very successful, and many of its ideas have reappeared almost unchanged in later theories. The success of a theory so far from the truth warns us that here an apparent agreement with experiment is not a safe guide, unless it is very far-reaching and very complete. There are some facts explicable in outline by the simple assumption that electrons are parts of atoms; and the partial explanation of these facts is a necessary consequence of any electronic theory. Thus any electronic theory will predict frequencies for the vibrations of atoms which are of the right order of magnitude to account for optical spectra. Any theory which supposes that atoms are distinguished by the number of their electrons, this number increasing with the atomic weight, will suggest periodicity in properties; for as the number of electrons is increased, some features of their arrangement are almost sure to recur. And any theory which supposes that atoms can lose or gain electrons can account for some kinds of chemical combination on the lines suggested long ago by Berzelius.

But the idea of Thomson's theory which has proved most permanent concerns the number of electrons in atoms. Thomson brought forward evidence from several sources (not all of which appear now to be reliable) that the number of electrons in the atoms of the various elements was about half their atomic weight. Now if the elements are arranged in the familiar sequence (which is roughly that of increasing atomic weight) characteristic of the periodic table, the increase in atomic weight in passing from one element to the next is about 2; actually it is 237 for the 91 steps from hydrogen to uranium. The conclusion is naturally suggested that the passage indicates an increase of one in the number of electrons, that hydrogen has one electron, helium two and so on. This conclusion is involved implicitly in all Thomson's speculations concerning the periodic table and the chemical properties of atoms. It was first put forward explicitly by van den Broek on the basis of evidence derived from radioactivity; it was finally established

by the work of Rutherford and Moseley. By the time it was established, the positive sphere theory had been abandoned, but it is important to realise that it is as much a consequence of that theory as of any other. Since the number of electrons in any atom, estimated in this manner, is far too small to account for any but an inappreciable fraction of the atomic weight, it followed, as Thomson had always maintained in the face of some arguments to the contrary, that the main part of the mass of the atom must lie in the positively charged portion.

2. **The Rutherford-Bohr atom.** The positive sphere theory, which had always presented serious difficulties, received its death blow when Rutherford proved indubitably that the main part of the mass of the atom and the positive charge required to neutralise all the electrons resided in a particle of dimensions far smaller than could be attributed to the atom as a whole. The positive portion must be a 'nucleus' of electronic rather than atomic dimensions, and the electrons must surround rather than be imbedded in it. A 'planetary' atom of this type had previously been suggested by Nagaoka, who however had not used it to explain anything which could not be explained equally well by the positive sphere atom. Rutherford's experiments produced the evidence necessary to convert a vague speculation into a theory of scientific value. But his theory necessarily involved the rejection of fundamental electrodynamic principles, according to which no such atom could be stable and permanent; for the moment there was nothing to put in their place. The dilemma was soon resolved. Within two years Bohr propounded his theory of atomic orbits, discussed in Chap. XV, and progress was once more possible along the path of his new principles.

Nobody today would think it worth while to discuss in detail any but a nuclear atom. And, as it seems to me, if we accept Rutherford's atom, we must also accept Bohr's principles which make it possible. Stated in the broadest manner, those principles are that classical electrodynamics provide a necessary, but not a sufficient, criterion for determining electronic arrangements. No arrangement is possible that would not be permissible (as distinct from stable or permanent) according to classical theory; but of

the arrangements so permissible only some fulfil a further condition that is necessary to actual existence[1]. But the reader should be warned that in accepting those principles for the determination of atomic structure, we are making them, in all probability, eternally inexplicable. For the various attempts that are made from time to time to explain quantum principles in terms of older conceptions all involve some special structure of the atom, which is on the one hand consistent with classical theory and on the other such as to make the atom behave effectively in accordance with quantum theory. It is impossible to adduce any kind of formal proof that such attempts are mistaken; any hypothesis can be made consistent with any facts if sufficient additional hypotheses are added. We must ultimately make the decision whether a theory which makes atomic structure a delicately balanced mechanism in which conflicting requirements are reconciled by ever increasing complexity of design really provides any explanation. For myself I have no doubt how to make the decision; and neither in this chapter nor in any other do I propose to take any account whatever of such attempts. Quantum principles as they are gradually elaborated in increasing beauty and simplicity to cover wider and yet wider regions of fact will always be the basis of our study. We shall accept them as the bed-rock of theoretical physics, and no more seek to ask why they are true than we ask why two charged particles should attract according to the inverse square law or why acceleration should be proportional to force. If he wants to regard the matter otherwise the reader must go elsewhere.

3. **Atomic number and isotopes.** Before we start on our detailed inquiry it will be well to sketch very briefly the theory we are going to discuss. Its outline is probably familiar to everyone who takes this book in hand: to refuse to describe its chief conceptions until evidence of their validity can be brought would be mere pedantry. The atom, according to the Rutherford-Bohr model, consists of a positively charged nucleus about which revolve electrons in quantum orbits. The great majority of the properties of the atom depend on the number and form of these orbits; and this number and form are determined again almost wholly by the charge on the

[1] See further footnote to p. 59.

nucleus. The mass of the nucleus is so great compared with that of an electron that, in reactions with electrons, it may be taken as infinite. Accordingly the mass of the nucleus (which is practically the same thing as the atomic mass), so far from being one of the most important properties of the atom, is one of the least important, except for certain purely practical purposes. The part played in classical chemistry by atomic weight will be played in most of our theory by the nuclear charge. This charge is always an exact integral multiple Ze of the electronic charge ϵ. Z is called the atomic number. In the list of the elements in Table I at the end of this chapter the number on the left of the conventional symbol of the element is its atomic number.

It will be seen that certain numbers are left vacant; they belong to elements not yet identified, which every modern electronic theory requires to be possible. In view of the interest chemists have always displayed in discovering new elements, it might seem that any element (with the possible exception of radioactive elements, which are almost all of atomic number greater than 80) which has not been identified so far can hardly exist among the material open to our inspection. And that was the view expressed in this place a few weeks ago. Quite recently, however, one of the elements previously missing (72) has been shown by Coster and Hevesy to be quite common and very widely distributed. Clearly it is too early to despair of the remainder. The truth is that only in the last few years have we had in X-ray spectroscopy the first adequate means of searching for and identifying elements.

In its normal state the number of electrons surrounding the nucleus is Z, and the atom is electrically neutral. When we mention an atom in this state (and indeed whenever we mention it without definitely implying that it is not in this state) we shall denote it by the conventional symbol of chemistry followed by the atomic number in brackets, thus: He (2), Na (11). When it contains a number of electrons other than the normal, this number will be substituted in the brackets; thus Na (10) will mean a sodium atom which has one electron less than the normal number and therefore bears a single positive charge. When the nucleus is mentioned, the brackets and the number in them will be omitted; thus He means the helium nucleus, which carries two positive charges. If much

depended on the reader immediately recognising from the symbol what charge is borne by the atom, the notation might be inconvenient; but actually it will always be clear from the context. However, the reader should realise that it is important nowadays that he should know immediately the atomic numbers of all the more important elements, just as an analyst is expected to know their atomic weights[1].

If it had been known thirty years ago that the mass of an atom had very little effect on all but a very small group of its properties, and in particular had practically no effect on its spectrum or chemical properties, doubts might have been raised whether all the atoms of what was classed as a single element had really the same mass. Such doubts, we know now, would have been justified. Fajans and Soddy arrived simultaneously at the conclusion that certain of the radioactive elements, perfectly distinct in their radioactive properties, must be almost identical in all others, and in respect of almost every property except radioactivity and mass should be regarded as the same element. To such elements, which would be placed in the same position in the periodic table, Soddy gave the name 'isotopes'. Isotopes are elements of the same atomic number and the same nuclear charge, but of different mass. They are not confined to the radioactive elements; J. J. Thomson suggested and Aston clearly established that neon in reality consists of two isotopes; and Aston has subsequently shown that mixed elements, consisting of several isotopes, are the rule and pure elements, the atoms of which all have the same mass, the exception. In Table I the masses of the various isotopes constituting the elements, referred in accordance with chemical custom to $O = 16$, are given after the conventional symbols where they are known; doubtful determinations being indicated by queries. (It is a very fortunate coincidence that oxygen happens to be a pure element.) Where the existence or the nature of isotopes is still undetermined, no mass

[1] Of course it is to be hoped that, since there is now something more important to record about an element than the fancy of its discoverer, some reasonable and scientific system of naming and denoting elements will be devised to take the place of a mere legacy from alchemy. But the problem is not easy; and the attempts to devise a system even for the limited class of radioactive elements have not been sufficiently successful to receive general recognition.

is given; the mean atomic weight of isotopes, which is all that we know in such cases, is of interest only to analysts.

A satisfactory nomenclature and notation for isotopes has not yet been invented. Aston has earned the gratitude of the scientific world by not attaching to all that he has discovered a series of pet names of his own devising. But it is usual to distinguish isotopes by an affix to the conventional symbol giving the atomic mass; thus Cl_{35} or Cl^{35}; but we shall not often have occasion to use this notation. The isotopes in radioactive elements can be distinguished without determination of their mass, and here the notation is determined by radioactive theory. When the whole group is mentioned the symbol of the most prominent member is usually employed; thus Pb(82) means the whole group. The Germans call a group of isotopic elements a 'Pleiad', but the term is apparently too picturesque for naturalisation in the English-speaking world. In what follows the true atomic weight of isotopes will be denoted by A; the mean atomic weight of an isotopic group by $\bar{A}$.

Just as we may have atoms of the same nuclear charge and different mass, so we may have atoms of the same mass but different nuclear charge; A^{40} (18) and Ca^{40} (20) give an example. Such elements are called 'isobares'; but the conception is not important. It is further possible that there may be isotopes which are also isobares and yet differ in some of their properties, especially radioactivity. But the existence of such pairs or groups does not seem to be established.

4. **Classification of atomic properties.** One further matter remains for discussion in this introduction. It might seem that a chapter on the structure of the atom must be in effect a compendium of all physics and all chemistry, if not of all human knowledge. For everything that we experience is a manifestation of the reactions of atoms and a complete theory of the structure of the atom should explain all their activities. But it is easy to set a limit to our inquiry. There are certain properties of material bodies which we associate much more closely than others with the properties of the atoms contained in them. They fall into two classes; in the first we have reason to believe that the property is actually the manifestation of the reactions of the atom when it is

under no external influence; to this class belong optical spectra, ionisation potentials, and other properties closely associated with them. In the second class, although the atom is probably not free from external influence, we find that the property is independent of that external influence; it is the same so long as the atom is the same, whatever its circumstances, and it is natural to conclude that it would be unaltered if we could realise the circumstances necessary to place it in the first class. To this second class belong X-ray spectra, radioactivity and the reactions of atoms to various kinds of rays. Properties of these two classes give us much the most definite evidence concerning atomic structure, and to them we shall pay attention first. We shall call them atomic properties; for though that name is usually confined to the second class, it is equally appropriate to the first for our present purpose.

When we have thus investigated the atom in isolation, we shall attempt to apply our conclusions to the atom in combination. At the outset of our inquiry we shall find a serious difficulty which arises from a doubt how far atoms when in combination retain their individuality: this difficulty may be left till it arises. But another more serious obstacle hinders this part of our study; we shall find ourselves much more doubtful than in the earlier part how to interpret the experimental evidence in terms of atomic structure. For it must be remembered that we never observe that structure directly; all that we can observe is something related by some well-founded theory to a distribution of electric charges, such as we imagine to compose the atom. And it so happens that the theories available to establish such relations are much less complete and much less certain for non-atomic properties than are those for atomic properties. This is the real obstacle at the present time to the full explanation of atomic combinations. But we have already good reason to believe that the complete explanation of some properties in combination will naturally follow from that of others; thus it is known that all mechanical properties are closely connected with each other and with thermal properties, and that if we can find some reason for associating any one of these connected properties with the structure we have determined from the atomic properties, we shall have gone as far as we can hope towards solving the problems presented by the whole group; the further development of

the explanation must wait on the progress of branches of the science that are not usually regarded as concerned with atomic theory.

Finally it will be convenient to make a division among the atomic properties which will be our chief study. Some properties can be regarded as belonging to the nucleus, others as belonging to the electrons which surround it. The distinction must not be pressed too far, for it is undoubtedly the properties of the nucleus which determine those of the electrons, but it will be useful in ordering the very miscellaneous data that we have to discuss. On the other hand we shall not adopt the usual but still less formally legitimate distinction between permanent and temporary electrons, the latter being generally called 'valency' electrons. For though the distinction undoubtedly represents an important feature in atomic structure, it is more fitly discussed by means of our division between atomic and non-atomic properties.

SECTION I

THE NUCLEUS

(*a*) *The charge on the nucleus*

5. **The scattering of charged particles.** The first definite evidence concerning the nucleus was derived from the study of the passage of charged particles (α- and β-rays) through thin material films.

When such rays pass through material bodies they suffer changes of two kinds. First, the particles are deflected from their original direction, the rays being scattered to a greater or less extent; second, the velocity of the particles is diminished and some actually stopped, so that the rays are absorbed. The earliest electronic theories of atomic structure recognised that scattering and absorption were due to the encounters between the particles and the charged centres, electrons and positive spheres or nuclei, of which the atom consists. We will therefore proceed at once to consider such encounters.

In Fig. 1 let the particle P, of mass m and bearing a charge e, enter a material medium at an infinite distance from the centre S along the line PO; let its initial velocity relative to the medium be v. It encounters the centre S, of mass M and bearing charge E, which forms part of the medium and is initially at rest relative to it; S is supposed to be so far from all other centres that they exert no influence on the encounter. (The particle and the centre may be precisely similar; thus they may both be electrons; but it is convenient to distinguish them.) Let $SN = p$ be the closest distance within which the particle would approach the centre, if it were undeflected. Actually it is deflected along the path PAP'. Let NOP', the angle of deflection, be ϕ; and let v' be the final velocity with which the deflected particle recedes. The centre will be set in motion relative to the medium with a final velocity U' making with NP an angle θ, measured in the same direction as ϕ.

We assume that the total momentum and energy of the particle and centre remains unchanged during the action, thus neglecting

the effect of any radiation that may be emitted. Then

$$mv = mv' \cos\phi + MU' \cos\theta \quad \text{.....(11.1)},$$

$$0 = mv' \sin\phi + MU' \sin\theta \quad \text{.....(11.2)},$$

$$mv^2 = mv'^2 + MU'^2 \quad \text{.....(11.3)},$$

which give

$$U' = 2v \cdot \frac{m}{m+M} \cos\theta \quad \text{.....(11.4)},$$

$$v' = \frac{v}{m+M} \{m \cos\phi \pm \sqrt{M^2 - m^2 \sin^2\phi}\} \quad (11.5),$$

$$-\tan\theta = \frac{M \cot\phi \pm \sqrt{M^2 \operatorname{cosec}^2\phi - m^2}}{m+M} \quad \text{.....(11.6)}.$$

Unless $m > M$ the upper sign must be taken in these ambiguities.

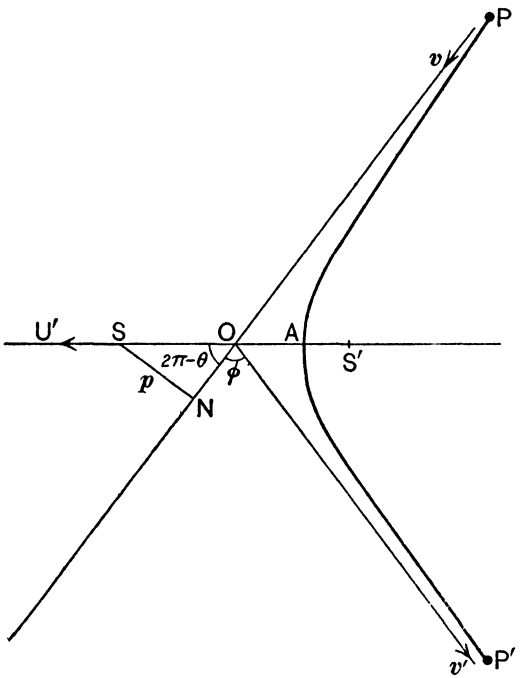


Fig. 1.

We must next consider the orbits of the particles. For this purpose we suppose first that M is infinite and that the centre is a point charge. Then if (as we shall always assume) v is so great that the centre cannot capture the particle as a satellite, PAP' will be a hyperbola with S in one focus. Fig. 1 is drawn on the

assumption that e and E are of the same sign so that the force between particle and centre is repulsive; if the force is attractive, S can be placed at S', the other focus, and the calculation will remain unchanged.

Let v_1 be the velocity of the particle at the apex A, and let $SA = a$. By the conservation of angular momentum we have

$$pv = av_1 \quad \text{.....(12.1).}$$

Since the decrease in kinetic energy must be equal to the increase in potential energy

$$\tfrac{1}{2}m(v^2 - v_1^2) = \frac{eE}{a} \quad \text{.....(12.2).}$$

From the geometry of the hyperbola $ON = OA$. But

$$SON = 2\pi - \theta,$$

so that $$a = SO + ON = -p \operatorname{cosec} \theta (1 + \cos\theta) \quad \text{.....(12.3).}$$

Eliminating v_1 and a from (12.1), (12.2), (12.3),

$$\frac{eE}{pv^2} \cdot \frac{1}{m} = -\cot\theta \quad \text{.....(12.4).}$$

From (11.6), when Mm is infinite,

$$-\tan\theta = \cot\frac{\phi}{2} \quad \text{.....(12.5).}$$

Hence $$p = \cot\frac{\phi}{2} \cdot \frac{eE}{v^2} \cdot \frac{1}{m} \quad \text{.....(12.6).}$$

Now let M be finite, the centre being still a point charge. Then a well-known theorem states that, if we substitute $\dfrac{mM}{m+M} = m'$ for m, we shall obtain the orbit of the particle P relative to the centre S. (12.6) will still be true if in place of ϕ we use the relative deflection ϕ_1, that is to say, the deflection measured on a diagram at rest relative to the centre S. But ϕ_1 is the angle between v and the resultant of v' and $-U'$; hence

$$\frac{\sin\phi_1}{\cos\phi_1} = \frac{v'\sin\phi - U'\sin\theta}{v'\cos\phi - U'\cos\theta} \quad \text{.....(12.7)}$$

$$= -\tan 2\theta \text{ by (11.1), (11.2), (11.3).}$$

Hence, $\phi_1 = \pi - 2\theta$, and $\cot\dfrac{\phi_1}{2} = -\tan\theta$. So that finally

$$p = -\tan\theta \cdot \frac{eE}{v^2} \cdot \frac{1}{m'} \quad \text{.....(12.8),}$$

where now $\tan\theta$ is given by (11.6) in terms of ϕ, m and M.

This equation cannot be applied directly to any experiment because we do not know p; it must be given a statistical form. Consider a plane sheet of material of unit area and small thickness t, containing n centres per unit volume, and suppose that spherical shells of inner and outer radii p and $p+dp$, drawn about the centres, are projected on its surface. If none of the shells overlap (an assumption to which we shall return), their total projected area will be $nt \,.\, 2\pi p\, dp$, and this will be the chance that a particle, entering the medium perpendicular to its surface, will pass through this area; it is also the chance that it will suffer a deflection between ϕ and $\phi + d\phi$, where ϕ and p are related by (12.8). If Q particles fall per second on a small area of the sheet, those that are deflected in this manner will emerge within an annular cone of solid angle $2\pi \sin\phi d\phi$; consequently the number emerging per second per unit solid angle making an angle ϕ with the original direction will be

$$Q_1 = Q \,.\, nt \,.\, \frac{p}{\sin\phi} \cdot \frac{dp}{d\phi} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13.1)$$

$$= Q \,.\, nt \,.\, \frac{e^2E^2}{m^2} \cdot \frac{1}{v^4} \cdot f(\phi) \quad \ldots\ldots\ldots\ldots\ldots\ldots (13.2),$$

where $f(\phi)$ is a complicated function of ϕ and $\frac{m}{M}$ which can be calculated from (11.6) and (12.8). Three cases are specially important.

(1) $\frac{m}{M}$ very small; $f(\phi) = \operatorname{cosec}^4 \frac{\phi}{2}$ $\ldots\ldots\ldots\ldots\ldots\ldots (13.3)$.

(2) $\frac{m}{M} > 1$; $f(\phi)$ is imaginary unless $\sin^2\phi < \frac{M}{m}$ and no particles are deflected through angles above this limit $\ldots\ldots\ldots\ldots\ldots\ldots (13.4)$.

(3) For all values of $\frac{m}{M}$, $f(\phi) = \infty$ for $\phi = 0$ $\ldots\ldots\ldots\ldots\ldots\ldots (13.5)$.

It is obvious from (13.5) and from (13.3) applied to very small values of ϕ that our calculation cannot be correct, for it leads to the conclusion that more particles should be scattered at very small angles than are incident. This false conclusion is due to the assumption that the spherical shells do not overlap; if p is sufficiently large they must overlap, however small is nt. Actually there must be a limit to the greatest distance at which a particle can pass a centre, and the deflection can only be strictly zero when the particle

passes always through points at which the forces due to the different centres counteract each other exactly. But this condition is impossible; every particle must be deflected slightly, although, if the centres are sufficiently distant from each other, the smallest deflection that can occur may be so small as to be inappreciable. Accordingly we must expect (13.2) to be accurate only when ϕ is above some finite limit; but since, on the other hand, we can detect scattering only when the deflection is above some finite limit, it may still be possible to find conditions in which (13.2) represents accurately the results of experiment. The necessary condition is that any deflection large enough to be detected experimentally is due to the encounter of the particle with a single centre; the centres must be so far apart that any appreciable deflection produced at a single encounter is due to a reaction with one centre only, and the sheet must be so thin that a particle, once deflected appreciably, practically never makes another deflecting encounter. When this condition is realised the scattering is said to be 'single'.

When it is not realised, and when the deflection of the particles may be due to several encounters with several centres, the scattering is said to be 'multiple' or 'compound'. The theory of multiple scattering is much more difficult. It is possible to consider how the particles, deflected in accordance with (12.8) at their first encounter, are deflected again at their second or third encounters. But the process is laborious and, when the number of encounters is very large, becomes practically impossible. On the other hand, when the number is very large another procedure becomes possible. We calculate the average deflection of a particle $\bar{\phi}dx$ in a film dx so thin that the scattering is single. We then suppose that every particle receives in each layer dx the average deflection $\bar{\phi}dx$, and inquire by the calculus of probabilities what will be the deflections resulting from the compounding of a large number of these infinitesimal deflections, the directions of which are distributed at random. The result is obtained that the average deflection $\bar{\phi}_t$ in passing through a layer of thickness t, in which there are many encounters, is proportional to $\sqrt{t}$, if $\bar{\phi}_t$ is sufficiently small, and that the probability of a particle being deflected through an angle not less than ϕ is proportional to $e^{-\phi^2/\bar{\phi}_t^2}$. The form of these results is independent of any assumption concerning the nature of the forces

between the particles and the centres; such assumptions affect only $\bar{\phi}$ and the constants of proportionality.

But there is a grave difficulty in calculating $\bar{\phi}$. $\bar{\phi}_t$ must always be small, say less than 10°, if the theory is to be valid; and since it is the resultant of many deflections, $\bar{\phi}dx$ must be very small. It will therefore lie in the region for which the theory of single scattering breaks down, because no scattering can be really due only to single encounters. We must take into account the fact that very small deflections are made under the influence of several centres; then the calculation becomes impossibly complex and requires a knowledge, not only of the number and character of the centres in the atom, but also of their distribution. Multiple scattering cannot be calculated as accurately as single scattering, and, if it could be, would give far less definite information concerning the structure of the atom, because many alternative hypotheses would lead to practically the same result. For this reason it is not proposed here to enter more fully into the theory of multiple scattering.

6. **Experiments on α-rays.** These considerations were first applied to the elucidation of atomic structure by Rutherford in 1911. Geiger and Marsden had investigated the scattering of α-rays by the very powerful but tedious method of counting the scintillations which the rays produce at impact on a zinc sulphide screen. They had shown that when α-rays pass through material films so thin that the average deflection is only one or two degrees, an appreciable fraction of them, about 1 in 10,000, is deflected through at least a right angle, and emerges on the side of incidence. Such a ratio of large to small deflections is inconsistent with the theory of multiple scattering, in which the observed deflection is made up of a large number of small deflections distributed at random; such a theory will always lead to the result that the deflections are distributed according to the 'error-function'. Rutherford showed that it was consistent with single scattering, according to the theory that has just been sketched. Interpreted by that theory, it indicated that the centres in the scattering material (gold) could not possibly be electrons; they must be massive compared with the α-particles and bear charges of the

order of 100 times that of an electron. On the other hand, the centre and the particle must be able to approach within 10^{-11} cm. of each other, a distance far smaller than any diameter that could be attributed to the atom as a whole. He was thus led to the nuclear theory of atomic structure, in which the greater part of the mass of the atom resides in a minute nucleus carrying a charge Ze, equal and opposite to that carried by the electrons surrounding it.

His conclusions depended entirely on the assumption that the scattering was single and not multiple. If the nuclear theory of the atom was true, it was clear at once that it must be single. For the number of gold atoms in the sheets investigated could be calculated from the density of the material and the mass of the gold atom, and it could be shown that the chance was infinitesimal that, in passing through such a sheet, a particle should make two encounters both sufficiently close to produce appreciable deflections. But up to that time a different theory of atomic structure had held the field, according to which the scattering of α-rays must be multiple. The α-particle was known to be a helium atom and therefore, on Thomson's theory, should have a positive sphere not much smaller than that of a gold atom. In order to explain how such a particle could pass through solid gold with closely packed atoms, it had to be assumed either that the helium atom worked its way between the gold atoms, or that it passed through them in such a way that the positive spheres interpenetrated. The first alternative obviously predicted multiple scattering, but it was clearly to be rejected, for the scattering would be so intense as to abolish all appearance of a beam of rays; the second also predicted multiple scattering, because the forces exerted on each other by interpenetrating spheres, at least if they reacted according to the laws of electrostatics, must be too small to produce any appreciable single scattering.

It was therefore of the first importance to establish by some more direct means whether the scattering is indeed single. If it is, the positive sphere atom must be false, and the way was opened for the nuclear atom. Such evidence was soon forthcoming. C. T. R. Wilson's beautiful method of making visible the tracks of ionising particles, by depositing water on the ions formed along their path, enabled the tracks to be photographed and examined

at leisure. They showed no general curvature, such as would result from multiple scattering, but only sharply defined kinks, representing sudden changes of direction of many degrees, which is precisely what must result from single scattering. The proportion of rays that are deflected at a single encounter through the larger angles is so small that it would have been impossibly laborious to collect sufficient evidence for a statistical examination; but the mere existence of these kinks was sufficient to establish the theory.

The later experiments of Geiger, Marsden and Chadwick, by the original method but with a greatly improved technique, would have finally removed any doubts, had any doubts remained in the face of confirmatory evidence pouring in from all sources. For they confirmed the accuracy of the theoretical equation (13.2) in almost every detail. It was first shown that if the atom is sufficiently heavy compared with the α-particle (10 times is practically sufficient), n is accurately proportional to $\frac{t \cdot \operatorname{cosec}^4 \phi}{v^4}$, in accordance with (13.3). The variation as v^{-4} is important, because it can be shown that it is inconsistent with any simple law of force between the centres other than the inverse square law. Further, by determining the absolute value of Q_1/Q for a given value of ϕ, E, the charge on the nucleus, could be determined; for the velocity, the mass and the charge of the α-particles are known. It was found that E, determined in this manner, was equal within experimental error to Ze, where Z is the atomic number, which, at the time that these later experiments were carried out, had been assigned from other evidence. Thus for Pt, Ag, Cu, Z was found to be 77·4, 46·3, 29·3, while the atomic numbers of these elements are 78, 47, 29.

Another confirmation of the theory, perhaps even more striking than these, was obtained from observations on the passage of α-rays through hydrogen. It was pointed out by C. G. Darwin, who generalised Rutherford's simpler theory of single scattering, that, when α-rays collide with hydrogen atoms, some of these atoms should be set in motion with velocities greater than that of the original α-particles. m/M for hydrogen centres and α-particles is 4; hence from (11.4), if the α-particle is originally moving directly at the hydrogen centre and makes with it an 'end-on' collision for which

$\theta = 0$, U', the velocity given to the hydrogen centre, should be 1·6 times v. In virtue of a theory of the absorption of charged particles (as distinct from their scattering) which will be noticed in a later section, the range of the hydrogen particles thus set in motion should be even greater than that of α- or helium particles of the same velocity. In fact by combining the two theories Darwin predicted that the range of the hydrogen particles should be about 4 times that of the particles by which they were excited. This prediction was very fully confirmed by Marsden, who detected the hydrogen rays due to the passage of α-rays through hydrogen, and showed that the range of those travelling in the direction of the original α-particles was about 3·5 times that of those particles, while the range of those emitted at an angle with this direction, for which θ was greater than 0, fell off with θ in very nearly the manner predicted by the theory. But further observations by Rutherford and Chadwick proved not completely in accord with the theory; in particular the number of hydrogen particles excited, though approximately that given by the theory when comparatively slow α-rays were used, was very much greater than that given by the theory when faster rays were used. But a simple explanation offered by Rutherford converted this apparent discrepancy into a yet more convincing support for his theory. For the predicted numbers are based on the assumption that the colliding particles act as point charges however close they approach each other. It is generally more plausible to suppose that atomic nuclei have some finite diameter, or, to express the matter more accurately, that there is some range within which they will repel another nucleus with a force very much greater than that corresponding to a point charge, and that there is some limit to the distance within which two nuclei can approach without serious internal disturbance to one or both. If there is such a distance at which the inverse square law breaks down, the excess of hydrogen particles emitted by very fast α-rays is immediately explained, for the fast particles will tend to approach nearer to a centre with which they collide than the slow particles, and thus enter into the region of very intense force.

According to (12.3) and (12.8) a, the distance within which the centre and particle will approach, is least in an end-on collision,

and is then equal to $\frac{2eE}{m'v^2}$. It will therefore be less the greater the velocity of the particles and the less the charge E on the centre. For the fastest α-rays on which experiments have been made $v = 2 \times 10^9$ cm./sec., $e = 2\epsilon$, $m = 4m_H$; for a gold nucleus $E = 79\epsilon$, $M = 197m_H$. Hence $a = 14 \times 10^{-13}$. On the other hand for a hydrogen nucleus $E = \epsilon$, $M = m_H$, and $a = 9 \times 10^{-14}$. If therefore the diameter of the helium nucleus lies between these values of a, that of the hydrogen nucleus being small compared with it, we should expect the theory that has been given to apply strictly to the collisions of α-rays with gold, but not to those with hydrogen; and, in hydrogen, to apply to rays with a velocity below 5×10^8 cm./sec., but not to those with considerably greater velocities.

That is precisely what is found. A detailed examination of the numbers of hydrogen particles excited with velocities corresponding to collisions very nearly end-on enables some suggestion to be made concerning the field of force surrounding a helium nucleus. Chadwick shows that it is such as might be expected if the nucleus were an oblate spheroid with diameters of 8×10^{-13} and 4×10^{-13} cm. respectively; but of course too much weight must not be attributed to the details of this speculation. The really important conclusion is that the nucleus, though minute, has a finite size.

7. **Experiments on β-rays.** Some further results of the study of the passage of α-rays through material bodies will be described later in this section. We must now devote a brief space to the similar study of β-rays. The experimental difficulties of deriving results similar to those for α-rays are great. Individual α-particles can be detected by means of the scintillations which they excite at impact on a zinc sulphide screen, and all the work that has been described has been conducted by this method. The scintillations excited by β-rays are much fainter, in virtue of the smaller energy of these rays (the energy of the fastest β-rays is only one third of that of the fastest α-rays), and are barely perceptible. β-rays have to be studied by ionisation or photographic methods which are necessarily less delicate. Nevertheless there is available a considerable amount of evidence concerning the scattering of β-rays, due largely to Crowther; and Rutherford's

examination of it indicated at first that β-ray scattering, at any rate in the thinnest films, might be single scattering by the nuclei of the atoms, similar in all respects to that of α-rays. This result did not necessarily follow from his theory, for with β-rays the collisions with the electrons, which with the nucleus form a neutral atom, might have to be taken into account. No mention has been made so far of these electrons, and it is easy to see that the collisions of α-particles with them cannot cause any appreciable scattering, although it may cause absorption. For since the mass of a particle is 7000 times that of an electron, the greatest deflection which an α-particle could suffer at such a collision would be, by (13.4), a very small fraction of a degree. On the other hand β-rays are electrons, and by collision with an electron could suffer a deflection of a right angle. However it appears that the deflections even of β-rays due to collisions with electrons must be small compared with those due to collisions with the nucleus. For there are Z electrons to one nucleus in an atom of atomic number Z. A β-particle will therefore make a collision, characterised by any given value of p, Z times as often with an electron as with a nucleus. But by (12.6) the deflection due to such a collision is $1/Z$ times as great as for the collision with the nucleus; so that, even if the electronic deflections were all in the same direction, they would only amount to a single nuclear deflection. In metal films in which observations can be made, Z is never less than 13 (Al); consequently multiple scattering due to the electronic collisions will always be much less than single scattering due to nuclear collisions.

Nevertheless a closer inquiry has shown that the scattering of β-rays is always somewhat greater, at least for the smaller deflections, than that predicted by the theory of single scattering which has been sketched. The discrepancy appears to have been explained completely by Wentzel. He draws attention to the considerations mentioned on p. 14 according to which the theory must break down at deflections for which p is comparable to the distance between two atoms. Since the energy of β-rays is much less than that of α-rays, deflections of a given magnitude will correspond to greater values of p with the former. Accordingly, while a deflection ϕ of an α-ray may correspond to a p much less than the distance between two nuclei, a similar deflection of a β-ray may correspond

to a p nearly equal to that distance. It is possible that while the deflection for which the theory breaks down may be inappreciable when the rays are α-particles, it is appreciable when they are electrons; detailed calculation shows that such is indeed the case. The theory of single scattering should be applied only to deflections of β-rays above a limit which is higher than the least perceptible, and when it is so applied it is in accordance with experiment. Further, even if limited to these large deflections, the theory must be applied only to the very thin films used in α-ray experiments; if thicker films are used, multiple scattering due to successive collisions with several nuclei may enter. Actually, owing to experimental difficulties, almost all experiments have been made on films rather too thick for the scattering to be strictly single.

There is then nothing in the scattering of β-rays which conflicts with the conclusions drawn from the study of α-rays. And that is the best that can be expected. For there is no further information concerning the nucleus unobtainable by means of the latter which we could expect to obtain from the former. Nor can we, as might appear at first sight, find out anything fresh about the electron; we cannot, for example, determine the size of the electrons as we determine that of the nucleus, because we cannot obtain electrons with sufficient kinetic energy to penetrate so near to the nucleus that the limitation of size becomes important[1]. We may therefore now pass to another property of the nucleus and another method of investigating it.

(*b*) *The mass of the nucleus.*

8. **The mass of isotopes.** Since (13.2) involves the masses of centre and particle, as well as their charges, it could be used to

[1] It may not be out of place here to say a word about the radius which is usually attributed to the electron, 2×10^{-13} cm. This radius is estimated on the assumption that the kinetic energy of an electron represents the energy of its magnetic field, and that the electrostatic field about an electron is that appropriate to a conducting sphere of definite radius. Both these assumptions are precarious, and all that the estimate gives is a lower limit to the distance from an electron at which the inverse square law can hold; it does not assign an upper limit, and there is no evidence at what distance that law breaks down. All that we can say is that the law of force between an electron and a nucleus is very nearly that of the inverse square down to distances comparable with the radius assigned to the nucleus.

determine these masses, if the experiments were capable of indefinite accuracy. But since m' differs little from the smaller of these two masses, unless they are nearly equal, and since it is practically impossible to use atoms heavier than helium, as 'particles' in scattering experiments, the only nuclei of which the mass can be determined with any accuracy are those of helium and hydrogen. But the results obtained with these two atoms are of far-reaching importance; they show that practically all the mass of the atom, as determined by the usual physical or chemical methods, resides in the nucleus; and if this is true for these atoms it would be quite unreasonable to doubt that it is true for all. This conclusion is inevitable, as we have seen (p. 3), if it is assumed that the atom consists of nothing but electrons and a nucleus, and that the number of electrons is equal to the atomic number; it may be regarded as supporting those assumptions, for which, however, there is more weighty evidence from other sources.

But even if it were possible to determine all nuclear masses by this method, little would be added to existing knowledge. For the scattering of the α-rays is determined by the average mass of the scattering centres; the method, like all others, would yield only the mean atomic weight $\bar{A}$. For the purposes of theoretical physics, the mass of the nucleus is important from one aspect only; it is different for isotopes, so that measurements of atomic mass enable isotopes to be distinguished. But that distinction cannot be made if only the mean atomic mass is determined: the only methods we need consider are those which give the true atomic mass A.

The methods at present available for this purpose are of two kinds. One depends on the study of the radioactive properties of the atoms and is applicable only to members of the radioactive series; it was the method by which the existence of isotopes was first suspected; it will be discussed later in this section; for the present we shall merely take the results for granted. The other depends on the study of positive rays; it is applicable to all elements, although so far the experimental difficulties of applying it to all have not been overcome.

Positive rays is a term applied to positive ions moving through a gas at low pressure with a speed derived from a fall through a difference of potential of several thousand volts. In one of the

usual methods of studying these rays, the positive ions are formed by ionisation by collision in a discharge through a gas at a pressure of about 0·1 mm. and are attracted to the cathode, which is pierced by a fine hole. The positive ions pass through this hole and enter a vessel in which a much lower pressure is maintained by powerful pumps against the leak through the hole. This method of production is applicable to elements which are gaseous or form not too unstable gaseous compounds. In another method the positive ions are generated in the form of 'anode rays' by the impact of electrons from a cathode on an anode containing the element in question; they again pass in a fine stream through the cathode to the region of examination. By whichever method the ions are generated, they are examined by deflecting the fine stream of positive rays in superimposed electrostatic and magnetic fields of measured intensity, and determining the deflection by receiving the rays on a fluorescent screen or photographic plate. In an electrostatic field of given geometrical form the deflection is proportional to e/mv^2, in a magnetic field to e/mv; by a knowledge of these two ratios e/m and v can be deduced.

The rays are never homogeneous in velocity; v usually varies from 0 up to a maximum corresponding to the potential applied to the discharge tube. Consequently the impression made by ions with a given value of e/m is not a point, but a line which is a parabola if the fields are uniform: the position and form of this parabola indicate the value of e/m for the ions concerned.

This method was first applied by J. J. Thomson, who used it primarily to elucidate the processes involved in ionisation. The determination of the mass of the ions forming a given parabola needs a knowledge of e, but this knowledge is usually easily obtained. Singly charged ions, bearing a positive[1] electronic charge ϵ, always appear whatever the nature of the ion; ions bearing a multiple of ϵ also appear sometimes, but they occur much more frequently when the ions are single atoms than when they are compound molecules. With these rules as a guide, the value of e,

[1] In the conditions of Thomson's experiments negative as well as positive ions often appeared, formed by the ionisation of the gas through which the positive ions pass behind the cathode. These, though important in Thomson's work, may be neglected in our present discussion.

and therefore of m, can usually be assigned to any parabola without difficulty. Thomson was able to show that chemical compounds are usually resolved in ionisation; the diatomic hydrogen molecule is broken into atoms, some of which combine to form a compound H_3, which has since been detected by its special chemical properties. Again many complex ions appear which correspond to compounds quite unknown to chemistry. Thus, if any gas containing carbon is placed in the discharge tube, singly charged ions CH, CH_2, CH_3, as well as CH_4, appear in the positive rays, formed by the combination of the carbon with hydrogen which is always present. But the results that interest us at present are those which bear on the mass of the elementary atoms and not on their compounds.

The first element shown plainly by this method to consist of more than one isotope was neon. Thomson found that when neon was present two parabolas always appeared, for which m/e (referred to the singly charged hydrogen ion as unity) was about 20 and 22, the latter being much fainter. The faint component might possibly have been due to a doubly charged CO_2 molecule (for the absence of C and O is difficult to ensure), but since no stronger line appeared at $m/e = 44$, corresponding to the singly charged molecule, this identification was highly improbable. Similar arguments excluded other possible identifications. Since the mean atomic weight assigned to neon was 20·2, it was strongly indicated that neon really consisted of a mixture of Ne^{20} and Ne^{22}. The conclusion was confirmed when Aston, who had been assisting Thomson in this work, subjected neon to a process of fractional diffusion and found that he could separate it into two components differing slightly in density.

Aston has since re-designed Thomson's apparatus so as to make the method capable of far greater accuracy, and has investigated with it what he terms the 'mass-spectra' of a large number of elements. The term 'spectrum' is appropriate, because in the photographs taken with his apparatus the lines corresponding to ions with different values of m/e appear not unlike those of an optical line spectrum. He can measure the value of m/e for any element with an error of about 1/1000 in favourable cases; or rather he can compare with this accuracy values of m/e not differing very greatly. As standards of reference he employs in the first

instance carbon and its four compounds with hydrogen, mentioned above, which appear on all plates; from these he derives secondary standards, often using for this purpose multiply-charged ions, and thus obtains standards over the whole range of m/e. Thus by comparing O with CH_4 he obtains the mass of O and of CO ($m/e = 28$); he can then measure Krypton ($m/e = 78$ to 86) by comparing its trebly-charged ion with CO. Occasionally identifications are doubtful on account of possible alternatives, but about his main results there is no doubt whatever.

They are given in Table I, where the work of others who have used or adapted his methods is included, together with the facts concerning radioactive isotopes. The main facts that emerge are these:

(1) Elements may be either 'pure' or 'mixed', consisting of a number of isotopes. It is difficult to decide quite definitely by experiment whether an element is pure, for the admixture of a very small proportion of a second isotope would escape detection. But there seems evidence for a real distinction in the fact that generally the elements of lower atomic mass tend to be pure and those of higher atomic mass mixed; thus of the first 18 elements 11 are pure, while of the remaining 24 that have been examined only 3 have not been resolved. The difference is quite as marked if we take into account the average number of isotopes per element; for the 18 light elements it is 1·5, for the 24 heavier elements it is 4. If all elements were really mixed, no such systematic relation would be expected. Moreover the relation found is intrinsically probable; for if the nuclei have any structure, this structure must be simpler in the lighter nuclei and therefore the number of possible alternatives less. Elements of odd atomic number have fewer isotopes than those of even atomic number.

(2) The masses of the nuclei, referred to O = 16, do not differ from integers by more than a few parts in a thousand. The only case in which a difference has been established quite certainly is that of H, where the actual mass is nearly 1 % more than the nearest integer, and agrees well with that determined by chemical methods; but there is good evidence that in Sn and Sb the masses of all isotopes are slightly less than the nearest integer. In Table I the values (except for hydrogen) are given only to the nearest integer.

The significance of these results will be considered when the additional evidence derived from radioactivity has been described. Of course they have excited the greatest interest, especially among chemists, to whom atomic weights, now shown to be often a mere fortuitous average, have been the most certain and fundamental data of their science. In particular, inquiry has been directed to determine whether the mean atomic weights are really constant, when samples from different sources are compared. It appears that they are, except when elements have doubtless been formed *in situ* by radioactive change during the history of the earth as a solid body. It has even been found that nickel from meteorites agrees with terrestrial nickel. The most plausible explanation of this constancy seems to be that at some time in the history of the earth, its materials have been thoroughly mixed with each other and with those of the rest of the solar system, probably in the liquid or gaseous form, and that since that time no formation of elements, other than those of radioactive series, has occurred. But such speculations lie beyond our province.

9. **The separation of isotopes.** Attempts, partially successful, have been made to separate the isotopes of elements known to be complex. Theoretically nuclei which differ in mass must differ to some small extent in every other property, and thus should be separable to some slight extent by any kind of change; but actually the most hopeful properties to use for the separation are those which depend most directly upon atomic or molecular mass. The properties which have actually been used successfully are diffusion and evaporation. The theory of the diffusion process was given long ago by Rayleigh. If out of a mixture of two gases consisting of X volumes of one with Y of another, another mixture of x volumes of the first with y of the second is selected by diffusion, then

$$R = \frac{x+y}{X+Y} = \frac{X}{X+Y} r^{\frac{\mu}{\nu-\mu}} + \frac{Y}{X+Y} r^{\frac{\nu}{\nu-\mu}} \quad \ldots\ldots(26.1),$$

where μ, ν are the diffusion coefficients of the two gases and $r = \left(\frac{y}{x}\right) \Big/ \left(\frac{Y}{X}\right)$. R may be called the fractionation coefficient, being the fraction of the mixture which is selected, r the enrichment coefficient, being the ratio of the proportions of the two gases

finally and initially. μ and ν are known to be inversely proportional to the square roots of the molecular weights. (26.1) shows that a separation of the constituents to any desired degree of perfection is possible, but it shows also how tedious and difficult it must be. For suppose that we start with equal volumes of the two isotopes of neon and require to obtain a mixture in which there is double as much of one as of the other, so that $r = 2$. $\mu/\nu = \sqrt{22/20} = 1{\cdot}048$, so that

$$R = \tfrac{1}{2}(2^{-21{\cdot}7} + 2^{-20{\cdot}8}) = 4{\cdot}8 \times 10^{-7},$$

i.e. we must continue the diffusion until only 1 part in 2 millions of the original gas has not passed through the diaphragm. In practice even this degree of success will not be obtained because perfect diffusion without leakage is impossible to attain. The highest value of r which has actually been obtained by this method for neon is 1·007; for gases with higher molecular weights the process is even less favourable for the same difference between the weights of the isotopes.

A second method is by evaporation at a very low vapour pressure. In these circumstances the rate of evaporation is proportional to the square root of the atomic weight; if the molecules are condensed immediately after they evaporate and have no chance of evaporating again a separation can be effected to which a formula very similar to (26.1) applies. The method has been applied with success to mercury, chlorine (in the form of HCl) and zinc. The substance is exposed in a vacuum at a temperature such that the vapour pressure is so low that the mean free path is several millimetres and above it is placed a cold surface (e.g. cooled by liquid air) on which the evaporated molecules are immediately condensed. Thus Brönsted and Hevesy, who first used this method, succeeded in obtaining samples of mercury differing in density by 5 parts in 100,000 and Harkins samples of chlorine differing by 1 part in 1000. Egerton has obtained differences in the density of zinc amounting to 53 parts in 100,000.

The only isotopic group that has been separated with any completeness into its constituents is Pb (82). Here the separation has been effected naturally and not artificially. The lead that is the final product of the disintegration of uranium (see p. 34) has an atomic mass 206, that which is the product of thorium has an

atomic mass 208. Values closely approximating to these have been obtained for lead extracted from uranium and thorium minerals, the atomic mass of 'ordinary' lead (which may or may not be a mixture of these two) being 207·2. It has been proved that the densities of these isotopes are accurately in the ratio of their atomic masses, so that isotopes have the same molecular volume. On the other hand Merton has detected a difference of 7 parts in 4 millions in the frequencies of certain lines in their spectra. This difference is rather puzzling. For according to the theory of Ch. XV, pp. 49, 50 this difference in frequency should be determined by a difference in $\frac{\mu M}{\mu + M}$, which in this case amounts to only 1 part in 36 millions. The theory given there should not apply directly when there are many electrons in the atom, but it would seem to indicate a difference of this order of magnitude. The discrepancy is unexplained; perhaps the effective mass of the system determining the frequency is not that of a single electron but that of all the 82 electrons; that hypothesis would give a difference of the right order, but is nothing but a speculation. McLennan thinks that he has detected a similarly abnormal difference in the spectra of the isotopes of lithium, but since these have not been separated completely the evidence is less certain. It may be added that a minute difference should be found in the rotational absorption spectra which depend on the moment of inertia of the molecule (see Ch. XV, pp. 106–108); but it has not been detected.

(c) *The structure of the nucleus.*

10. **Artificial radioactivity.** The fact that the masses of nuclei are so nearly integral multiples of a single unit naturally suggests, in accordance with Prout's hypothesis, that they are built of common parts. That hypothesis remained a mere speculation till some condition could be found in which the atom (or rather that part of it which determines the mass) could be divided. Such a condition is found in radioactivity, and all speculations concerning the structure of the nucleus must be based mainly upon the evidence of radioactive change.

Two kinds of radioactivity are now known, natural and artificial;

and since the latter is the less complex it will be well to describe it first, although its discovery is much more recent.

In studying the scattering of α-rays by the methods described in the first part of this section, Rutherford found that when α-rays passed through nitrogen they excited rays which, like those excited in their passage through hydrogen, had ranges greater than that of the original rays. These could not be nitrogen atoms, for though the atoms of a gas by which α-rays are scattered must always be set in motion by the reaction (as indeed Wilson's photographs show, see p. 16), the theory shows plainly that, if their mass is greater than that of helium, their range will be so small that they will be inappreciable by experiment. At first Rutherford was inclined to attribute these rays to traces of hydrogen present as an impurity in the nitrogen, but this possibility was soon excluded. The most careful attempts to exclude hydrogen compounds produced no diminution of the rays; they did not appear in oxygen or carbon monoxide, even when contaminated with water vapour; and—most conclusive of all—the range of the particles was distinctly greater than that of the secondary rays excited in pure hydrogen. This last result was especially striking; for, according to the theory of scattering that has been discussed, it should be impossible for any secondary rays to be excited having ranges greater than that of these hydrogen particles; in helium α-rays might excite secondary rays of the same velocity and the same range as the primary; in gases with heavier nuclei the velocity of the secondaries, and still more the range, must be less than that of the primaries; that conclusion is a direct result of the principles of the conservation of energy and of momentum, if the α-ray reacts with the nucleus as a whole. Rutherford therefore suggested that this condition is not fulfilled in the reaction between α-rays and nitrogen nuclei, but that these nuclei were broken up by the collision, parts of them being ejected with additional energy and momentum derived from the disintegration.

Later work has confirmed this suggestion completely. Similar long range rays have been excited in boron, fluorine, sodium, aluminium and phosphorus, but not in any other elements; in all these elements the range of these rays is still greater than in nitrogen; in aluminium the range is three times that of the fastest hydrogen

particles excited in hydrogen, and therefore three times greater than any which the simple theory of scattering would predict. Further it was shown that these long range particles are emitted in all directions from the atoms struck by the primary α-rays, and not merely in directions making a very small angle with that of the primaries; those emitted backward have ranges less than those emitted forward, but still, except in nitrogen, greater than that of the hydrogen secondaries. The number of the long range particles is very small compared with that of the primaries, the ratio being only about 1 in 300,000; it does not vary greatly with the element in which they are excited, so long as it is one in which they can be excited at all. Their range falls off with the range of the primaries and approximately in proportion. Lastly measurements of the magnetic deflection of the long range particles make it almost certain that they consist of hydrogen nuclei from whatever element they come.

The following table summarises the chief results; the gain of energy takes account of all directions of emission and is calculated on the assumption that the total momentum is conserved.

TABLE II

Range of primary rays (He) in air at N.T.P. ... 7 cm.
Range of secondary rays (H) in hydrogen ... 29 cm.

Range in hydrogen of rays due to disintegration of nuclei.

Elements disintegrated	Forward Range	Backward Range	Gain in energy
	cm.	cm.	%
Boron	58	38	+42
Nitrogen	40	18	−13
Fluorine	65	48	+35
Sodium	58	36	+ 6
Aluminium ...	90	67	+42
Phosphorus ...	65	49	+15

Rutherford suggests that these hydrogen nuclei are revolving in orbits as satellites to the main part of the nucleus; the momentum with which they are emitted over and above that which they could receive from the primary rays represents their momentum in their

orbits. The faster the primary rays, the further they can penetrate into the nucleus; and since the satellites nearer the main portion are probably travelling with greater velocity, the greater the momentum of the satellites which they liberate. We shall have more to say presently concerning the distinction between those elements in which the nucleus can be disintegrated in this manner and those in which it cannot (p. 39); but it may be noted that we should expect the nuclei of high atomic number to belong to the second class, because the charge on them is so great that, as the experiments on scattering show, the primary α-rays cannot penetrate beyond the region in which the nucleus acts as a point charge—a region which must obviously be free from satellites. However it is doubtful whether on this account we should expect the first class to end at an atomic number as low as that of phosphorus.

The experiments have attracted universal attention, for they present the first solution of the ancient problem of the artificial transmutation of the elements. Under the impact of α-rays nitrogen is undoubtedly transmuted into other elements, of which one is hydrogen and the other probably carbon. (The quantities concerned are too minute for there to be any chance of detecting the carbon chemically.) The transmutation is always in the direction of a decrease of atomic weight, but after all it was in that direction that the alchemists strove when they sought to turn lead into gold; however that particular problem seems less likely than ever to be solved on account of the high atomic numbers of these elements. Again, a transmutation in the direction of higher atomic weight seems beyond our reach; Ramsay, who was always turning lighter elements into heavier, was working on a theory as worthless as his experiments. And perhaps it is well to note, in view of journalistic vapourings, that though there is a gain of energy in a very minute proportion of the collisions between α-rays and certain atoms, the loss occurring at the overwhelming majority of these collisions far outweighs that gain.

11. **Natural radioactivity.** The facts are so well known in outline that a summary will suffice. Natural radioactivity consists in the spontaneous emission of α-rays or of β- and γ- rays, these last two kinds being always associated. It is a purely atomic process;

the energy of the α- and β-rays (which determines their range or absorption) and the frequency of the γ-rays (which determines their absorption) are characteristic of the element concerned in the emission, and so is the rate of emission; they are totally unchanged by any variation in the chemical or physical condition of the element that has yet been effected. The average rate of emission is proportional to the number of atoms of the radioactive element present, but is subject to fluctuations of the kind characteristic of fortuitous events. The emission of rays is always accompanied by a disappearance of the emitting atoms and by the substitution for them of atoms having different chemical properties and constituting a different element. According to the theory of Rutherford and Soddy, which is the basis of all modern work on the subject, radioactivity consists essentially of a disintegration of the radioactive nucleus, the α-particles and some of the β-particles being fragments of the nucleus ejected as it passes from a less to a more stable condition. The disintegration is fortuitous in the sense that there is a definite chance, λdt, that a given atom will disintegrate during the time dt, λ being characteristic of the atom and totally independent of its circumstances or of the time that has elapsed previous to the disintegration. It follows that if m is the mass of a large and initially homogeneous collection of atoms left after time t,

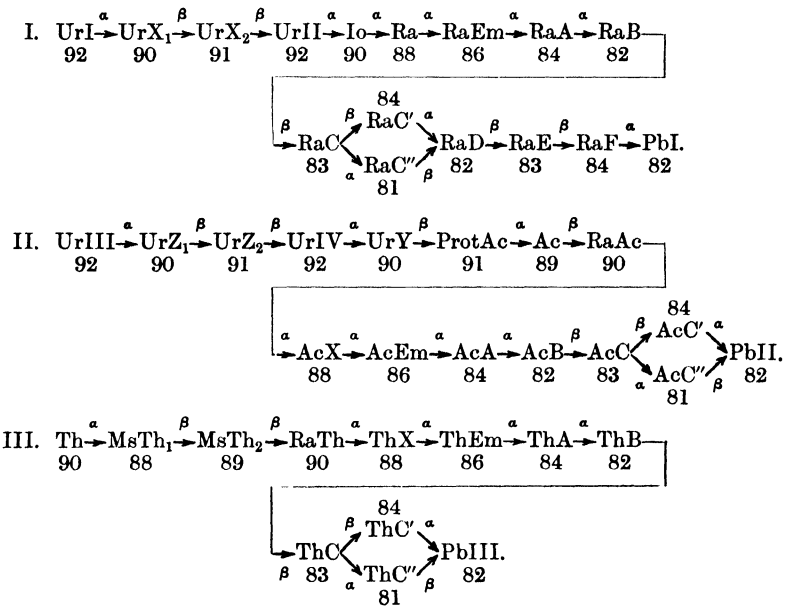
$$m = m_0 e^{-\lambda t} \quad \text{.....(32.1),}$$

where m_0 is the mass at time $t = 0$. λ is therefore called the 'decay constant', and $T = 1/\lambda$, which is the period in which the mass falls to $1/e$ of its original value, is called the 'life' or 'period'. (In place of T some writers employ the period required to fall to half value.) The term 'period' is the better, for radioactive atoms differ from living beings in the fact that the expectation of persistence does not vary with age. T varies over a very wide range, from 10^{10} years to a small fraction of a second; the very long and very short periods cannot of course be measured directly, but are deduced from other measurements.

With two exceptions, all known radioactive elements are of atomic number greater than 80; all the elements, including isotopes, of atomic number greater than 83 are radioactive; of those of atomic number 81, 82, 83 (thallium, lead, bismuth) some are radioactive

and some not; no elements of any kind are known of atomic numbers 85 and 87. The two exceptions are K (19) and Rb (37), which emit β-rays in a manner indistinguishable experimentally, except in degree, from that characteristic of the other radioactive elements. No sign of atomic disintegration has here been found in connection with the emission, but, since their periods are doubtless immensely long, that is not a proof that it does not occur. But the elements are in some way anomalous, and will not be included in the general statements which follow unless explicit mention of them is made.

TABLE III



The normal radioactive elements can be arranged in 3 series (of which only 2 are certainly independent—see p. 41), such that each member except the first is produced by the disintegration of the preceding member; the member with which the series ends is not radioactive. These series are given in Table III, in which each element is denoted by its conventional symbol with the atomic number written underneath. The arrow represents the production

of each element from its 'parent', and the letter beside the arrow the nature of the rays emitted during the production. The following features should be noted.

(1) Except when 'branching' occurs (to be discussed more fully later) no single radioactive change is accompanied by the emission of both α- and β-rays. But the evidence for this fact is not always direct: for some of the periods are so short that the corresponding emission is not experimentally separated in time from its predecessor. Further, α-ray emissions occur in a long sequence, while β-ray emissions occur in pairs succeeding each other immediately or with one intervening α-ray emission. At a branch these two alternatives are represented in the alternative branches, the emission preceding the branch being β-ray.

(2) There is a close parallelism between the three series. Each begins with an α-ray followed by 2 β-rays; there is in each a long series of α-rays in the middle, leading to a branch which is similar in all three series. In fact the parallelism is closer than appears from the table, for if the λ's for corresponding elements in the three series are compared (e.g. those for the first three changes, or for the 4 α-ray changes preceding the branch, or for the elements in the branch) it is found that the ratio of these λ's is approximately constant.

(3) The change in atomic number is determined by the ray emitted during the change; an α-ray emission causes a decrease of atomic number by 2, a β-ray change causes an increase by 1. This is the 'displacement law' of Fajans and Soddy. These changes are exactly what we should expect according to the theory of Rutherford and Soddy; for when the nucleus ejects a helium nucleus bearing 2 positive electronic charges, the charge on it decreases by 2; when it emits an electron its charge increases by 1. Since 1 α-ray and 2 β-ray changes restore the original atomic number, isotopes are of frequent occurrence both in a single radioactive series and among members of different series. It was the recognition of the displacement law which led to the clear recognition of isotopes and their naming by Soddy. All three series end in an element of atomic number 82, isotopic with lead; the final product of the first series, descended from uranium ($A = 238$) through 8 α-ray emissions, should have an atomic weight 206; that of the

third, descended from thorium (A = 232) through 6 α-ray emissions, should have an atomic weight 208. These predictions have been confirmed, as has been mentioned already. The extremes that have actually been obtained are 206·05 and 207·77; the divergence from the numbers expected is doubtless due in part at least to the impossibility of finding quite pure minerals. Further radium, descended from uranium by 3 α-ray changes, should have an atomic weight 226; this is the value actually found.

The agreement of prediction and experiment in these cases justifies the application of the method to determine the atomic masses of radioactive isotopes for which no other method is available. Radium is the only radioactive isotope, known to be pure, of which the atomic weight has been determined with any accuracy[1] by the older methods, or by any method other than this. It is assumed that naturally occurring thorium and uranium are pure elements, so that chemical methods determine the true atomic weight. For thorium this assumption is highly plausible, but it is not nearly so certain for uranium; the fact that the chemical atomic weight of uranium is 238·2 (and not 238·0, as it should be if it is to agree with radium) may be due to the presence of more than one isotope in natural uranium, but it may possibly represent the 'packing effect' (p. 38).

The values assigned to the other radioactive isotopes in Table I are calculated from those of these three elements by means of the displacement law. Since it is uncertain from what isotope in group 92 the actinium series is descended, and since no member of this series has been determined directly, the atomic masses of all this series are doubtful.

12. The composition of the nucleus. Such are the facts. We have now to consider the light that they throw on the structure of

[1] Ramsay attempted to determine the molecular weight of radium emanation by direct weighing. The value he gave was 220, which is in all probability 2 units wrong. On the ground of this 'determination' he claimed the right to rename the element, which had been known for ten years and of which all the chief properties had been established, mainly by Rutherford. His claim appears to me a disgraceful attempt (and not the only one of which he was guilty) to steal scientific credit to which he had not a shadow of right. I protest vehemently against the practice of some writers who assign to element 86 the name which he put forward in place of Emanation (Em), which was thoroughly established and has never been abandoned by British and German physicists.

the nucleus. Since hydrogen nuclei and helium nuclei can appear as the fragments of disintegrated nuclei of greater mass, it is natural to suppose that these simpler nuclei are among the constituents of which the more complex are built; indeed if we do not accept that view there is no evidence that the nucleus has a structure at all. And it is natural to proceed a step further and to suppose that these two kinds of nucleus, together with electrons (which also appear as fragments of nuclei), are the only ultimate constituents[1]. We might even take another step and suppose that the helium nucleus itself is composed of four hydrogen nuclei, to which the mass would be due, together with two electrons, which would give the right nuclear charge; but that hypothesis, intrinsically probable as it is, has not so far led to the explanation of any facts, and we may leave it on one side; so far as experiment has indicated as yet, the helium nucleus is indivisible. We should also not overlook the fact that no complex nucleus has yet been shown to contain both a hydrogen and a helium nucleus; the former appears in artificial, the latter in natural disintegration; but since we have never been able to effect more than a partial disintegration, this negative evidence need not shake our faith that complex nuclei may contain both of these simple kinds.

However, one apparent difficulty to the view that all other nuclei are made up of these three kinds of building stones must be mentioned at the outset. If mass is truly additive, in the building of nuclei as well as in the building of chemical compounds, the theory cannot be true. As we have seen, the number of electrons, limited by the known nuclear charge (nobody has yet been bold enough to deny that charges are not truly additive), is always so small that their mass cannot amount to as much as one thousandth of the whole. Accordingly, on our view, the mass of any complex nucleus should be represented to this order of accuracy by the sum

[1] Thomson in his experiments on positive rays and Rutherford in his experiments on artificial radioactivity thought at one time that they had detected particles of mass 3 and charge 2 which, if they are atomic nuclei, would be isotopes of helium. No evidence of such particles has been found among the α-rays from radioactive bodies, but since the mass of all α-rays has not been determined their absence is not absolutely certain. But later work seems to have thrown doubt on the existence of such particles. Their existence is involved in certain theories of the constitution of complex nuclei, but we shall exclude them from our consideration.

of integral numbers of hydrogen and helium nuclei. This condition is not fulfilled. Even if the masses of all nuclei, except hydrogen, are integers referred to O = 16, they are not integers referred either to He = 4 or H = 1·008, nor are they of the form $4p + 1{\cdot}008q$. If we entertain our theory at all, and still more if we speculate that the helium nucleus is made up of hydrogen nuclei, it must be on the assumption that mass is not strictly additive. This is not really a very serious difficulty, for it is obviously quite illegitimate to conclude from experiments on chemical or physical combination, involving mere re-arrangements of the nuclei, anything about what happens when they are made or destroyed. However, we must notice an argument that has been used to remove it.

It is based on a result obtained in Ch. XVI, p. 49, eqn. (13.8). It was shown there that, according to the principles of relativity, the mass of a body must be a function of its energy, or that energy E possesses a mass E/c^2. If this is so, two bodies which unite with loss of energy will have less mass than the sum of the individual masses before combination. Accordingly, if we suppose that, when four hydrogen nuclei unite to form a helium nucleus, energy is lost in the process, as it is in the formation of an exothermic compound, we can calculate the amount of energy that must be lost in order to account for the loss of mass, and find (as might be expected) that it is very much greater than any lost in the formation of the most stable chemical compound by the most violent reaction. The explanation is therefore in complete accordance with the observed difficulty of resolving the combination.

Though this explanation is constantly made the basis of elaborate calculations, all so far unchecked by experiment, it seems to me a very doubtful and difficult interpretation of the relativity result. What was actually proved in Ch. XVI is that it will require a greater amount of work to cause a given increment in v^2 for a particular charged body if v, its velocity relative to the system supplying the work, is already great. The extension to bodies that are not charged, such as neutral atoms, is perhaps in accordance with the general ideas of relativity, but the step from kinetic energy to potential energy is much more serious; for potential energy, so far as I can see (cf. Ch. XVI, p. 75), is a conception foreign to relativity. Consider a very simple case. An electron is

at rest at an infinite distance from a nucleus, which is at rest relative to the observer. It falls towards the nucleus, losing potential and gaining kinetic energy. When it reaches the nucleus all its energy is kinetic; the mass of the electron should have increased, according to our result, because its velocity is greater; that of the nucleus has not changed; and it would therefore be reasonable to suppose that the mass of the combination is greater. But the total potential and kinetic energy has not changed; here we would seem to expect change of mass without change of energy. Now stop the particle. Nothing in the relativity argument indicates that the mass is different from that when the nucleus and electron were infinitely distant and equally at rest. But according to the view we are discussing, the mass is not only less than it was when the electron was moving but, since energy has been lost by the system of nucleus and electron, less than it was when the system was infinitely dispersed. The view may be correct—that experiment alone can decide; but there seems nothing in relativity to justify it.

However, we may leave the matter there, simply assuming that there is a 'packing effect' (as the supposed change of mass with energy is usually called), and that the evidence of atomic masses is not inconsistent with the building of more complex nuclei from H and He. We may then treat the matter as if all nuclear masses were integral multiples of that of hydrogen, rounding off the masses actually observed to the nearest integer.

The question now arises how many H and how many He there are in the more complex nuclei. Certain conditions are imposed by the atomic mass and charge. Thus, neglecting as usual the mass of the electrons, a nucleus consisting of n He, p H, and q electrons must have an atomic mass and number given by

$$\left.\begin{aligned} A &= 4n+p \\ Z &= 2n+p-q \end{aligned}\right\} \quad \text{.....(38.1).}$$

If we know A and Z, we have two equations to determine the three unknowns n, p, q: since n, p, q are integers there are usually several possible solutions, but the number is limited.

A further limitation is imposed by all who have speculated on this subject. It is that p is never greater than 3, and that, consequently, p is equal to the residue obtained by dividing the atomic

weight by 4. There are two lines of argument that support this assumption.

(1) Rutherford never obtained hydrogen particles from elements with atomic weights that are multiples of 4; it is therefore a reasonable conclusion that, when the residue is 0, p is 0. If the assumption is true in this case, it is not unlikely that it is true in others.

(2) It has long been observed that the lighter elements, those namely with atomic numbers up to 20, can be arranged in two series in which the atomic weight increases from one member to the next by 4.

For one of these series $A = 4n$, where n is the series of integers, while $Z = 2n$, so that $A = 2Z$: for the other series $A = 4n + 3$, $Z = 2n + 1$, so that $A = 2Z + 1$. Thus one series includes the elements of even atomic number, the other of odd atomic number. These two series are shown in the following table in which, when there is more than one isotope, the predominant isotope is considered. Where the rule breaks down, the infringing member and its atomic mass are shown in brackets.

TABLE IV

Z	$A=2Z$	$A=2Z+1$
1	—	(H=Z)
2	He	—
3	—	Li
4	(Be=$2Z+1$)	—
5	—	B
6	C	—
7	—	(N=$2Z$)
8	O	—
9	—	F
10	Ne	—
11	—	Na
12	Mg	—
13	—	Al
14	Si	—
15	—	P
16	S	—
17	—	Cl
18	(Ar=$2Z+4$)	—
19	—	K
20	Ca	—

If we neglect H (1) on the ground that the series do not start until $A=4$, there are only three discrepancies, and they are all relatively rare elements; for, though nitrogen is familiar, it does not form a large proportion of the earth's mass. The abundant elements without exception (as Harkins has insisted) fall into the two series which make up between them by far the greater part of the materials known to us. Fe (26) and Ca (20) are the only really abundant elements missing, and the chief isotope of Ca (20) belongs to the $4n$ series; but Fe (26) cannot belong to $4n$. From the fact that the abundant elements can be classified readily in these two series, we may argue that the classification denotes something real, and that the expression of the atomic mass in the form $4n+p$, where p is never greater than 3, gives a true clue to the composition of the nucleus. If we accept that conclusion, we are driven to believe that the part of the nucleus other than the electrons is composed of He with a number of H never greater than 3 and determined by (38.1). We shall return to this line of argument presently.

Another and more detailed suggestion may now be mentioned which is due to Meitner and intended to explain certain features in the radioactive elements, to which alone it is strictly applicable. It will be observed in Table III that each series has one branching place, which always succeeds the emission of a β-particle, both branches consisting of an α-particle and another β-particle. Again when β-ray emission occurs without branching two β-ray emissions always occur either in immediate succession or separated by a single α-ray emission. Meitner suggests that the two β-particles which are thus concerned in a branch are very closely associated in the nucleus with an α-particle, forming a sub-nucleus, which may be denoted by $(\alpha'+2\beta)$, acting throughout the disintegrations preceding the branch almost as a single particle and breaking up at the branch. She goes further and suggests that all the intra-nuclear electrons are thus associated either with α'-particles or hydrogen nuclei. Thus, e.g., the nucleus of Ur ($A=238$, $Z=92$) would be composed of 46 α-particles not associated with electrons and giving the atomic charge, together with 13 α'-particles, each neutralised by a pair of electrons, and two hydrogen nuclei each neutralised by a single electron; but this hypothesis is not really necessary to

the main idea. If the $(\alpha' + 2\beta)$ group breaks up and any part of it is emitted, the rest must follow soon. If the α'-particle is emitted first, the remaining two β-particles are equivalent and there can be no branching; but if one of the β-particles comes off first, it is possible (but not necessary) that in some cases the second β-particle may follow, in others the α'-particle, so that branching occurs.

The idea is ingenious and attractive, if somewhat speculative; but two minor pieces of evidence can be brought in its favour. If it is true, we might expect to find some difference between α-ray changes (when an unneutralised helium nucleus is emitted) and α'-ray changes (when the helium nucleus was neutralised). Now ThC, RaF, AcC, AcC′ which, on the Meitner theory, must all be α'-radiators, do not fit into Wolff's relation (see below) which applies to most α-radiators. AcX also does not fit in; but this is also anomalous in the Geiger-Nuttall relation (see below). On the other hand RaC, RaC′, ProtAc, ThC′, which should also be α'-radiators, do fit in (UrI and Th can hardly be tested); but perhaps this is a matter in which positive facts outweigh negative. Second, the theory can be used to account for another kind of branching not shown in Table III. In that Table the actinium series is shown starting from an isotope of UrI and UrII. It seems to be held by those most familiar with this very specialised branch of science that it arises as a branch from UrI and perhaps from UrII as well; these two possibilities are indicated by the following schemes:

$$\mathrm{UrI}\begin{cases}{}^{\alpha}\mathrm{UrX_1}\overset{\beta}{-}\mathrm{UrX_2}\overset{\beta}{-}\mathrm{UrII}\overset{\alpha}{-}\mathrm{Io}\overset{\alpha}{-}\mathrm{Ra}\ldots\ldots \\ {}_{\alpha}\mathrm{UrZ_1}\underset{\beta}{-}\mathrm{UrZ_2}\underset{\beta}{-}\mathrm{UrIII}\underset{\alpha}{-}\mathrm{UrY}\underset{\beta}{-}\mathrm{ProtAc}\underset{\alpha}{-}\mathrm{Ac}\underset{\beta}{-}\ldots\end{cases}$$

$$\mathrm{UrI}\begin{cases}{}^{\alpha}\mathrm{UrX_1}\overset{\beta}{-}\mathrm{UrX_2}{}^{\beta}\\ {}_{\alpha}\mathrm{UrZ_1}\underset{\beta}{-}\mathrm{UrZ_2}{}_{\beta}\end{cases}\mathrm{UrII}\begin{cases}{}^{\alpha}\mathrm{Io}\overset{\alpha}{-}\mathrm{Ra}\ldots \\ {}_{\alpha}\mathrm{UrY}\underset{\beta}{-}\mathrm{ProtAc}\underset{\alpha}{-}\mathrm{Ac}\underset{\beta}{-}\ldots\end{cases}$$

In either case there must be branches both of which consist of α-ray emissions. If this is so, Meitner's theory clearly suggests that one branch represents an α-, the other an α'-emission. In fact it will be seen that the first of the two schemes just given fits in admirably with the theory, if in the top branch UrI gives α, UrII α', and the rest α, while in the lower branch UrI gives α', UrIII α

and ProtAc α'. But endless space could be occupied, and probably wasted, in discussing these possibilities. The direct experimental evidence is so slight and complicated that none but an expert would attempt to estimate its bearing. The latest view of Hahn, who is such an expert, seems to be that all the alternatives presented here are incorrect.

13. **The dynamics of the nucleus.** By the application of these ideas, the number and nature of the constituents of the nucleus may be determined. But we shall not have a complete theory of the nucleus until we know, not only how many particles of each kind compose the nucleus, but also what is their arrangement and what are the changes that lead to instability. Such a theory will doubtless be based on a study of the numerical laws relating the various radioactive constants, the life and the number and energy of the particles emitted. Accordingly we shall proceed to consider such numerical laws as are known already.

The most definite and certain laws of this nature concern the relation between β- and γ-rays. The β- and γ-rays emitted in a single radioactive change are not homogeneous, like the α-rays. The velocities of the β-rays vary over a wide range, far too wide to be accounted for by an absorption of the rays in passing from their place of origin to the place of examination; and the γ-rays have long been known, from experiments on their absorption, to be usually of more than one kind. Detailed examination of the deflections of β-rays in a magnetic field has shown that they consist of several sharply defined groups, each characterised by a definite velocity, superimposed on a general distribution of continuously varying velocities. From the appearance of the photographic plates on which the measurements are made, the sharply defined groups are known as the line spectrum, the remainder as the continuous spectrum of the β-rays.

The frequencies of some of the γ-rays have been measured by Rutherford and Andrade, who adapted to this purpose the method of crystal reflection which has given us most of our knowledge concerning the X-rays, from which γ-rays differ only in frequency. They showed, in fact, that some of these γ-rays were nothing but part of the X-ray spectrum of the disintegrating atoms, excited by

the β-rays just as they might be excited by the electron stream in an X-ray tube; for, though this X-ray spectrum has not been measured in the ordinary way, its nature is known from that of elements of neighbouring atomic number by means of Moseley's law. But in addition to these X-rays, arising from the *K*- and *L*-extra-nuclear electrons, there were other frequencies in the same region of the spectra to which nothing corresponded in the neighbouring non-radioactive elements. These frequencies they attributed to true γ-rays, arising from the nucleus itself. Further it is known from measurements of the absorption of γ-rays in metals that there are other γ-rays much harder, and therefore of higher frequency, than these. The same method cannot be applied to these harder γ-rays, because their wave-length is too short compared with the spacing of the planes of any crystal; they lie beyond the range of crystal analysis in just the same way as X-rays lie beyond the range of optical analysis. Their frequencies must be determined by some other method; a simple and elegant theory of the relation between β- and γ-rays, due to Rutherford and Ellis, provides the necessary means.

According to this theory the β-rays of the line spectrum are secondary rays due to the detachment of the extra-nuclear electrons of the radioactive atom by the γ-rays from the nucleus travelling among them. (The possibility that the γ-rays from one nucleus may detach extra-nuclear electrons surrounding a neighbouring nucleus will be noted later.) There is one obvious and direct method of testing the theory. If the γ-rays from a radioactive element are allowed to fall on a non-radioactive element of neighbouring atomic number, that substance should emit a β-ray line spectrum closely resembling the β-ray spectrum of the radioactive body; the difference between the two should be capable of being explained by the difference in the states of the extra-nuclear electrons in the two elements as revealed by X-ray spectra. Indeed in some cases, and these of greatest experimental importance, the test can be applied more simply; for there may be a non-radioactive isotope of the radioactive elements, having the same atomic number and therefore the same states for its extra-nuclear electrons. Such an element should give a β-ray line spectrum identical with that of the radioactive element. The test has been applied with RaB and

lead and with ThD and bismuth. The result is so far satisfactory that all the lines given by the non-radioactive element are identical with some lines of the radioactive; but the converse is not true. The absence of some of the lines of the radioactive element from the spectrum of the non-radioactive may merely be due to the far lesser intensity of the latter in any possible conditions. It is at least proved that some of the β-ray lines arise in the manner suggested by Rutherford; the question whether all so arise requires further examination.

This examination has been conducted recently by Ellis, who has used his results to measure the frequencies of γ-rays inaccessible to other methods. The principle involved is this. We know from quantum theory that, when radiation of frequency ν is absorbed by an electron, it gives to that electron an energy $h\nu$; we know also, from Bohr's theory of spectra, that with each extra-nuclear electron is associated a definite amount of energy, W, which is that required to set it free from the atom. Accordingly if radiation of frequency ν is absorbed by an electron characterised by W, that electron must leave the atom with kinetic energy $h\nu - W$. Again from the X-ray spectrum of its isotope (or, if there is no non-radioactive isotope, from Moseley's law applied to elements of neighbouring atomic number) we know what are the values (W_r) characteristic of the various extra-nuclear electrons in the radioactive atom. If then we can find a set of frequencies ν_s such that every line in the β-ray spectrum of a radioactive atom corresponds to an energy given by one of the alternatives ($h\nu_s - W_r$), then we may begin to suspect that Rutherford's theory is true and that this set of ν's truly represents the frequencies of the γ-rays emitted by that radioactive atom.

But of course, whatever the lines might be, some values ν_s could be found to account for all of them. In order to be sure that we are not merely juggling with arithmetic, we must apply two checks which are similar to those which we noted (Ch. XV, p. 11) when discussing the evidence for the principle of combination and the existence of spectral terms. First, the number of ν's, over and above those determined experimentally, which we have to introduce in order to explain all the β-ray lines must be less than the number of the lines explained, and some explanation must be forth-

coming of the expressions $h\nu_s - W_r$ which are *not* represented in the β-ray spectrum. Second, we must seek for some relation between the ν's which shows that they are not arbitrary and artificial selections.

Both these tests are fulfilled. Thus, Ellis finds that in order to account for 33 of the 37 lines in the β-ray spectrum of ThD, he has to assume 18 ν's for the γ-rays. Again, to account for all the 12 lines in the β-ray spectrum of RaB, he has to assume 6 ν's for the γ-rays. The strongest β-ray line attributed to excitation by each γ-ray generally corresponds to the same W_r, and energies $h\nu_s - W_r$ unrepresented in the β-ray spectrum are those which correspond to a ν_s and a W_r both of which give weak lines in other combinations. The scheme is thus coherent. Agreement of the calculated ν's with those observed cannot be tested, for the γ-rays of ThD have not been measured, while all those attributed to RaB lie outside the range within which the crystal method is applicable. There is here nothing inconsistent with the theory; for it is the hardest γ-rays which are much the most effective in exciting β-rays in other substances; those excited by the soft γ-rays, including all those in the region of the X-ray spectrum, are usually too faint to be detected. But the results are even more striking when the second test is applied and the ν's are compared amongst themselves. For if the mechanism of the emission of γ-rays resembles at all that of X-rays, we should expect that the principle of combination would apply to these ν's, and that they could all be represented as the differences between a smaller number of terms. Actually 8 terms are necessary to account in this manner for the 18 γ-rays from ThD; and, though 5 terms are required to account for the 6 rays of RaB, the same 5 terms will account also for all the lines (4 in number) in the γ-ray spectrum of that element which have been detected by the spectroscopic method in the region of slightly lower frequency. In this last case the connection between the frequencies predicted by the theory and those measured directly is established definitely.

By these observations the theory of the line spectrum is confirmed and an extremely important result obtained. Though the electrons giving the β-ray line spectrum do not come from the nucleus, they give us much information about it. They enable us to

determine the frequency of the γ-rays which undoubtedly do come from it. They show in particular that the principle of combination and therefore Bohr's first principle concerning 'possible' (or 'quantum' or 'stationary') states applies within the nucleus, and so lay down the principles on which any theory of its constitution must be based. As yet no progress has been made in applying to the nucleus Bohr's second principle or Sommerfeld's extension of it; we have as yet no idea why the quantum states are what they actually are; but probably developments in this direction will soon follow.

There remains the continuous β-ray spectrum. According to Ellis, this represents the emission of electrons from the nucleus. He imagines that the whole process of β- and γ-ray activity takes place in two stages. In the first, one of the constituents of the nucleus falls from one of the quantum states, represented by the γ-ray terms, to another, and thereby emits a γ-ray which in passing through the atom ejects an electron of the β-ray line spectrum. This change leaves the nucleus in a state of instability and at some subsequent time, following immediately or at some finite interval, an electron is ejected from the nucleus, giving the continuous spectrum. The variation in the energies of these electrons would be due to differences in the manner in which the instability occurred and might be related to the preceding transition between γ-ray states. The idea is plausible and some parts of it can be tested to some extent by experiment. Thus, if, as is supposed, the γ-ray of RaB (say) is emitted before the electron is ejected from the nucleus, the extra-nuclear electrons, over which it passes and one of which it ejects, should be characterised by the W's of RaB: if, on the other hand, the electron from the nucleus is emitted before the γ-ray, the W's ought to be those characteristic of the next element of the series, RaC, of which the atomic number is one unit higher. The experiments seem to support the first alternative, but their accuracy is hardly sufficient to settle the matter. Besides it is possible that the electron of the line spectrum comes, not from the atom emitting the γ-ray but from a neighbouring atom, which has not yet broken up. But if this were so, as the substance decayed and the proportion of RaC to RaB in it increased, the line spectrum ought to change gradually from that representing the W's of the

former to that representing the W's of the latter: no such change seems to have been observed; it is probable therefore that the electrons of the line spectrum come from the extra-nuclear region of the very atom emitting the γ-ray. Again, on this theory, since we have every reason to believe that the atom ejects from its nucleus only one electron in disintegrating, the number of rays emitted in the continuous γ-ray spectrum ought to be equal to the number of atoms disintegrating, and the total number of β-rays in the line and continuous spectra greater than this number. The testing of these predictions is difficult, because β-rays are not counted nearly as easily as α-rays: but the observations available confirm the second prediction and are not inconsistent with the first. Lastly there should be no close relation between the γ-rays and the continuous spectrum when different atoms are compared. It is found that the two are almost independent; thus, while in RaC and RaD the energy of the γ-rays is an appreciable fraction of that of the β-rays, RaE emits a continuous β-ray spectrum with hardly any trace of γ-rays or of a line β-ray spectrum.

It should be mentioned that an alternative theory of the relation between β- and γ-rays was put forward by Meitner before Ellis's full evidence was available. According to it some of the β-ray lines represent primary electrons from the nucleus, and the γ-rays are secondary rays due to the emission of these electrons. But the experimental evidence as well as the general coherence and simplicity of the ideas are in favour of the Rutherford-Ellis theory.

We may now turn to the α-rays, but here far less information is to be gained. The only numerical relations known in which α-ray emission is involved are those between λ, the decay-constant of an element emitting such rays, R the range of the rays, and the atomic mass and number; but these relations are all largely empirical and not even of universal validity. The energy E and velocity v of the rays are closely connected with R; if R is measured in cm. in normal air,

$$R = 1{\cdot}35 \times 10^8 . E^{\frac{3}{2}} = 1{\cdot}13 \times 10^{-27} v^3 \ldots\ldots\ldots (47.1).$$

The best known of these relations is that of Geiger and Nuttall:

$$\log \lambda = A + B \log R \ldots\ldots\ldots\ldots\ldots (47.2).$$

A relation of this form holds between all the α-radiators in a

single series (except AcX, which for some unknown reason is anomalous), but different values of A are required for each of the three series. If the logs are to base 10, A lies between $-36{\cdot}9$ and $-39{\cdot}6$, B is $53{\cdot}3$ for all three series. But the same facts are covered equally well by two other relations of rather different form due respectively to Swinne and H. A. Wilson,

$$\log \lambda = a + bv \quad \text{.....(48.1),}$$

$$\log \lambda = \log v + c + dv^{-2} \quad \text{.....(48.2).}$$

On the other hand there is Wolff's relation involving A and Z in place of λ,

$$\log R = \log (\tfrac{3}{4}A - Z + c) + \eta \quad \text{.....(48.3),}$$

but this has a more limited scope; it fails for ThC, RaF, AcX, AcC, AcC′, while Ra and ThX are doubtful.

14. **The stability of the nucleus.** We have still to discuss why some nuclei exist with values of A and Z, while others which are equally possible according to (38.1) do not. To this question there is as yet no answer that pretends to be complete, but some indication of the kind of evidence on which an answer must ultimately be based can be obtained by developing further the considerations of pp. 39–42. It is reasonable to suppose that different possible combinations of the component parts of the nuclei differ in stability, and that we may gain some clue as to what arrangements are relatively unstable by relating instability to rarity in the earth's crust and, when the element is radioactive, to a short period; the justification of this assumption is that we arrive at much the same conclusions whichever of these two properties we consider. Proceeding on this line of argument, we conclude from our previous examination that nuclei of the forms $A = 4n$, $Z = 2n$ or $A = 4n + 3$, $Z = 2n + 1$ are especially stable; the former have no electrons, the latter two. Let us therefore proceed to relate stability to the number of nuclear electrons. For this purpose we may write (38.1) in the form

$$q = \frac{A}{2} - Z + \alpha,$$

where α is never greater than $\frac{3}{2}$. If we are content with an approximation we may put $\alpha = 0$ and the number of electrons in the nucleus

equal to $\frac{A}{2} - Z$. We now plot q, derived in this way, against Z. We do not know A for all elements, since not all have been examined for isotopes; but since we are going to deduce merely statistical conclusions from our results, we may safely substitute $\bar{A}$ for A; for by so doing we are merely taking means in proportion to abundance. We find (Fig. 2) that all elements lie very closely about a curve, the smoothness of which is evidence that the assumptions on which it is based are essentially correct. This curve is parallel to the axis of Z, with q between 0 and 1, till $Z = 18$; then it rises,

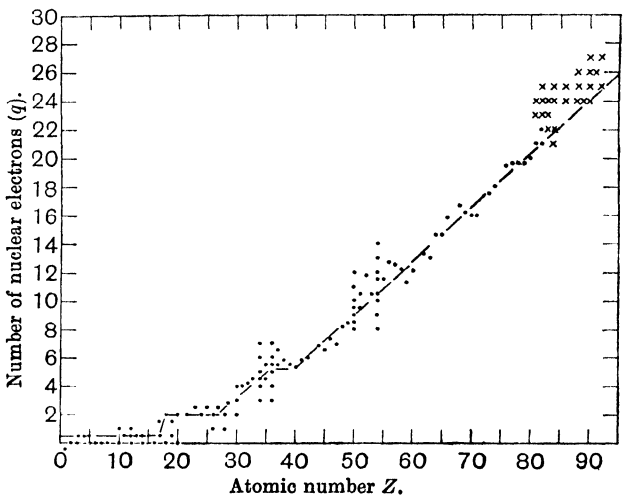


Fig. 2.

and for elements of higher atomic weight is straight and sloped so that q increases by 1 for an increase in Z of 2·7. It is reasonable to interpret this mean curve as representing the relation between simple nuclei and electrons which gives the most stable element: and we may expect that the further an element is from it, the less abundant it will be in nature and the shorter its life will be. Actually it is found that the less abundant isotopes generally lie further from the line than the more abundant. It is also found that almost all the radioactive elements (indicated by ×), which are not completely stable, lie above this line and therefore contain too many electrons for perfect stability. Further an empirical rule

(originally due to Fajans) states that the further a radioactive element is above this line, the more likely it is that it will lose an electron and approach the line, the less probable that it will lose a helium nucleus and recede from it; that is to say, the shorter will be its life if it is a β-radiator, the longer if it is an α-radiator. One further fact may be noted. q first rises sharply at $Z = 18$, where the first irregularity in the periodic table occurs, Ar having a mean atomic weight greater than that of K. (Of course this irregularity is a result of the sudden appearance of an appreciable q, and so is the breaking off of the series of Table IV.) Now it is just here that the first β-radiator occurs, namely potassium; it is tempting to regard it as evidence of instability arising from excess of electrons in the nucleus.

Similar arguments have been developed by Harkins in voluminous papers and, with more restraint, by Fajans and others. As a result of their work we know several empirical rules for connecting the stability of an element with its nuclear constitution as determined from (38.1), on the assumption that p is never greater than 3. It appears, for example, that nuclei with an odd number of electrons are much less stable than those with an even number; of those with an even number the most stable are those for which the number is 0, or in which the $2n$ electrons are associated with $3n$ hydrogen nuclei, as they are in the series $A = 2Z + 1$ among the lighter nuclei. On the other hand elements of the form $4n$ with odd atomic numbers (which must consist of helium nuclei together with an odd number of electrons) are particularly unstable; they are without exception short-lived β-radiators, having a very pronounced tendency to lose electrons. The relations of this kind that have been found are interesting and suggestive; some of them are well established, though others suggest arithmetical coincidences. Someday they will doubtless be welded together into a consistent theory; but since that time has not yet come, we will devote no more attention to them.

But one question remains, the most difficult perhaps in the whole field of nuclear constitution. We have used the term 'stable' indifferently to mean abundant elements and the radioactive elements of relatively long period: that association of meanings would be perfectly justifiable if all elements were radioactive, for then

those with the shorter life would necessarily be the less abundant. But in spite of the labours of many investigators, there is no evidence of radioactivity among elements other than those which we have classed as radioactive. Radioactivity, which is true instability of some kind, is definitely confined to the elements of high atomic number (with the exception of K (19) and Rb (37)). No theory of the nucleus will be complete until we have some explanation of this association. Rosseland has recently put forward an interesting suggestion. He points out that, according to Bohr's theory of electronic orbits, which we shall consider in the next section, some of the extra-nuclear electrons in the elements of highest atomic number must pass very near to the nucleus. He suggests that elements of atomic number higher than 92 cannot exist, because, if they did, the extra-nuclear electrons would have to pass actually through the nucleus; and that those of atomic number near this limit are unstable because the intra-nuclear orbits are perturbed by the close proximity of the extra-nuclear. He supposes further that there may be some kind of resonance between the two sets of orbits, and that in this resonance is to be found the explanation of the anomalous nuclei K and Rb; it so happens that in these two elements the conditions for resonance occur. All this is very speculative.

And even if it is true, a grave problem remains. The instability manifested in radioactivity is of a very peculiar kind. Dynamically unstable systems usually break up in a period after their formation which is not long compared with the period of their oscillations. But in radioactive atoms the ratio of the average 'life' to any period that we can conceive as characteristic of the atom is enormous; uranium has an average life of a thousand million years; the longest period we know of in the atom is not as much as one thousand-million-millionth of a second. How comes it that this vast number of orbitary periods can be performed without disaster and yet disaster occur ultimately? Moreover there is the puzzling fact that the life is only an average life. We can prepare UrX_1 (say) in which we know that the age of the oldest atom present is not more than a few minutes; the average life of the atoms is several days; and yet within a few seconds of their birth the same proportion of atoms will disintegrate as when they are all a year old. Radioactivity cannot be thought of as some regular natural process; it must be

due to some kind of 'chance', but of what nature this chance can be we do not know and find it hard to make a reasonable guess. One reasonable suggestion has been offered by Lindemann; if we consider it briefly, it is rather to make clear the difficulties of the problem than to put forward a really plausible solution of them.

Stated very broadly Lindemann's suggestion is that the instability which results in disintegration is due to the fortuitous attainment of some peculiar configuration of the particles of the nucleus[1]. Let us take a very crude illustration. Suppose that the constituent particles are all moving in circular orbits. The periods will not be commensurable, and the relative phases of the orbits will change so rapidly and so irregularly that the configuration at any moment may be regarded as due to chance. Imagine now that we know that the atom will disintegrate if all the particles happen to fall at the same instant on a single straight line, and consider the chance that such an event will occur within some period t. This chance will depend on P, the number of particles; indeed general probability theory indicates that P must occur in the form α^P. If it is only the geometrical configuration of the particles that matters, α will be independent of the frequencies ν of the orbits, so long as they are all very great compared with $1/t$, and will be determined simply by how nearly all the particles must be to the straight line in order that the disintegration may occur. But a simple modification will introduce the frequencies. If all the particles have to cross the same straight line within some fixed interval τ, and if the frequencies, though incommensurable, are all of the same order of magnitude, general considerations again show that α must be of the form $\alpha'\tau\nu$, where now α' is a mere geometrical constant. Accordingly the chance that a single glance at the particles would disclose that they are in a critical state must be proportional to $(\alpha'\tau\nu)^P$. But if t is so long compared with the periods of the orbits that during t the effects of the initial configuration are completely wiped out and another random configuration, independent of the first, is attained, then we can make, as it were, several trials during t. The number of trials we can make during any assigned t is proportional to ν. Hence finally we arrive at the conclusion that, of

[1] I have not followed Lindemann's statement of his theory at all closely because the calculation he gives appears to contain a slight error. The equation from which he starts is wrong dimensionally.

a large number n of atoms, the number dn disintegrating in time dt is given by

$$-dn = \lambda n\,dt \propto n\,.\,(\alpha'\tau\nu)^P\,.\,\nu dt \quad \text{.....(53.1).}$$

Now suppose that the frequency ν is connected with the energy of an α-ray liberated on disintegration by the usual quantum relation $E = h\nu$, then from (47.1) and (53.1)

$$\log \lambda = \log \nu + P \log C + \tfrac{2}{3} P \log R \text{.....(53.2),}$$

where C is a constant involving α', τ, h and the factor of proportionality.

Comparing (53.2) with the Geiger-Nuttall relation (47.2), we may identify $P \log C$ with A and $\frac{2}{3} P$ with B. But the first term of (53.2), which involves R through ν, has no counterpart in (47.2); however it is small compared with the last and we shall neglect it. We may then calculate P, the number of particles in the nucleus B; we find that P is about 80 for all radioactive atoms. Of course it should not be the same for all atoms in a series, since the number of particles decreases as disintegration proceeds; we must regard (53.2) as only an approximation and P as a mean value. But as a mean value it is not unreasonable; for if we regard the nucleus of Ra as made up according to formula (38.1), we must have $n = 56$, $p = 2$, $q = 26$; if helium nuclei, hydrogen nuclei and electrons are all equally particles for our present purpose, $P = 84$. Lindemann's idea is thus very attractive, and it has consequently received much attention. It suggests at once an explanation on the same lines of Wolff's relation (48.3); for A and Z on the right of (48.3) determine P. But it is decidedly speculative, mainly because it is by no means certain that many other hypotheses would not lead to the same kind of agreement with experiment. Indeed it is quite possible that we are wrong in attempting to 'explain' the peculiarly fortuitous character of radioactivity: it may turn out to be more fundamental than anything in terms of which we can hope to explain it. For radioactivity, as we know now, is a quantum process, and it is likely that we shall have to recognise chance as an integral part of all such processes, inseparably connected with the discontinuity that is their most striking feature. However these are deep matters which it would be inappropriate to discuss at the end of this section; for the time being, atomic instability must be left as one of the mysteries of modern physics.

SECTION II

THE EXTRA-NUCLEAR ELECTRONS

15. **Evidence from ionising rays.** The central problem of atomic structure, since the advent of the first electronic theory, has been the determination of the number and arrangement of the electrons; for, beyond doubt, it is this number and arrangement that determines all the properties of the atom outside the special, and experimentally not very important, group that we have considered in the last section. Today any solution that can be offered must be based mainly on the study of spectra; but before an adequate theory of spectra was available much more weight was placed on evidence from other sources. It will be well to consider this evidence before passing to the more modern aspects of the problem.

If any property of matter could be found in determining which all electrons play the same part, the determination of their number should follow immediately. Thomson from the first suggested that such properties were to be found in the effect of matter upon X-rays and β-rays passing through it, at any rate if the rays were so hard that their period, in the one case, or time of passage through an atom, in the other, was very much shorter than the period of vibration of any electron; if this condition is fulfilled, the reaction should be almost independent of the forces binding the electron in the atom, and depend only on its mass and charge.

The property to which he attributed most importance for this purpose was the scattering of X-rays, of which he gave a simple theory. According to Stokes's theory X-rays were electromagnetic pulses emitted, in accordance with Maxwellian theory, during a sudden change in the motion of an electron. This theory leads (see Ch. XI, p. 278 et seq.) to a relation between the acceleration of the emitting electron and the electric displacement D at any point in its neighbourhood; or, by Poynting's theorem, between the acceleration and the energy radiated. But an electron over which

the radiation passes, if it is effectively subjected to no other forces, will receive an acceleration $f_1 = \frac{4\pi\epsilon D}{\mu}$; from the value of f_1 so determined the energy radiated can again be calculated. It is therefore a simple matter to find the ratio of the energy of the scattered radiation due to such an electron to the intensity of the primary radiation in its neighbourhood. If there are n electrons per unit volume, it appears that σ, the ratio of the energy emitted per second from this volume as scattering radiation to the energy of the primary radiation passing through it per second, should be given by

$$\sigma = \frac{8\pi}{3} \cdot \frac{\epsilon^4}{\mu^2 c^4} \cdot n = 6{\cdot}95 \times 10^{-25} n \quad \text{.....(55.1).}$$

Let ρ be the density of the substance, n' the number of electrons per atom, so that

$$n = \frac{n'}{A} \cdot \frac{\rho}{m_H} \quad \text{.....(55.2),}$$

then

$$\sigma/\rho = 0{\cdot}424 \cdot \frac{n'}{A} \quad \text{.....(55.3).}$$

Barkla's experiments showed that σ/ρ was constant over a considerable range of materials and was equal approximately to 0·2. Accordingly

$$n' = A/2 \text{ approximately} \quad \text{.....(55.4),}$$

and the number of electrons per atom is about half the atomic weight.

This was the result that led Thomson to the conclusion that inspired all later work. Unfortunately, as so often happens, the evidence for a perfectly true conclusion appears very much less convincing when examined later. Barkla's result is neither accurate nor general: for very hard rays, especially γ-rays, σ/ρ is only about 0·04; it is not constant even for softer rays, increasing with the atomic number of the scattering material and being generally less than 0·2. But, even more serious, the basis of the whole argument is doubtful; the classical theory of dispersion (which is implied in the calculation) and, still more, the classical theory of emission are no longer tenable, although they appear to give nearly the right result in applications similar to these. There is nothing in the modern interpretation of scattering to throw doubt on Thomson's

conclusion; but neither theory nor experimental data are sufficiently certain to support it.

The earlier attempts to deduce similar information from the scattering and absorption (or loss of velocity) of β-rays are now known to be even less reliable. Scattering, as we have seen, is determined mainly by the nucleus; absorption is determined by the electrons; but the assumption that it is not affected appreciably by the forces binding them in the atom is quite unjustifiable. For a simple calculation shows that if the electrons are perfectly free, and if there is no limit to the distance at which two electrons can act on each other, the absorption must always be infinite. Sundry additional hypotheses were introduced to remove this difficulty, but Bohr has shown that the only adequate way to deal with the matter is to take the forces into account. He relates the absorption directly to the natural frequencies of the electrons, which are of course determined by the forces binding them; he is then able to show that the absorption of β-rays (and also of α-rays) of different velocities in some of the elements of lower atomic number is consistent with what we know on other grounds of the number of electrons in them and the frequencies as determined by optical and X-ray data. But the calculation involves many simplifying assumptions which cannot be wholly true, and the agreement between theory and experiment is only approximate. Estimates based on such grounds can at best confirm those derived from more reliable sources.

However it is probable that in the future the study of the reactions between ionising rays and the electrons in the atoms through which they pass will yield valuable information concerning atomic structure. Some indication of the kind of information that may be obtained is already forthcoming. The reflection of X-rays at crystal planes is a manifestation of the scattering on which Thomson's conclusions were based; the recent work of W. L. Bragg and his associates on the intensity of this reflection leads to some conclusions of which the importance will appear presently. The regular reflection of X-rays arises from the distribution of the scattering centres in evenly spaced planes, the distance between successive planes being that between the atoms (or molecules) of the crystal. The centres must be electrons, the nuclei being too

massive to exert any influence. But unless all the electrons in an atom lie in one plane, it is impossible that the atomic 'planes' at which reflection takes place should be perfectly sharp; if the electrons are arranged, for example, on a spherical shell about the nucleus, the atomic planes must have a width equal to the diameter of this shell. This diffuseness of the atomic planes necessarily makes the reflection less intense than it would be if the planes were perfectly sharp; for, if the planes were perfectly diffuse and the distribution of the electrons throughout the crystal uniform, there would be no reflection at all. Further it is not difficult to see that this diffusion will diminish the intensity of reflection the more, the higher the order and the larger the glancing angle at which reflection takes place. (Rays which result from the interference of radiation scattered with a difference of path $n\lambda$ are said to be reflected in the nth order.) Accordingly by the study of the relative intensity of reflection in different orders and at different crystal planes, which give different glancing angles, it is possible to estimate the diffuseness of the planes. The theory is difficult and will not be attempted here; moreover, even with a perfect theory, there would be necessary limitations to the knowledge that could be gained about electronic distribution; for example, the method can give nothing but a time-average of the distribution, so that, if the electrons are moving, it can tell nothing about the forms of the orbits. But the broad features of the distribution can be determined with some certainty. Thus it appears that the number of the electrons in a given volume must increase rapidly as the nucleus is approached; if an attempt is made to devise an arrangement of electrons on concentric spherical shells which shall accord with the determined diffuseness of the planes, the number of electrons on the inner shells must be greater than that on the outer shells. In the atom of Na (10), for example, an arrangement consistent with the experimental facts would be one in which 7 of the 10 electrons lay on a sphere of radius $0{\cdot}26\mathring{A}$, while 3 lay on a sphere with radius $0{\cdot}76\mathring{A}$; Cl (18), on the other hand, requires at least three shells, one of radius $0{\cdot}25\mathring{A}$ with 10 electrons, another with radius $0{\cdot}86\mathring{A}$ and 5 electrons, another with radius $1{\cdot}46\mathring{A}$ and 3 electrons. ($1\mathring{A} = 10^{-8}$ cm. The reason why 10 and 18, not 11 and 17, electrons are attributed to these atoms will appear in Section III.)

Many other arrangements are possible, but they all show the same feature of rapidly increasing density towards the centre.

When we turn to rays consisting of charged particles, some interesting but limited conclusions can be based on Millikan's experiments, in which the chance is determined that a ray will liberate more than one electron from an atom in an ionising encounter. It was found that the chance is so small for most atoms that a double ionisation at a single encounter has never been observed certainly in many hundreds of observations. The only exception among the atoms examined is helium; two electrons are liberated from this atom in about 1/6 of all the encounters which result in ionisation. From the energy required to remove an electron the theory of pp. 11, 12 will tell roughly how near the charged particle must pass to an atomic electron in order to eject it; the knowledge that a particle very rarely approaches near enough to two electrons in its passage through the atom sets a limit to the possible density of the distribution of the electrons in any part of it. Such arguments confirm the conclusions reached by Bragg. The more easily detached electrons, which lie on the whole further from the nucleus, must be much more sparsely distributed than the more firmly attached, which lie nearer to the nucleus and require a much closer encounter with a charged particle in order that they may be ejected.

Lastly there are some observations which, though they do not determine directly the electronic arrangement, throw light on the principles according to which it must be determined. Ramsauer measured the mean free path of electrons moving with a speed of a few volts through various gases. In the rare gases, and especially argon, he arrived at the remarkable conclusion that, as the velocity is decreased, the mean free path increases, reaching a maximum at about 1 volt; and that the diameter of the atom, determined from this free path, is very much smaller than any estimated by the usual methods. The only possible conclusion is that these very slow electrons can pass right through the extra-nuclear electrons and even very close to the nucleus without suffering any deflection. Hund has suggested that this conclusion may be brought into line with general quantum theory by assuming that, when the conditions are such that the energy of the radiation which, according to

classical theory, would be emitted at a deflection of the particle is greater than the kinetic energy that the particle possesses, then no reaction occurs and the particle proceeds unhindered on its course[1]. But all this is still speculative; its interest for our immediate purpose is the indication given that the knowledge to be obtained from a study of the familiar process of ionisation by charged particles is by no means exhausted.

16. **Evidence from spectra.** Indeed the obstacle to pursuing these lines of inquiry further is not the lack of suggestive facts or any experimental difficulty; it is that we have not any adequate theory by which to interpret experiment. The reaction of ionising rays with the electrons over which they pass is a comparatively simple matter according to the older electrodynamics, which is involved to some extent in all the interpretations we have just discussed. But we know now that within the atom the older electrodynamics is not always true. It is sometimes true, completely or up to a point; thus it seems completely true in the reactions of two nuclei moving relatively to each other with high velocity; it is true up to a point in interpreting dispersion. But it is sometimes completely untrue, for instance in its account of ionisation by X-rays. We do not know at present when it is likely to be true and when it is not; and as a consequence all the arguments which depend on its assumptions are precarious; we can never be sure that we have drawn the line at the right place. There is only one property of matter concerning which we have a satisfactory theory whereby to derive information about electrons in the atom from our measurements.

This theory concerns series spectra and formed the subject of Ch. XV. It consists of two distinct parts. One (previously called the second assumption) lays down the principles according to which the orbits of charged particles in electric fields are to be determined. It is applicable to every kind of phenomenon that is an expression

[1] In his latest paper at the time of writing Bohr suggests that quantum orbits are 'permissible' according to classical electrodynamics only when they are such that the retarding force due to the radiation from them is small compared with other forces on the electron. This view is clearly in accordance with Hund's suggestion.

of the form of such orbits, and therefore, according to any electronic theory of the atom, to all atomic and molecular properties, except possibly those considered in the preceding section; and, as we have seen, it is probably applicable to these as well. If we could be sure that these principles were true to the last detail and if we were not limited by analytical difficulties, this part of the theory would give a complete formal solution of our problem. We know the nuclear charge and the number of electrons in each atom; we believe that the fields due to their charges obey the familiar electrostatic laws (except when the charges approach very closely); and it should be merely a matter of straightforward calculation to deduce the electronic orbits. But even if we could obtain such a solution we should still need something more; we should need some principle according to which properties measurable experimentally could be attributed to any given system of electronic orbits; for it is only if we have such principles that we can relate our theory to experiment, and so produce any evidence for it. And while we cannot apply the 'second assumption' as completely as we should like, such additional principles are all the more necessary: for actually our only method for deciding between alternatives, all of which are equally possible according to that assumption (so far as we can tell with our limited powers of analysis), is to inquire which of them is in accordance with experimental data. The other part of Bohr's theory (previously called the first assumption) supplies such principles, but it is applicable only to spectra; it lays down the relation between electronic orbits and emission or absorption spectra, so that, if the orbits are known, the spectra can be deduced. There is at present no principle applicable to phenomena other than spectra which establishes in so direct and definite a manner relations between these other phenomena and the nature of the electronic orbits. It is for this reason that the study of spectra must play a part in the investigation of atomic structure quite different from that of any other branch of experiment. From spectra alone can we derive information that is perfectly determinate, though it may be limited.

We will then proceed to the consideration of spectra and, at the outset, remind ourselves what is Bohr's first assumption. It is that the frequency ν of every spectral line is the difference between

two terms T_r, T_s[1], and that each T_r is proportional to the energy required to remove an electron from one of the electronic orbits to the boundary of the atom. If W_r is this energy, then

$$W_r = hT_r,$$

where h is Planck's constant. The spectral line in question appears in the emission or absorption spectrum when an electron in the atom passes from one of these orbits to the other. If then we can determine the terms, we shall know the energy of the electronic orbits, and thus have made a great step towards elucidating all their characteristics.

These considerations apply equally to optical and X-ray spectra; but there is a difference between these two classes that is of great importance for our immediate purpose. It is (see Ch. XV, p. 29) that the electronic orbits concerned in X-ray spectra are those which form part of the permanent structure of the atom in its normal and undisturbed state, whereas those concerned in optical spectra are characteristic of a state of the atom that is not normal and is only produced by disturbance (see further p. 75). The distinction made on this ground between the two classes does not coincide exactly with that ordinarily made, which is based simply on the experimental methods applicable to the range of frequency within which the lines lie. Thus some of the terms concerned in the helium spectrum, which lies in the optical range, represent X-ray terms, according to our classification; again certain features in lines lying within the X-ray region must be referred to electronic orbits representing abnormal states. But on the whole the division is so very nearly the same whichever method of classification we adopt that the terms optical and X-ray may be applied conveniently and without confusion to the newer and theoretical classification.

17. X-ray spectra. If then we want to study normal atoms, it is natural to begin with X-ray spectra. A very rough outline of the facts concerning X-ray spectra was given in Ch. XV, but a brief recapitulation may be useful in slightly different form, and with some additions and reservations that are now necessary.

[1] Following Bohr's recent notation, the terms will be denoted by T, the frequency of lines by ν. In Chapter XV ν was used for both.

The X-ray spectra of all elements are essentially similar. To every line in the emission or absorption spectrum of one element corresponds a similar line in the spectrum of every other element within a certain range of atomic number on one or both sides of the element in question. The relation between the frequencies ν of corresponding lines is given approximately by Moseley's equation

$$\nu = a(Z - z)^2 \quad \text{.....(62.1),}$$

where a, z are constants characteristic of the particular line. Thus the frequency of the line and the hardness of the rays increase with the atomic number.

The lines can be divided sharply into at least three groups, denoted by K, L, M, in order of decreasing frequency. There are several lines in each of these groups, but the members of one group differ in frequency among themselves far less than they differ from those of other groups. The constant z in (62.1) is nearly the same for all lines of the same group. Rays belonging to a fourth and fifth group N, O, of still lower frequency, have been detected in the elements of high atomic number; but since the difference between successive groups diminishes as we pass in the direction KLM, N or O rays are not very clearly distinguished from M rays. The distinction between the K, L, M groups, which alone are open to detailed examination and accurate measurement, is very well marked.

The absorption spectra, which appear experimentally as absorption 'edges', are much simpler than the emission spectra; there is only one K- and only three L-absorption edges, whereas there are at least five K- and twenty L-emission lines. The frequencies of absorption edges are (at least very nearly) the terms, the differences between which are the emission lines.

It will be convenient here to introduce some important work published since Ch. XV was written. It confirms the fundamental ideas upon which our interpretation of X-ray spectra is based and thus supports our use of X-ray evidence for the elucidation of atomic structure; and it leads to some new ideas which are necessary for that purpose.

(1) Some very beautiful experiments, based on the ideas which we discussed on p. 44, have been carried out by de Broglie. Ac-

cording to fundamental quantum theory, an electron can absorb from radiation of frequency ν_0 only an amount of energy $w_0 = h\nu_0$. If work W_r has to be done in order to remove an electron from the atom, it must emerge with kinetic energy $w_0 - W_r$. If the atomic states, and consequently the values of W_r, are discrete, the kinetic energies with which electrons leave the atom must also be discrete. Therefore if we observe the deflection in a magnetic field of the secondary electrons emitted from an element under the action of X-rays of frequency so high that w_0 is greater than any W_r, we should obtain a line spectrum, the energies associated with the different lines being $w_0 - W_r$. We shall have to take into account that the electrons may lose some part of their energy in emerging from the substance after leaving the parent atom, and we shall expect the lines to be diffuse on the side of lower energy: but the side of higher energy ought to be perfectly sharp. de Broglie found that the facts are precisely in accordance with expectation; his experiments enable the values W_r to be determined without a knowledge of ν_0. For some of the electrons will come from the surface of the atom where W_r is practically zero. These electrons will emerge with the full energy w_0; any other electrons will have a lesser energy. So, by measuring the difference in energy between the fastest electrons emitted, which appear experimentally as a definite limit to the spectrum of magnetically deflected rays, and each of the lines of the spectrum, we determine directly the values of W_r. A slight complication is introduced by the excitation of the X-ray spectrum of the element by the primary X-rays. If $\nu_1, \nu_2, \ldots$, are the frequencies of the lines of this spectrum, and $w_1 = h\nu_1$, we shall have, superimposed on the magnetic spectrum $w_0 - W_r$, due to the primary X-rays, other magnetic spectra $w_1 - W_r, w_2 - W_r, \ldots$, due to the secondary X-rays. But the disentangling of the spectra is only a matter of patience; and the fact that all the different spectra give the same values W_r is additional confirmation of the theory.

The work is particularly interesting because, in principle at least, it enables the energies W_r to be determined without any spectroscopic or other measurements involving the conceptions of the wave theory; and, since at present the gulf between these conceptions and those of quantum theory is unbridged except by Bohr's purely formal rule, there is a clear gain of logical independ-

ence. Actually we do still require spectroscopic measurements to explore the details of atomic structure, because the frequencies of X-ray lines can be determined with much greater precision and much greater completeness than can the energies of the secondary electrons. But since the two methods agree perfectly within the limits of experimental error, one slightly disquieting difficulty underlying all our discussion is removed.

(2) Kossel has pointed out that, according to Bohr's theory and his own interpretation of the absorption spectrum (see Ch. XV, p. 29), the absorption edges should not be perfectly sharp. In optical spectra absorption lines are fewer in number than emission lines, because all absorption lines must have one term in common, namely that representing the orbit of the displaced electron in the normal atom. In X-ray spectra they are fewer for a slightly different reason. More than one of the orbits in the normal atom are concerned, for any of the extra-nuclear electrons, and not merely those most lightly attached, can be ejected; but on the other hand an electron cannot pass from one normal orbit to another, because all the normal orbits are occupied; if it is ejected at all, producing absorption, it must be ejected clear of the atom. Consequently all absorption lines must have in common the term representing the 'orbit' of an electron free from the atom (to which we have by convention attributed the value zero), so that the frequencies of the absorption edges are simply those of the terms representing the normal orbits within the atom. But on further consideration it appears that the expression 'clear of the atom' is not definite. All that is implied in Kossel's explanation of absorption edges is that, in absorbing energy, an electron cannot pass from one normal orbit to another; but it should be able to pass from a normal orbit to an abnormal orbit, which is not normally occupied. Now the abnormal orbits are represented by the terms of the optical spectrum. Accordingly, in place of a single absorption edge representing the transition between a normal orbit and the 'outside of the atom', there should be many absorption edges or lines representing all the transitions between this normal orbit and the abnormal orbits of the optical spectrum, the frequencies of these lines being the differences between the term representing this normal state and the terms of the optical spectrum. It is too much to expect that

all these lines should be separately distinguishable, since the range of frequency covering all the optical terms is very small compared with the value of any X-ray term; but we should expect to find some sign of their presence in a finite width of the absorption edge. The high frequency edge of the band should represent electrons which receive just enough energy to carry them to an infinite distance from the atom; the low frequency edge those carried to the first abnormal orbit, represented by the second largest term of the optical spectrum. Careful inquiry by Fricke has shown that this is precisely what we do find; absorption edges are not perfectly sharp; they are really bands in which sometimes a fine structure can be detected. And the width of these bands is precisely what Kossel's theory predicts. For since the greatest term of an optical spectrum is always approximately Rydberg's number N, and the least term is zero, the width of the band should be approximately N. The values actually measured for the width lie between $1{\cdot}3N$ and $0{\cdot}9N$, the least frequency of any absorption band measured so far being about $200N$. Moreover there are definite signs of lines within the band, corresponding to intermediate optical terms. In general the probability of a transition, and therefore the intensity of the absorption, decreases as the amount of energy involved in it increases; but the presence of this fine structure of the absorption band shows that an electron will take the larger energy required to carry it into a quantum state rather than the smaller energy which would carry it into an intermediate and non-quantum state, if such were possible[1].

A most interesting but indirect confirmation of this theory has been obtained. The optical spectrum, determined by the abnormal orbits, is always entirely different for a chemical compound and for

[1] Though it is not relevant to our present discussion, a word may be said about electrons which receive more energy than is required to carry them to rest at infinity, and therefore leave with a finite velocity. Epstein has suggested that even here there may be discontinuities in the possible states, and that there are hyperbolic, in addition to elliptical, quantum orbits. The idea is attractive, but at present there is little evidence for it; and there are other considerations which suggest that the ordinary quantum relations are not applicable to a 'free' electron. At any rate the sharp high frequency edge of the band, separating electrons which leave with a finite velocity from those which do not, shows that the probability of hyperbolic quantum states, if they exist, is much less than that of elliptical, even when allowance is made for the greater energy.

the elements contained in it; it would follow therefore from the theory that the fine structure of an absorption edge and the position of the beginning of the edge should vary with the state of chemical combination of the element. This prediction has been confirmed by Bergengren and Lindh. Thus variations in the absorption edge of sulphur have been detected according as it is free or combined and, indeed, according to the state of combination; the absorption edge differs according as the sulphur is acting as a divalent, quadrivalent, or sexvalent element; similar results have been reported with phosphorus and chlorine. This discovery does not change the conclusion that the X-ray emission spectrum is independent of the state of chemical combination, although the terms of this spectrum are the frequencies of the absorption edges. For since chemical combination will change the position of all absorption edges in the same manner, the emission lines, being the differences between absorption edges, will be unaffected.

18. **X-ray terms.** We saw in Ch. XV that, for theoretical purposes, the terms of the spectrum, rather than the lines, are important; our discussion must next concern the identification of these terms. Hitherto we have described the facts of X-rays by speaking of lines, partly because lines are immediately accessible to experiment, and partly because the difficulties arising in the determination of the terms had not been wholly solved. But great progress has been made recently in the solution of those difficulties; and since it is only if they are solved that definite information about atomic structure can be derived from the study of X-rays, we shall always henceforward speak of terms and not of lines, unless the contrary is explicitly stated.

The chief workers who have been concerned in the later developments (the list is given now to avoid the constant mention of names later) are Siegbahn, Stenstrom, Duane, de Broglie, Dauvillier, Coster, Wentzel, Kossel, Sommerfeld and Bohr; those whose names are earlier in that list have devoted more attention to the experimental side of the problem, those later to the theoretical. All are agreed on the main features of the solution of our problem, but there is still some divergence concerning the details, which may be of great theoretical importance. No attempt will be made here

to state all the facts; here, as always in this book, the broad and general ideas require our attention[1]. It will be convenient therefore to adopt for consideration a single solution and to notice later some alternatives. The solution that will be chosen for this purpose is that of Bohr and Coster; it is not less in agreement with the facts than any other, and it is very directly based on Bohr's theory of atomic orbits of which much will be said later.

According to this scheme the X-ray spectrum of the elements of highest atomic number has at least 25 terms, which can be subdivided into 1 K-term, 3 L-, 5 M-, 7 N-, 5 O-, 3 P-, 1 Q. An L-term (say) is denoted by that symbol because it is closely connected with the L-lines in two ways; first, the L-terms are the frequencies of the L-absorption edges, that is to say, of those edges which lie in

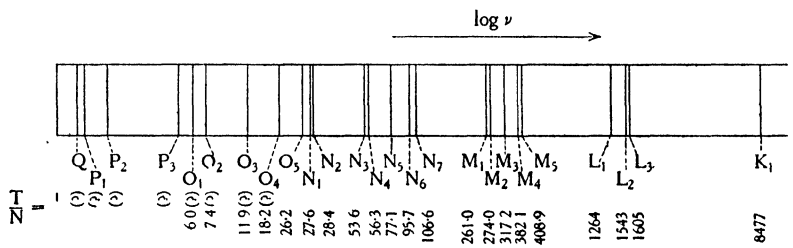


Fig. 3.

the range of frequency of the L-emission lines; second, they represent the final orbits concerned in the emission of L-lines and, consequently, are the larger of the two terms between which such a line is the difference. The arrangement of these terms for Ur (92) is shown diagrammatically in Fig. 3, which is analogous to Fig. 1 of Ch. XV; the only differences are that in Fig. 3 the scale of frequency is logarithmic, in order that the terms may be shown conveniently separated, and that the lines are wholly omitted. The distance of a term from the left-hand end of the line is proportional to the logarithm of the term T. The terms are denoted by the conventional symbols (but see p. 77) and under each is written the value of T/N, where it is known, N being Rydberg's number; where it is not known, the indication of the term in Fig. 3 must,

[1] Having no first hand knowledge of the subject, I cannot be sure that all the smaller details of facts are given correctly. The facts are rather difficult to disentangle because there is some difference of nomenclature as well as of theories. Moreover small corrections to previous measurements are always being made.

of course, be taken to show nothing but the existence of the term (see p. 81). T is sometimes conveniently expressed in volts[1]; the numerical value of a term so expressed is approximately $13{\cdot}54\ T/N$ volts.

The terms of the spectra of elements of lower atomic number differ from those given in the Table by their number and their value. The number decreases, but not regularly, as the atomic number decreases, the terms on the left disappearing first; the details of this change will be one of the main topics of subsequent discussion. The value of the terms is related to the atomic number approximately by Moseley's law, the approximation being the better the further the term concerned is towards the right; the approximation is very good for the K-term, less good for the L-, and so on. In fact, as we saw in Ch. XV, p. 53, Moseley's law is explicable theoretically only on the ground that it applies in the first instance to terms. It is valid for lines partly because z is small for the K- and L-lines, so that a mean z, which is not the true z for either of the two terms, will represent the facts sufficiently well; and partly because the terms for which it is not approximately true (the N-, O-, etc. terms) are so small compared with the K- and L-terms that they have little effect on the frequency of the line in which they are concerned. When Moseley's law is not true, there is still a regular, but more complicated, relation between T and Z, which enables the terms of one element to be correlated with the corresponding terms of another and so permits reliable interpolation to elements (such as the rare gases) of which the X-ray spectra cannot be determined directly. Indeed the regularity of the relation between T and Z and the possibility of interpolation are bound up intimately with the scheme of terms; for a limitation to the scheme, which all accept on theoretical grounds, is that there must be such a relation; the evidence for the existence of particular terms is based just as much on the comparison of the spectra of neighbouring elements as on the examination of each particular element. Without this guiding principle the establishment of a scheme of terms would be quite impossible.

[1] See Table I, p. 24, Ch. XV. By an unfortunate blunder the first line of that Table is wrong. ν (or as we now call it, T) for Hg is $8{\cdot}42 \times 10^4$, and the corresponding value of h is $1{\cdot}232 \times 10^{-4}$.

And now what is the evidence for this scheme?

The most satisfactory way of establishing this or any other solution would be to measure the terms directly as the frequencies of absorption edges and to show that the emission lines were all differences between such terms. For though the identification of terms with absorption edges involves an element of theory, it is quite independent of the assumption that emission lines are the differences between terms, and the proof that they were such differences would afford the strongest possible support for the scheme adopted. The complexity of the absorption edges would not affect the cogency of this proof; for, since the fine structure of all absorption edges is similar, the differences between terms will be independent of the part selected if the same part of the structure is always measured. But unfortunately the proof is impossible, partly because the complexity of the edges diminishes somewhat the accuracy of measurements on them, so that we know the terms, determined in this manner, less accurately than the lines; but much more because only a few of the absorption edges can be measured at all. The K- and L-edges have been measured for almost all the elements of which the X-ray spectrum can be examined with any completeness; the M-edges only for a few elements of large Z; the remaining edges, indicated by the terms, lie in a region where the general absorption is so great that they are quite inaccessible to experiment. But it is very important to realise that, in so far as the test can be applied, its results are completely favourable. There is no doubt that the two strongest K-lines are given with all the accuracy of the most refined experiment by $(K_1 - L_1)$ and $(K_1 - L_2)$, if the terms are taken to be the measured values of the edges. The next strongest K-lines agree well with $(K_1 - M_3)$ and $(K_1 - M_4)$, and many of the L-lines agree well with differences between the L- and M-absorption edges; but owing to the lesser accuracy and to the smaller number of elements examined, the agreement is not so absolutely convincing. In addition there are at least four pairs of L-lines the differences between which agree well with the difference $(L_2 - L_1)$; these may be plausibly represented as arising from a transition from the same higher orbit to this pair of orbits, so that their frequencies are of the form $(L_1 - x)$ and $(L_2 - x)$. There are other pairs of lines the

differences between which agree well with the differences measured between pairs of M-absorption edges; and there are some other slightly more complicated relations of the same nature which support further the identification of absorption edges with terms.

So far, so good. But there remain many lines that cannot be interpreted directly by measured terms. They must involve N-, O-, ... terms or, possibly, K-, L- or M-terms that do not appear as absorption edges. (This last alternative is not actually adopted, and would be inconsistent with the theory.) The only way to discover these terms is to analyse the lines in the manner adopted in the resolution of optical spectra. But the facts that have just been mentioned show that this method is likely to be attended by some difficulties. Thus, although the K_1 and L_3 terms can be identified by absorption edges, there is no strong line corresponding to a transition between L_3 and K_1 (there may be a very weak line of this origin); it is clear therefore that we cannot test any suggested set of terms by the most certain method, namely by examining whether there is a line which is the difference of every pair of terms; it is certain at the outset that there are some pairs to which no line corresponds. There is nothing surprising in this conclusion, for exactly the same feature is found in most optical spectra. It is only in the simplest optical spectrum that the converse of the principle of combination, as we have stated it, holds, and to every difference between terms corresponds a line. In the more complex this proposition is not true, but it can be replaced by a very simple rule (to be noted presently) which states the 'principle of selection' determining whether a difference between any given pair of terms will give rise to a line. In X-ray spectra we may hope to find a similar principle of selection; and if we can find one simple, all-inclusive, and intrinsically probable, the evidence that the terms are real, and that we are not merely misled by numerical coincidences, will be just as complete as if the simplest rule of all, the converse of the principle of combination, were still valid[1].

[1] It is very important to insist on the possibility that numerical relations found between lines may be mere arithmetical coincidences; for it seems certain now that many relations discovered by earlier workers on optical spectra, who had no adequate theory, were wholly or mainly of this nature. Some of them cannot be pure coincidences, for, if they were, the probability of their occurrence would be unreasonably small. But on the other hand, they cannot represent directly anything physically

Unfortunately such a rule has not yet been established certainly, and while it is still lacking, some uncertainty in our conclusions must remain. But rules have been found that have all merits except universality; they cover the greater part of the facts, and all the stronger lines obey them; but there are some exceptions which are not wholly explained away. Moreover the evidence for any one rule is weakened somewhat by the fact that there are others, differing slightly, to which the facts conform just as well or just as badly. The rule underlying the solution that we are considering is indicated in Table V, p. 72. Here to each of the terms is attached, first, a symbol of the form n_k, where n and k are integers, and second, a letter a or b; n is 1 for the K-term, 2 for the L-terms and so on, while k takes all values from 1 to n. It will be seen that the assignment of the k's and also of the a's and b's to the various terms follow simple and definite rules, which the reader can appreciate for himself. The theoretical significance of these symbols will be considered presently; here we shall use them only to state the principle of selection.

It consists of three parts: at a transition (1) n always changes; (2) k remains unchanged or changes by one unit in either direction; (3) a changes to b or b to a. The last part of the rule is perhaps the most remarkable, for it implies that the terms fall into two sharply divided classes, such that transitions never occur between terms in the same class, but occur only between terms in different classes. One consequence of this division is that no line can be the difference between two other lines. For a difference between lines is a difference between two terms only if the lines have one term in common. But if they have, then our rule demands that the terms which they have not in common belong to the same class, and therefore that no transition between them occurs. In this manner the absence in X-ray spectra of the relations (13), p. 39 of Ch. XV, is completely explained (it is generally spoken of as the 'combination defect'), although such relations are prominent in optical spectra and, indeed, gave rise originally to the principle of combination. There is subsidiary evidence from the terms them-

important, because they involve constants (usually the mean atomic weight) which are now known to be without simple physical significance. The explanation of these delusive coincidences is a very important problem as yet unsolved.

selves that the distinction between a and b terms is significant; for there run throughout X-ray spectra two series of doublets, which are known respectively as 'regular' (or 'relativity') and 'irregular' (or 'screening') doublets. The frequency difference

TABLE V

Symbol / Term	1_1 b K	2_1 b L_3	2_1 a L_2	2_2 a L_1	3_1 b M_5	3_1 a M_4	3_2 a M_3	3_2 b M_2	3_3 b M_1	4_1 b N_7	4_1 a N_6	4_2 a N_5	4_2 b N_4	4_3 b N_3	4_3 a N_2	4_4 a N_1
$1_1\,b$ K	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$2_1\,b$ L_3	×	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$2_1\,a$ L_2	Ka_2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$2_2\,a$ L_1	Ka_1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$3_1\,b$ M_5	...	...	$L\eta$	Ll	...	...	...	...	...	...	...	...	...	...	...	...
$3_1\,a$ M_4	$K\beta_3$	$L\beta_4$	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$3_2\,a$ M_3	$K\beta_1$	$L\beta_3$	×	...	...	...	...	...	...	...	...	...	...	...	...	...
$3_2\,b$ M_2	...	×	$L\beta_1$	La_2	...	...	...	...	...	...	...	...	...	...	...	...
$3_3\,b$ M_1	...	×	...	La_1	...	...	...	...	...	...	...	...	...	...	...	...
$4_1\,b$ N_7	...	...	$L\gamma_5$	$L\beta_6$	...	×	×	...	...	...	...	...	...	...	...	...
$4_1\,a$ N_6	$K\beta_2$	$L\gamma_3$	...	...	×	...	...	?	...	...	...	...	...	...	...	...
$4_2\,a$ N_5	$K\beta_2$	$L\gamma_3$	...	...	×	...	...	?	×	...	...	...	...	...	...	...
$4_2\,b$ N_4	...	...	$L\gamma_1$	?	...	×	?	...	...	...	...	...	...	...	...	...
$4_3\,b$ N_3	...	×	...	$L\beta_2$	...	...	$M\gamma$	...	...	...	...	...	...	...	...	...
$4_3\,a$ N_2	...	...	×	×	...	...	...	$M\beta$	Ma_2	...	...	...	...	...	...	...
$4_4\,a$ N_1	...	...	...	...	...	...	...	...	Ma_1	...	...	...	...	...	...	...
$5_1\,b$ O_5	...	...	×	$L\beta_7$	...	?	×	...	...	...	?	?	...	...	...	...
$5_1\,a$ O_4	?	$L\gamma_4$	...	...	?	...	...	×	...	?	...	...	?	...	...	...
$5_2\,a$ O_3	?	$L\gamma_4$	...	...	×	...	...	?	?	?	...	...	?	?	...	...
$5_2\,b$ O_2	...	...	×	?	...	×	?	...	...	...	?	×	...	...	?	...
$5_3\,b$ O_1	...	...	...	$L\beta_5$	...	...	×	...	...	...	...	×	...	...	?	?
$6_1\,b$ P_3	...	...	?	?	...	?	?	...	...	...	?	?	...	...	...	...
$6_1\,a$ P_2	?	?	...	...	?	...	...	?	...	×	...	...	?	...	...	...
$6_2\,a$ P_1	?	?	...	...	×	...	...	?	×	×	...	...	?	?	...	...
$7_1\,b$ Q	...	...	?	?	...	?	?	...	...	...	?	?	...	...	...	...

between the members of corresponding pairs of regular doublets varies approximately as Z^4, increasing very rapidly with the atomic number, while that between members of corresponding pairs of irregular doublets is approximately proportional to Z and increases

far less rapidly[1]. Now it appears that when the doublet is regular in this sense, the terms in which the pair of lines concerned differ are consecutive in Table V, both being a or both b (e.g. L_1 and L_2), while if the doublet is irregular these terms are consecutive, one being a and the other b (e.g. L_2 and L_3). There is therefore a meaning which can be attributed to this distinction wholly independent of the principle of selection.

Accordingly the principle of selection suggested is simple and intrinsically probable; how far it is all-inclusive is shown in Table V. The terms in the vertical column represent initial orbits in a transition, those in the horizontal row final orbits. Lines are indicated at the intersection of the column and row of the terms between which they are differences, the larger term being, of course, always the final level; thus all L-lines (e.g.) appear in the column under the L-terms. The stronger lines, for which all writers use the same notation, are given by their conventional symbols; the weaker, for which the notation varies, by crosses. When a line should occur according to the principle of selection, but has not been found, the place is marked by ?. When it should not occur, but has apparently been found, the cross is underlined, once if one of the three rules is broken, twice if two are broken. When it should not occur, and has not been found, the place is left blank.

The omissions of predicted lines, indicated by ?, are not serious in any part of the table which is mainly occupied by them; for they merely indicate the difficulty of detecting lines in this region —either because the lines are very near together or because the rays are too soft to be investigated easily; but there are some which almost certainly represent real infractions; if there is no sign of a line where it ought to appear the rule must be broken. But the appearance of unpredicted lines does not show a breach of the rule so certainly; for the infringing line may not really represent the difference between the two terms; it may have some other source and merely happen to appear at the right place. No attempt can

[1] The distinction between regular and irregular doublets is expressed in a form convenient for experimental examination by the rule that regular doublets show a constant difference in wave-length, while irregular doublets show a constant difference in $\sqrt{T}$. Since $T=\frac{c}{\lambda}$ is approximately proportional to Z^2 this rule is approximately the same as that given in the text.

be made here to discuss all the difficult and complicated considerations that have to be taken into account in deciding whether a line appearing on the photographic plate is 'real'; the chief difficulties arise from impurities and from the possibility of a confusion between lines in spectra of different 'orders'; the general conclusion would seem to be that there are some infractions, although they occur in relatively small proportion and only among weaker lines. It is noteworthy that rule (1) is never broken; a very careful search for lines representing transitions between two L-levels, which if they occur ought to be easily detectable, has clearly established their absence; but both (2) and (3) are sometimes broken. The rules are probably not false, but merely incomplete; there are some other conditions limiting the occurrence of lines that have not yet been discovered. And if this conclusion is accepted, all that is important for the study of the structure of the atom is secured; for there will remain no doubt that the terms really and truly measure the energy of the possible electronic levels.

However there are some lines which do not fit in the table at all; they cannot be represented as differences of the terms shown. Here again the reality of some of these lines is still in dispute, but those which are undoubtedly real are all weak 'satellites' of very much stronger lines. Indeed it is because they are such satellites that it is difficult to fit them in; they demand for their interpretation terms very close to other terms which are very well known because they are concerned in the strong lines. A very satisfying explanation of some of these satellites has been offered; it is that the discrepant lines come from atoms that have lost two electrons and not merely one. The account that has been given of the absorption edges and of their relation to the emission lines implies that the normal lines, which are differences between terms identical with the absorption edges, arise from atoms in which one electron has been ejected from some normal orbit to beyond the confines of all normal orbits; the emission of the lines represents the replacement of an electron so ejected by another coming from a more distant (but still normal) orbit. But if, before the replacement occurs, a second electron is ejected from the atom, the state of the atom during the replacement of either of the ejected electrons will not be the same as it was when only one electron had been ejected;

there will be one less electron in it and the orbits, which must depend on the mutual action of the electrons as well as on the forces due to the nucleus, will be correspondingly modified. The exact modification cannot be calculated at present, but certain features of it are clear. Thus, since the effect of the electrons is in general opposite to that of the nucleus, the removal of one electron must in general increase the forces and therefore the energy of any orbit. The satellites arising from doubly ionised atoms should therefore occur on the high frequency side of the main line from the singly ionised atom. Again, the separation should be greater the smaller the charge on the nucleus and the less the atomic number, and should vary nearly as the atomic number. And the intensity of the satellite relative to the main line should increase with the intensity of the electronic bombardment by which the X-rays are excited; for the chance that an atom will be doubly ionised is thereby increased. All these expectations are realised; there is no doubt that some of the satellites which are not accounted for by the ordinary terms are indeed to be explained in this manner, a possible method of accounting for others will be noted later (p. 114).

According to this theory these discrepant satellites are related to the main lines in somewhat the same way as the spark optical spectra to the arc spectra (Ch. XV, p. 22). But the analogy is not quite complete; for in the emission of the arc spectra, but not in the emission of the main X-ray lines, the displaced electron is still in one of those levels, transitions between which give rise to the spectrum in question; in other words the arc spectra are emitted from neutral atoms to which the full complement of electrons is still attached, the main X-ray spectra from singly charged atoms, which have ceased to exert any appreciable influence on the displaced electron[1]. But it is sufficiently close to warrant the appli-

[1] The question may be asked what is the spectrum emitted when the ionised atom, having emitted X-rays, is finally neutralised; i.e. to what orbit does the electron, ejected from one of the orbits represented by X-ray terms, fall when it returns from an abnormal orbit or from an infinite distance. Of course in some cases it may return direct to one of the X-ray orbits, and in that case should give a line lying within the absorption band; but as such lines are seldom, if ever, observed, we must conclude that the interior normal orbits are usually filled up from the exterior, and that it is only the most exterior orbits of all that are filled up from outside. The rays emitted in such transitions would lie in the almost inaccessible region between X-rays and optical spectra.

cation of the term 'spark spectra' to the collection of X-ray satellites that can be accounted for in this manner. It may also be noticed that the theory implies that strictly it is illegitimate to speak of the individual orbits, as if they were independent; the L_1-orbit (e.g.) cannot be quite the same when an electron passes from it to the interior K-orbit as when a vacancy in it is filled up from an exterior orbit. The energy which we have associated with an orbit such as L_1 is really the energy of a complete atomic state in which one L_1 electron is missing or, more accurately, the difference between the energy of the whole atom when this electron is present and that when it is absent. Most writers nowadays are careful not to associate the terms with particular *orbits*; they speak of atomic states or, still more concisely, of levels ('niveau') represented by the terms. But the term 'levels' is unfortunate and subject to an objection which we shall presently raise against 'interior' and 'exterior'; while 'states' is undesirably vague. Language does not matter so long as its meaning is carefully explained; and with the explanation that has just been given the continued use of 'orbits' is justifiable and convenient. However it is important to realise that it is surprising that we can attribute the same value to terms independently of whether they are acting as initial or final terms; but it seems that within the limit of present accuracy we can. A difference of this nature between initial and final levels was suggested in Ch. XV, p. 91 to account for the 'combination defect'; but we have seen that it is not needed for this purpose. On the other hand it may possibly have some bearing on the relation between a terms and b terms.

Before leaving X-ray spectra two points should be mentioned in which the classification of the terms adopted by other writers differs from that just described. First Bohr has recently adopted a different notation for the various terms, and consequently a slightly different principle of selection. In accordance with the suggestions of Sommerfeld and Wentzel, he has abandoned the a and b classification, and introduced three integers, n, k_1, k_2, in place of the two n, k. At the same time he has reversed the order of the suffixes appended to the capitals in the notation of the terms of each group. The new and the old notations are compared in the following

scheme, which the reader will readily extend to the higher terms:

Old	Symbol	K	L_3	L_2	L_1	M_5	M_4	M_3	M_2	M_1
	n_k	1_1a	2_1b	2_1a	2_2a	3_1b	3_1a	3_2a	3_2b	3_3b
New	Symbol	K	L_{I}	L_{II}	L_{III}	M_{I}	M_{II}	M_{III}	M_{IV}	M_{V}
	$n(k_1,k_2)$	1(1,1)	2(1,1)	2(2,1)	2(2,2)	3(1,1)	3(2,1)	3(2,2)	3(3.2)	3(3,3)

The following are now the rules of the principle of selection: (1) n changes, (2) k_1 changes by one unit, (3) k_2 changes at most by one unit. The results of these rules are exactly the same as those of the rules given previously.

In the scheme of X-ray levels proposed by de Broglie and Dauvillier each term is again characterised by three integers instead of two; at the same time the number of levels is increased so that there are 6 M-, 10 N-, 6 O-levels in place of 5, 7, 5. A rather different principle of selection is also adopted; but again exceptions to it have to be recognised. It is not proposed here to discuss in detail the relative advantages of the two schemes, between which it would not be easy to decide if there were no general theory of atomic structure to be taken into account. The scheme given here has been preferred because it is directly based on such a theory.

19. **Optical spectra.** We must now notice a few recent developments concerning optical spectra and, more particularly, concerning spectra which lie between the X-ray and optical regions according to the experimental classification. The methods adopted in investigating this region have already been indicated in Ch. XV, p. 25; that which seems to have the widest scope was devised by Richardson and Bazzoni. It is one of the consequences of Kossel's theory (p. 64) that an X-ray line involving a given term as the final orbit cannot be emitted unless the atom has received an amount of energy at least as great as that corresponding to that term. Accordingly, if the emission is excited by the impact of electrons, the line is not emitted unless the incident electrons have at least this energy. Experiments in accessible regions have definitely established that such a limitation exists; the determination of the energy of incident electrons necessary to excite the various lines in a material on which they fall is a sound method, but not a very accurate one, of measuring normal terms. In order to apply the

method in regions otherwise inaccessible it is necessary to find some method of detecting the rays emitted; for this purpose the photoelectric effect is used, the electron current emitted from a metal plate to which the rays have access being measured. If this current is plotted against the energy of the electrons striking the material under examination, sudden increases are noted at certain points, which indicate the occurrence of an absorption edge and the emission of the characteristic radiation the lines of which involve, as the final orbit, the term corresponding to this edge.

By applying this and similar methods, the curves of Fig. 2, Ch. XV, which represent Moseley's law in the region where they are drawn full, can be traced through the region in which they are there shown dotted. (Actually the curves in that figure show lines, not terms; but, as has been said already, they would show the same characteristic form if, as we suppose now, they represented terms.) The results can be presented from two points of view, according as we trace the same term through the series of elements, or consider the various terms belonging to the same element. Taking the first point of view, we may sum up the results briefly by saying that the K-term obeys Moseley's law very approximately throughout the whole range of elements down to H (1); the curve relating $\sqrt{T/N}$ to Z is very nearly straight. On the other hand in passing from Ne (10) to lower elements, the L-curve takes a sharp turn to the left; among these lower elements, the term varies with Z far less rapidly than Moseley's law would predict. At Li (3) the curve stops; there is no L-term for He (2) or H (1). The results for the M-term are less complete and certain; but a similar sharp turn seems to occur at Ar (18), and the term seems to disappear at Na (11).

Taking now the second point of view, we find that H (1) and He (2) have K-terms but no higher term: the K-term here represents the energy required to detach the least firmly bound electron, that is to say, the ionisation potential of the normal atom. Elements from Li (3) to Ne (10) have K- and L-terms, but no M-term; the L-term represents the ionisation potential. Similarly in the elements from Na (11) to Ar (18), there are M-terms, but no higher terms, and the M-term represents the ionisation potential. Experimental evidence of this kind is not available beyond this point,

and our knowledge of where the higher terms (N, O, ...) enter is derived from other sources. But there is no reason why all the information should not be obtained in time by this perfectly direct method, though considerable refinements will be necessary before a distinction can be made between the different L-, M-, N-terms, which have been treated as identical in the statements just made.

These results have a most important bearing on the classification of the terms of purely optical spectra. We saw in Ch. XV that when the optical spectrum can be resolved into normal series, the largest term, which is the 'limit' of the principal series, represents the ionisation potential according to the quantum relation $W = hT$. If the K-term in H (1) and He (2) represents the ionisation potential, it must be the largest term of the optical spectrum, and, if the optical spectrum can be resolved into typical series it should appear as the limit of the principal series. Similarly the L-term (or rather one of the L-terms) must be the largest optical term in the elements from Li (3) to Ne (10), and one of the M-terms must be the largest optical term in the elements from Na (11) to Ar (18). When the optical spectrum has been resolved into typical series, these predictions are confirmed; it can be shown that the X-ray term, determined by the methods appropriate to this intermediate region, actually agrees with the largest optical term determined from the optical spectrum. In accordance with our general theory, we find that there is one term, representing the orbit of the electron (or electrons) most loosely attached in the normal atom, which is the largest term of the optical spectrum and the smallest of the X-ray spectrum; it belongs equally to both. And as we trace any term shown in Fig. 3 and Table V through the elements, we find that it is an X-ray term for the elements of higher atomic number and an optical term for those of lower atomic number[1].

[1] Of course an objector might say that there is a distinction between optical and X-ray terms, which is slurred over in the text and yet indicates that the identification of the largest optical term with the smallest X-ray term is doubtful. It arises from the fact that, just where the X-ray term becomes an optical term, Moseley's law breaks down and there is a change in the relation between T and Z. This must be admitted, though it might be replied that there is always one element, just at the kink of the curve, which is free from this objection. The real answer, apart from theory, is that, as we shall see presently, precisely similar anomalies in the curve between T and Z occur in regions where the terms are undoubtedly part of the X-ray spectrum.

But if this is so, the largest optical term, the limit of the principal series, should be denoted by the notation appropriate to the X-ray terms. This term for the elements between Li (3) and Ne(10), being an L-term, should be represented by 2_k, for the elements between Na (11) and Ar (18) by 3_k, and so on. The question therefore arises whether, by assigning k suitably to this term of the optical spectrum, and both n and k suitably to the other terms of the optical spectrum, we can find a principle of selection for optical spectra similar to that for X-ray spectra and expressed, like that rule, in terms of n and k. We must not expect the same rule, for the optical terms, other than the largest, undoubtedly differ in character from the X-ray terms; but if our notation represents anything real we must expect similarity. We can find such a rule (cf. Ch. XV, p. 92). If we assign the value $k=1$ to the s-terms, $k=2$ to the p-terms, $k=3$ to the d-terms, $k=4$ to the b-terms; and if further we suppose that the smallest value of n for each series is that determined in the manner we have just discussed by the relation of the largest s-term to the X-ray terms; then we find that the principle of selection for many spectra can be expressed by the rule that k in a transition always changes by one unit in either direction. n may or may not change, and there is nothing corresponding to the a and b distinction; rules (1) and (3) for X-ray spectra are further limitations imposed on the rule for such optical spectra. But in other and more complex spectra, the principle of selection is also more complex.

There is therefore definite experimental support, derived from both X-ray and optical spectra, for the notation of terms shown in Table V; that notation must represent something physically real. The reader is probably perfectly aware already that the details of that notation have been determined very largely by the theoretical considerations to which we are just about to proceed. But it is important to realise that the classification adopted is not wholly theoretical, and that it does express certain experimental facts, independently of any interpretation of them; for this reason, even at the risk of some pedantry, it has been well to discuss the matter first, as we have done, without any mention of the theory. But before we pass on, it should be noted that some features of the scheme presented in Table V have no justification apart from the

theory. Thus there is no experimental evidence for saying that there must be 3 P-terms and 1 Q-term in the spectrum there shown, and very doubtful evidence for 5 O-terms. All that we know from X-ray spectra is that there are some terms beyond the O-group, and that one of these must be the largest term of the optical spectrum. We do not even know, for any of the elements to which the complete scheme of terms shown applies, what is the value of this term; for none of their spectra have been fully resolved into series. In view of this uncertainty no distinction was made on p. 67 between different elements of 'highest atomic number'. Table VI below suggests that the terms of Table V apply only when $Z = 87$ or 88; but so far as known terms are concerned, the scheme is the same so long as Z is greater than 72.

20. **The normal electronic orbits.** To explain why the X-ray terms are what they are, we must have recourse to the second assumption of Bohr's theory. Hitherto we have used only the first.

Until quite recently all electronic theories of the atom agreed in one thing, namely in arranging the electrons in shells or rings round the nucleus. Such an arrangement was perhaps partly an inheritance from the Thomsonian atom, partly based on mere simplicity and apparent plausibility. It was characteristic of Bohr's earlier theory, suggested by his original study of circular quantum orbits, and it was sketched for the explanation of the X-ray terms in Ch. XV. There we suggested that the electrons corresponding to the K-, L-, ... terms might be revolving in concentric rings about the nucleus, the inner ring being the K-electrons, the next the L-electrons, and so on. And this simple arrangement seemed to explain some features well, especially the general form of Moseley's law.

However, since then definite experimental evidence has been obtained that this arrangement cannot be correct. The most conclusive evidence comes from W. L. Bragg's experiments on X-ray reflection (p. 56); his work shows conclusively that the electrons are arranged far more densely about some planes than the arrangement sketched permits. If the electrons are arranged on rings or shells at all, the inner rings must contain more electrons than the

outer. Since this conclusion is inconsistent with the values of z in Moseley's equation, the only possible deduction is that the electrons are not arranged in rings or shells. Similar but less definite conclusions follow from Millikan's work on multiple ionisation.

But in truth such an arrangement is no longer even plausible. There was something to be said for it, so long as our theory of electronic orbits was based on the original second assumption of Bohr that such orbits were all circular. But in Ch. XV we have had abundant reason for abandoning that assumption and for substituting for it the generalisation of Sommerfeld, which permits, and indeed requires, orbits that are very far from circular. We concluded from that generalisation that the orbits of an electron round a single nucleus must be characterised by two quantum numbers and not, as Bohr originally assumed, only by one. These two numbers were called the radial and azimuthal numbers, and were previously denoted by m_1, m_2; they will now be denoted by n', k. The sum of these numbers, or total quantum number, previously denoted by m, will now be denoted by n. If we neglect for the moment the 'relativity' correction and suppose Newtonian mechanics applicable, we find that the energy of the orbit and its greatest dimension are determined wholly by n, so that the work required to remove the electron from the orbit to infinity is

$$W = Nh\frac{Z^2}{n^2} \quad \text{.....(82·1),}$$

while the major axis of the ellipse is given by

$$a = \frac{1}{2}\frac{\epsilon^2}{Nh}\cdot\frac{n^2}{Z} \quad \text{.....(82·2).}$$

On the other hand, when n is fixed, the partial quantum numbers determine the shape of the orbit. If $k = n$ the orbit is circular: if k is less than n (it can never be less than 1), the orbit is elliptical, the eccentricity increasing as k diminishes. The latus rectum $2l$ of the ellipse is given by

$$l = \frac{\epsilon^2}{2Nh}\cdot\frac{k^2}{Z} \quad \text{.....(82·3).}$$

As the reader will doubtless have realised, these considerations determine the notation for the terms of the X-ray spectrum we have adopted. Without further explanation, we may identify the

symbols n, k used in that notation with the quantum numbers, and assume that the term n_k represents an orbit of which the total quantum number is n, the azimuthal quantum number k, and the radial quantum number $n' = n - k$. (We could, of course, have used n', k to describe the orbits, modifying our principle of selection accordingly; but it is more convenient to use one total and one partial number.) For the moment we leave the symbols a, b without any significance other than that implied by the principle of selection, and shall treat a pair of terms differing only in these symbols as a single term.

But the terms of actual X-ray spectra do not agree with these simple formulae, applicable to the orbits of a single electron round a nucleus. And it is not to be expected that they should; for the mutual action of the electrons surrounding the nucleus will doubtless have some perturbing effect on the orbits. This fact has already been recognised in Ch. XV; the divergence between the orbits thus calculated for a single electron and those found in actual atoms has been taken into account by the introduction of an 'effective nuclear charge' $Z - z$, differing from the true nuclear charge by a relatively small number z, which represents the 'screening effect' of the electrons on the nucleus or their action in partially neutralising the nuclear charge.

The introduction of this screening effect enabled us to determine the values of n, the total quantum number, for the K-, L-, M-terms, and to guess from the magnitude of z in Moseley's law that there are 2 electrons in K-orbits[1] and 8 in L-orbits. Further we found it possible in some cases to determine k. For this purpose the 'relativity correction' had to be taken into account. The variation of the mass of the electron with its velocity leads to a dependence of the energy of the orbit on k as well as on n; to a first approximation (82·1) must be replaced by[2]

$$W_{n,k} = \frac{NhZ^2}{n^2} + \frac{NhZ^4}{n^4} \cdot \left(\frac{2\pi\epsilon^2}{hc}\right)^2 \cdot \left(\frac{n}{k} - \frac{3}{4}\right) \ldots\ldots (83{\cdot}1).$$

[1] The number in the K-ring was erroneously given as 1 in Ch. XV, p. 54.

[2] This is equation (96), Ch. XV, p. 85, translated into our present notation. In equation (97) following for $\frac{a^2}{4m^2}$ read $\frac{a^2}{4m^4}$.

By means of this equation the existence and magnitude of the L-doublet (which represents the difference between the terms we now call L_1, L_2) could be explained, if it were assumed that both the orbits represented by these terms had the total quantum number $n = 2$, but differed in their azimuthal quantum numbers, one being the circle for which $k = 2$, the other the ellipse for which $k = 1$. But here again agreement between theory and experiment could be produced only if the distinction between true and effective nuclear charges were recognised and Z in (83·1) replaced by $Z - z$. Choosing the value which fits best the measurements, z was very nearly independent of Z and equal to 3·6 for the L-terms.

But at this stage a discrepancy enters; for z thus determined from the relativity doublet does not agree with that determined by Moseley's law; in other words, in order to make (83·1) fit the facts for the L-terms, we have to adopt different values for the screening effect in the first and second terms. And now other and more serious discrepancies are known; Moseley's law breaks down altogether for the elements of lower atomic number and the terms of higher n; and if we attempt to interpret the group of M-terms as forming a relativity triplet, M_1, M_2M_3, M_4M_5, we find that we have not only to assume different values of z in the first and second terms of (83·1), but also to allow for a variation of z with Z. But if we permit ourselves so much latitude in assigning z, it becomes doubtful whether the agreement with prediction that we ultimately attain has any evidential value. The truth is that the simple screening effect, denoted by the introduction of a z independent of Z, gives an adequate account of the mutual actions of the electrons only when these mutual actions are relatively unimportant compared with the forces due to the nucleus; and when the whole correction is small, the fact that it can be adequately explained by some hypothesis gives little ground for accepting it. If we are still to retain and develop the conception of a screening effect, producing a difference between the real and effective nuclear charges, we must inquire rather more deeply; we must justify more fully the increasingly complex assumptions that we are forced to make.

When we consider generally the orbits of many electrons round a nucleus, the first question that has to be settled is whether we are right in assuming that those orbits can be described by two

quantum numbers only. According to quantum theory, that assumption is true if, and only if, the orbits are two-dimensional, a condition that cannot be fulfilled strictly unless all the orbits lie in a plane. For if there are orbits in different planes, a distinction is possible between otherwise similar plane orbits of one electron according as their planes are differently related to the planes of other electronic orbits; even if the orbit is actually plane, it will be formally three-dimensional and a third quantum number will be required to describe it completely. On the other hand, it may still be true that, though three quantum numbers are required fully to describe the orbit, two are sufficient to define its energy; that the orbits are actually nearly plane; and that the energies of two similar orbits are the same although they lie in different planes. This is the assumption that we are actually making, since we are concerned so far with nothing but the energy of the orbits. It is not without intrinsic plausibility; Bohr maintains that it is a consequence of the principle of correspondence; and it is supported by some work on the Zeeman effect, which belongs strictly to Ch. XV, but is too recent to have been included there. It has been shown that the more complex forms of the Zeeman separation can be explained by taking into account the third quantum number, and supposing that the orbits are nearly plane, while their planes are slowly rotating round the axis of the magnetic field. The energy associated with this rotation, and therefore with the third quantum number, is very small compared with that associated with n' and k; for the purposes of such approximate calculations as we may hope to make it can be neglected.

And here we must revert for a moment to the alternative methods of p. 77 in which it is proposed to attribute symbols to the terms of spectra. In Bohr's second notation, as in his first, n is the total quantum number; k_2 the azimuthal quantum number. On the other hand k_1 is not a quantum number in the sense of Sommerfeld's general theory; no physical significance can be attributed to k_1; it merely expresses the same difference, at present inexplicable, as a and b. It is dangerous to differ from Bohr; but there certainly seem to be great advantages in the earlier notation which made perfectly clear this very important difference between the meanings of k_1 and k_2. On the other hand de Broglie and Dauvillier definitely

identify the three integers which they use to describe their terms with three quantum numbers, radial, azimuthal and equatorial; and it is because they so identify them that they introduce additional terms (*e.g.* 10 in place of 7 N-terms), which are necessary to represent fully all the possible combinations of these numbers, although they are not required to explain observed lines. Since the available evidence seems to show that the third quantum number is not important in determining the energies of orbits, and therefore the magnitudes of terms, the additional complication of their scheme does not seem to bring with it any compensating advantages.

We assume then that the number of orbits having substantially different energy will not be changed by the presence of additional electrons round the nucleus; that there will still be two quantum numbers defining the energy, and that their general geometrical significance will be unaltered. n will in general determine the size of the orbit, and k its shape. We may also suppose that the influence of k on the shape is still of the same nature; the orbits will not be exactly ellipses or circles, but those for which $n = k$ will probably be nearly circular, while the remainder are the more elongated the less is k. If this is so, it is immediately clear that the relation of the energy of the orbit to n and k must be somewhat changed, and that the whole effect of k on the energy of the orbit cannot now be represented by (83·1). For consider the orbits with a large n and therefore with large linear dimensions. If n is large enough, the orbits for which $k = n$ will be nearly circles, lying wholly outside the collection of the nucleus and the other electrons, and will approximate very closely to the orbits which an electron would describe round a nucleus, the charge on which is the algebraic sum of the charges on the nucleus and the electrons; if the atom as a whole is neutral and of atomic number Z, the effective charge determining these orbits will be not $Z\epsilon$, but ϵ. On the other hand the orbits for which k is less than n will approximate to ellipses; their aphelia will lie even further from the nucleus and its surrounding electrons than the circles; but their perihelia will lie well within the circles and, if k is much less than n, may approach to the immediate neighbourhood of the nucleus. In that neighbourhood they will be under the influence of the full nuclear

charge Ze, and their form will approximate to that of orbits described under that influence. But for the same quantum number n, the energy varies as the square of the nuclear charge. Hence we must expect that, when the nucleus is surrounded by electrons, the effective nuclear charge will increase as k decreases. The relativity correction also makes the energy of an orbit with a small k greater than that of an orbit with a larger k, the total quantum numbers n being the same in the two cases. This new change of energy with k is in the same direction as that given by (83·1); but it is perfectly independent of it and may be much greater or less than that change according to circumstances.

The relation between the forms of the orbits with different values of n and k is so important that it is well to illustrate it diagrammatically. In Fig. 4 there are shown the orbits 1_1, 2_1, 2_2, 3_1, 3_2, 3_3, 4_1, 4_2, 4_3, 4_4 round a single nucleus, the mutual actions of the electrons being neglected. Of course this mutual action will modify the orbits, for it is exactly that modification that we are trying to determine; but the figure shows the general relation between the orbits that we may expect. The most striking feature is that, in the neighbourhood of the nucleus, the orbits with the same k are similar, whatever the n, because the latus rectum is determined by k. (Orbits with the same k are shown by the same kind of line, different lines of the same kind corresponding to different n's.)

These ideas are fundamental in Bohr's theory of atomic structure and distinguish it from all others. In all other electronic theories, the electrons less firmly bound and requiring less work to detach them have been considered to be permanently further from the nucleus than those more firmly bound; that is the essence of the older conception of rings or shells of electrons. We now see that such an arrangement is not necessary or even probable. On the quantum theory the less firmly bound electrons have higher total quantum numbers; and if we compare the approximately circular orbits, for which $k = n$, with different n, it is still true that the orbits of the less firmly bound lie outside those of the more firmly bound. But if we consider the approximately elliptical orbits we find a perfectly different relation. Part of the 3_1 orbit (say), which is highly elongated, will lie not only within the circular 3_3 orbit, but probably also within the circular 2_2 orbit although the latter

has the smaller total quantum number and therefore the higher energy. The importance of this feature for our subsequent considerations is immense. It explains at once W. L. Bragg's results which were mentioned on p. 57. There is no doubt that in the

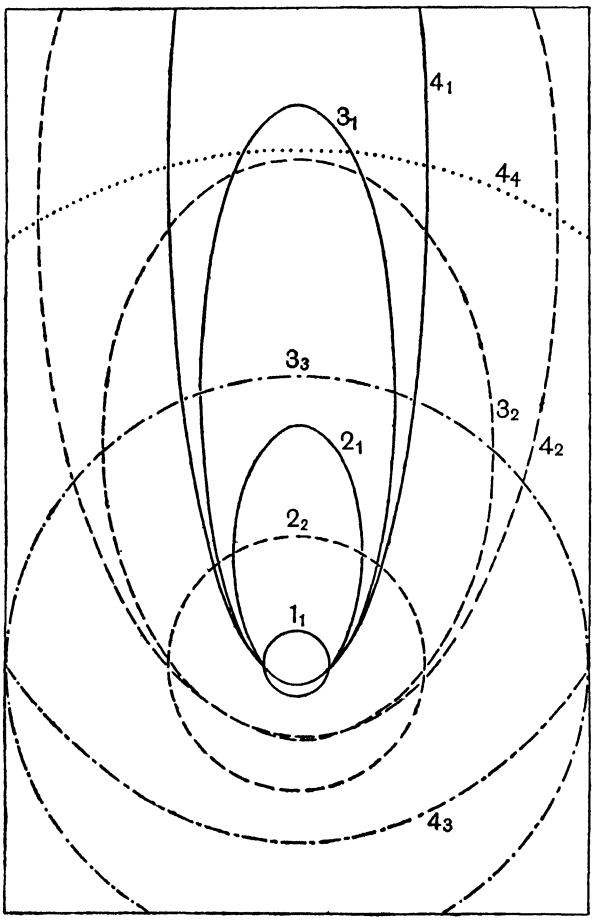


Fig. 4.

sodium atom there are more L-electrons than K-electrons. If the L-electrons, being less firmly attached, must all lie outside the K-electrons, his experiments are hard to explain; but if some of these electrons, those namely in 2_1 orbits, approach during part of

their orbit nearly or quite as close to the nucleus as the K-electrons in 1_1 orbits, it becomes clear why his measurements, which determine the time-average of the distances of the electrons from the nucleus, show an increasing density of distribution of the electrons as we approach the nucleus.

If the screening effect of the other electrons can vary in this manner for different parts of the orbit of the same electron, it is clear that we cannot expect to account completely for the mutual actions of electrons by means of a single screening constant z. Nevertheless the conception of effective charge may not be wholly valueless. Let us now write in place of (83·1)

$$\frac{T}{N}=\frac{W}{Nh}=\frac{(Z-\gamma)^2}{n^2}+\frac{(Z-\delta)^4}{n^4}\cdot\left(\frac{2\pi\epsilon^2}{hc}\right)^2\cdot\left(\frac{n}{k}-\frac{3}{4}\right) \quad \ldots(89\cdot1).$$

We must expect γ and δ to be functions of k and of Z, as well as of n; and if we allow ourselves in this manner to vary the two terms of (89·1) independently, it will always be possible to make it fit the observations. But if we find that the values of γ and δ that we have to adopt in order to produce a fit show the kind of regularity we should expect on general considerations based on our discussion of the forms of the orbits, then we may hold that the conception is of some use in enabling us to understand why the terms of spectra are what they are. We shall not have established any definite and complete theory—we do not pretend to have such a theory to propound—but we shall have proved that the general ideas from which we are working are not inconsistent with the facts.

Now this regularity is found. Thus δ is always considerably less than γ. Since the second term of (89·1) is determined by the part of the orbit in the neighbourhood of the nucleus, where the velocity is greatest, while the first is determined by the whole orbit, this relation is to be expected. Again values of δ can be assigned which make it certain that the M-triplet, and the corresponding N-quartet $\{(N_7N_6), (N_5N_4), (N_3N_2), N_1\}$, are to be explained by the relativity correction, and represent according to (89·1) the differences in the values of k assigned to these terms; this explanation is in accordance with the fact that the frequency difference between corresponding pairs of terms is approximately proportional to Z^4. Further

both γ and δ increase with n; and there are regularities in the increase of γ with Z which will be noted later. Lastly some indication is obtained of the meaning of the a, b distinction, which we have been leaving temporarily out of account. The frequency difference $T_a - T_b$ between a pair of ab terms (*e.g.* L_3L_2 or M_5M_4) is approximately proportional to Z. We can account for such a difference by supposing that the values of γ for the pair differ by a constant amount; for approximately

$$\frac{n^2}{N}(T_a - T_b) = (Z - \gamma_a)^2 - (Z - \gamma_b)^2 = 2Z(\gamma_b - \gamma_a) \quad \ldots(90{\cdot}1).$$

We may suppose, therefore, that the separation of these pairs, or 'screening doublets', is due to the fact that orbits with the same n and k may differ slightly in the effective charge to which they are subjected—an idea which is clearly in accordance with our general examination of the orbits, even if we cannot give any definite account of what the difference is. Bohr supposes that it represents an interaction between orbits all of which have the same values of n, k (see p. 95), but the interaction cannot be described with any precision as yet.

But perhaps the most striking success of a very approximate theory of this kind has been attained by Schroedinger and Fues, who have applied it to optical spectra. We have seen (Ch. XV, p. 33) that the terms of optical series spectra, or at least of the simplest of them, can be represented with good approximation by Rydberg's formula

$$T = (m, a) = \frac{N}{(m + a)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(90{\cdot}2),$$

where m is an integer, increasing regularly throughout the series of terms, and a is a constant characteristic of the series. But the ideas that we have been considering suggest that we might write in place of (90·2)

$$T = \frac{NZ_1^2}{n^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(90{\cdot}3),$$

where Z_1 is the effective nuclear charge and n the total quantum number, thereby relating (90·2) closely to (89·1) and to our theory of X-ray terms. (90·3) will be identical with (90·2), if we put

$$Z_1 = \frac{n}{m + a} \quad \ldots\ldots\ldots\ldots\ldots\ldots(90{\cdot}4).$$

If we adopt this course, and assign values for n to the optical terms in the manner suggested on p. 80, we shall find that Z_1 is always greater than 1. Thus for sodium the term $(1, s)$ is 41449 and $m + a = 1{\cdot}6267$. To this term we assign the quantum numbers 3_1, so that $n = 3$ and $Z_1 = 1{\cdot}85$; similarly the term $(1, p)$ to which we assign the notation 3_2 is 24476, so then $m + a = 2{\cdot}1165$ and $Z_1 = 1{\cdot}42$. n and m both increase by unity as we pass to the higher members of these series, so that Z_1 approaches unity asymptotically. All this is exactly what we should expect. Z_1 is 1 for the orbits of high n because these orbits lie wholly outside the remainder of the atom, consisting of a nucleus and $(Z-1)$ electrons. If all orbits were circular, those of lower n would also lie outside; for it must be remembered that all the orbits considered here are abnormal and not permanently occupied by electrons. But some of them are elongated, and these orbits penetrate within some of the normal and permanent orbits; for such orbits Z_1 is greater than 1, and the increase in Z_1 will be the greater the more elongated the orbit. Since those for which $k = 1$ are the most elongated, we expect, as we find in this case and in all the simpler series spectra, that the s series, for which $k = 1$, has the highest effective charge and the highest frequency.

Since $n/(m + a)$ approaches 1 asymptotically as we pass up the series, it would be convenient if we could identify n and m. There is no real objection to our doing so. As was pointed out in Ch. XV, p. 34, the assignment of the value 1 to m for the largest term is largely arbitrary; several reasons have led to the conventional choice, of which one is the fact that, if this choice is made, a turns out always to be a positive proper fraction, of the same order of magnitude for corresponding terms in the spectra of allied elements. Now that we have a theoretical reason for making another choice, we may safely identify n and m, substituting for a the appropriate negative value a'. Thus in place of writing the s-terms of sodium $(1, a)$, $(2, a)$, $(3, a)$, where $a = +0{\cdot}627$, we may write them $(3, a')$, $(4, a')$, $(5, a')$, where $a' = -1{\cdot}373$. Arithmetically there is no difference between the two notations, but there is a material difference in physical suggestiveness. For now another way of looking at the matter occurs to us. In place of the idea of an effective charge, different from the true charge, we may keep the true charge $Z = 1$

and introduce the idea of an effective total quantum number n_1, different from the true number, n; we may transform (90·2) once more and write it

$$T = \frac{N}{n_1^2} \quad \text{.....(92·1),}$$

where $n_1 = n + a'$ and a' is negative. Of course n_1 will not generally be an integer, as every true quantum number must be, but there is no greater objection to fractional effective quantum numbers than to fractional effective atomic charges. If we adopt this course, $-a'$ is conveniently called the 'quantum defect'.

We may now express Rydberg's law that a is constant throughout a series, by saying that the quantum defect is constant. Since k is constant through the series, the quantum defect must be determined by k and be independent of n; the question now arises whether we can give any reason for this remarkable fact. A complete explanation cannot be hoped for, since that could only come from a complete determination of the quantum orbits in the very complicated system of a nucleus with many electrons, but an interesting attempt has been made by Fues to show that the result is quite consistent with the general theory. His procedure may be described generally as an attempt to discover a law of force in the region about the nucleus which will account for the facts and at the same time resemble generally the law which we expect to hold about a nucleus surrounded by electrons. The argument will be sketched very briefly.

It starts with the assumption that the orbits represented by the optical terms may be taken approximately to be central orbits, in which the force on the electron is always directed towards the nucleus. This assumption implies that the remaining electrons are always distributed with spherical symmetry about the nucleus; it is doubtless not strictly true, but as an approximation it is reasonable. Now in any central orbit

$$W = V + \frac{1}{2m}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right) \quad \text{.....(92·2),}$$

where V is the electrostatic energy, and p_r, p_ϕ are the radial and azimuthal momenta (Ch. XV, p. 60); p_ϕ is constant. From the fundamental quantum equations we have

$$\int p_r dr = n'h; \quad \int p_\phi d\phi = kh \quad \text{.....(92·3),}$$

so that $$p_\phi = \frac{kh}{2\pi} \quad \text{.....(93·1)}$$

and $$\int \left\{ 2mW - 2mV - \frac{k^2 p^2}{4\pi^2 r^2} \right\} dr = n'h \quad \text{.....(93·2).}$$

Now let us write $V = V_1 + V_2$, where $V_1 = -\frac{\epsilon^2}{r}$, the electrostatic energy due to the true charge ϵ supposed concentrated in the nucleus, and V_2 is the 'correction' which is due to the ellipticity of the orbits and the cause of the quantum defect. Then we may write (93·2)

$$\frac{1}{h}\int \sqrt{P - Q}\, dr = n' \quad \text{.....(93·3),}$$

where $$P = 2mW - \frac{2m\epsilon^2}{r^2} - \frac{k^2 h^2}{4\pi^2 r^2} \quad \text{.....(93·4),}$$

$$Q = 2mV_2 \quad \text{.....(93·5).}$$

Now from the optical terms we know W for all relevant values of n and k, and therefore of n'; we therefore know P as a function of r for these values. Q does not involve the quantum numbers; it is a function of r only. Can we guess a form of this function $Q = f(r)$ such that, if we combine it with the function P, we shall make (93·3) true for all values of n' and k? Fues finds that he can guess such a function Q, and he finds further that the function has the general form characteristic of a central charge partially neutralised by outlying electrons. Again it is possible to give a physical meaning to the quantum defect by relating it to certain features of the integral in (93·3), expressed geometrically.

The latest development in this direction is an attempt to explain on these lines the relation (corresponding to Moseley's law in X-ray spectra) between the optical spectra of different elements of similar properties. It has long been known that there are such relations, but none of them have received any theoretical explanation. The only case treated in any detail is that of the Na(11) arc and Mg(12) spark spectra (cf. Ch. XV, p. 23); nothing approaching to a general law can yet be formulated. But at last progress in this direction, so long overdue, appears to have begun in earnest.

21. **The distribution of the electrons.** The primary object of the long discussion which began on p. 81 and has just ended has been to decide whether the general quantum principles of Bohr

and Sommerfeld are competent to explain the facts concerning spectral terms. We shall now conclude that they are, and that the many subordinate features which have to be left without complete explanation arise merely from a complexity of the intra-atomic electric field which it is beyond the power of analysis to resolve at present. If that conclusion is accepted, we have solved one part of our main problem, the determination of the structure of the atom; for we know accurately from spectroscopic measurements the energy associated with the various electronic orbits, or the work required to drag an electron from any one of them, and we know something about their geometrical form. But there is another part of the problem that we have not touched as yet. There are 25 terms in the X-ray spectrum of Ur (92), and consequently 25 different normal orbits with different forms and energies. But there are 92 electrons. Either some of these electrons do not give rise to terms at all, or several electrons must give rise to the same term. The first alternative may be dismissed at once; it has no intrinsic plausibility, and is utterly inconsistent with all the ideas that are inspiring our inquiry. The question therefore arises how the 92 electrons are distributed among the 25 orbits.

We have already given a tentative and partial answer to this question. In Ch. XV evidence was produced—which is quite untouched by the more detailed discussion of this chapter—that there are 2 electrons in the single K or 1_1 orbit; that there are about 8 in the L-orbits, and probably many more than 8 in the M-orbits. But even if we could go further, divide up the 8 L-electrons among the 3 L-orbits, and extend our conclusions in detail to the other orbits and to all elements, a most important question would remain. When we say that there are 2 electrons in the K-orbit, do we mean that 2 electrons follow each other in precisely the same path, or that there are 2 orbits, identical for the purposes of spectra, each of which is occupied by a single electron? And if we adopt the latter alternative, what is the difference between these two orbits? Until quite recently opinion on this matter seems not to have been clear; the question had not been considered directly, but on the whole the tendency was towards the first alternative. In Bohr's earliest sketch of his theory, and in later modifications of it by other writers, orbits containing several electrons, following

each other in the same path, were definitely supposed to form part of the normal structure of the atom. Nowadays, however, there is no doubt that the second alternative must be adopted. Recently (in the interval between this chapter and Ch. XV) Bohr has put forward a theory of atomic structure, far more detailed and at the same time far more successful, than any attempted before; we shall consider it in the following pages[1]. This theory definitely assumes that no normal electronic orbit in an atom contains more than one electron, in the sense that two or more electrons follow each other in the same path. Bohr supports this assumption by means of arguments based on his principle of correspondence, showing that it is impossible that an electron entering or leaving such a multiply occupied orbit could emit the homogeneous radiation which represents a transition between terms. Again, in one element, which we shall discuss presently, there is direct experimental proof of its truth. But perhaps even more convincing support for it is to be found in the order which it introduces into atomic theory and in the simplicity and naturalness of the conclusions to which it leads.

But if some or all of the orbits we have been considering are really multiple, consisting of two or more different orbits, in each of which a single electron revolves about the nucleus, how are these orbits distinguished? The answer is obvious; they are distinguished by lying in different planes. When, on p. 85, we rejected the assumption that the energy of the orbits is determined materially by the third quantum number, we were not deciding that this number had no significance at all; for it must be significant according to our general principles. The different orbits, which have the same n' and k, and therefore the same energy according to our assumption, appearing as a single term, differ in the third quantum number (which we may call for the moment l). We cannot say at present how the planes of two orbits with the same n', k but different l will be related to each other; but one conclusion, supremely important for our coming discussion, we can draw at once. The number of values of l that can occur will be limited, and there will therefore be a limited number of orbits, each occupied by a single

[1] It must not be supposed that all the ideas in the theory were entirely new. Many of them had been foreshadowed by other writers, especially Vegard and Kossel. But Bohr first welded the older ideas with the newer into a coherent form.

electron, represented by the same term. Further we may expect the number of possible values of l to increase with n; indeed we should expect it to be equal to n or at least not greater than n. At first sight we should expect each of the L-terms ($n = 2$) to be double and to represent two electronic orbits; each of the M-orbits to be triple and to represent three. And though this is not the conclusion at which we shall ultimately arrive, it is sufficiently near the truth to guide our thoughts through the rather complicated argument that we shall have to follow. But one attractive proposal, which will doubtless occur to the reader, must be negatived at the outset. It would be agreeably simple if we could explain the puzzling *ab* classification, which we have had to leave unexplained, by a difference in l, giving rise to a small but just appreciable difference in energy. But that view leads nowhere. The *ab* division is probably connected somehow with the difference in the planes of atomic orbits, but not in the simple way that first suggests itself. In what follows we shall have once more to neglect this division entirely, identify completely terms which differ only in this respect, and discuss the evidence as if there were only 2 L-, 3 M-, 4 N-, 3 O-terms[1].

This principle of individual electronic orbits is one of the foundations of Bohr's theory of atomic structure. Another principle which is involved may be termed that of the permanence of orbits. The fact that the same spectral terms can represent both initial and final states in the transitions that are accompanied by radiation proves that the electronic orbits cannot be very greatly perturbed by the re-entry of the ejected electron; the removal of an electron must change the remaining orbits slightly, but it does not change them to the extent of altering their quantum numbers. Now the removal of an electron has the same effect on the total charge on the atom as the addition of one unit to the nuclear charge; and, though the orbits are determined by the distribution of the charge as well as by its total magnitude, it is not unreasonable to suppose that, in general, the orbits are permanent in this particular feature when the nuclear charge is increased, just as they are when an

[1] Bohr's adoption of the three integer notation explained on p. 77 may indicate that he is about to explain the *ab* division in terms of a third quantum number; but he has not done so yet.

electron is removed. If this principle is admitted, the discussion of atomic structure is greatly simplified. For suppose that we know the quantum numbers of all the electronic orbits of an atom of atomic number Z. If the nuclear charge is increased by one unit, the nuclear charge and the number of normal orbits are those characteristic of the simply ionised atom of atomic number $Z+1$. But by our principle, the Z orbits already present in this ionised atom of number $Z+1$ have the same quantum numbers as the orbits in the neutral atom Z; they will doubtless differ, being all of rather greater energy, but this feature is preserved. Accordingly in order to determine the structure of the neutral atom of atomic number $Z+1$, to the extent of deciding what are the quantum numbers of the orbits, we have only to solve the problem for a single orbit, namely that of the $(Z+1)$th electron. But the nature of this orbit is revealed by the optical spectrum; to it corresponds the greatest term of the arc spectrum (which is also the least term of the X-ray spectrum); when the optical spectrum has been resolved into series the requisite information is immediately forthcoming. When we have thus determined the atom $Z+1$ we can proceed in the same manner to $Z+2$. Since we know in detail the structure of H(1), we could by this procedure determine the structure of all atoms by a method in some degree analogous to that of 'mathematical induction'.

The same argument can be expressed in a rather different way, to which frequent reference will be made in what follows. In place of tracing the development of the electronic orbits in the various atoms as we pass up the scale of atomic number, let us consider the building up of the orbits in a single atom. Regarded from this standpoint the principle of the permanence of orbits means that as successive electrons are allowed to fall into their normal orbits round the nucleus, the pth electron will always fall into an orbit with the same quantum numbers whatever the nuclear charge. n_k is simply a function of p; the 10th electron, for example, will fall into an orbit with the same n and k, whether it is completing the last normal orbit in an atom of Ne(10) or one of the earlier orbits of Em(86). Whether we are thinking of the development of orbits throughout the sequence of elements or the development of the orbits in a single atom as it takes up electrons, the order in

which the orbits are presented to us is the same. Moreover, since in the development of each atom each incoming electron will fall into the most stable orbit (that is to say, the orbit in which it is most firmly bound and has the highest ionisation potential), the order in which the orbits appear will also be that of increasing firmness of binding.

But two conditions must be fulfilled if this method of examining the arrangements of electrons is to be completely successful and exhaustive. First the underlying principle of the permanence of orbits must be true; second the optical spectra of all elements must have been resolved into series and terms, so that we always know the quantum number and the energy of the last bound electron. Actually neither of these conditions is fulfilled. We shall see that, when the principle breaks down, exceptional circumstances occur which indicate very clearly that it has broken down and what is the change that has occurred; indeed the study of the infringements of the principle provides the most convincing evidence for the truth of the theory; this is one of those cases where the exception truly proves the rule. But our ignorance of spectra is by far more serious, and at present prevents the full application of the principles to determine in detail the structures of all atoms. To this extent the theory is incomplete; but it is complete as no other theory has ever been in bringing clearly to light all the factors which must determine the structure and all the kinds of evidence that are, or will some day be, available for filling in the details. The comprehensive truth of the theory cannot be doubted as we study the elements in turn, and find all their properties falling into line with our principles.

But before starting on that study, it may be convenient to point out the general nature of the results that we attain. The $(Z+1)$th electron will, of course, always fall into the orbit of greatest energy which is still open to it; and, on the whole, the orbits with lesser n and lesser k are those of greater energy. Accordingly we shall expect the first few elements (proceeding upwards from H (1)) to contain only 1_1 orbits. After a certain number of these orbits have been filled, no more are possible because the spatial grouping represented by the third quantum number is complete. 2_1 orbits appear; these are filled in due course and 2_2 orbits appear, followed

again by 3_1 orbits—and so on. The sequence of the elements in order of atomic number is simply the sequence in which these orbits are filled up, generally in the order indicated; the problem is to determine how many orbits of given n_k there can be, before this group is filled up and a new group with higher n or higher k begins to be formed. We can express our conclusions in a simple table, stating how many electronic orbits in each group there are for each of the elements. The table at which we shall ultimately arrive is best given here, in order that the reader may follow the argument as it develops. Table VI gives the number of orbits with the quantum numbers at the head of the column in the element at the beginning of the row. When the number is doubtful it is bracketed; when several numbers are doubtful, the element is omitted. Table I has also been drawn with these conclusions in view.

After these preliminaries let us start on our course. In the normal state of the hydrogen atom the single electron is in a 1_1 orbit, revolving in a circle round the nucleus. Consequently, when we pass to the helium atom ($Z = 2$) one of the electrons must be in a 1_1 orbit, which again must be a circle or very nearly a circle, but will be of a different radius. In what orbit will the second electron move in the normal state? In this instance some answer can be given to this question by direct calculation of the possible quantum orbits according to the general criteria. One possibility appears to be that both electrons revolve round the nucleus in the same circular 1_1 orbit, an arrangement which would be inconsistent with Bohr's assumption of individual orbits. Another possibility is that the second electron revolves in a 1_1 orbit similar to that of the first but inclined to it at an angle of about 120°. The remaining possibilities are that the second electron occupies an orbit with n greater than 1. A decision between these alternatives ought to be possible on the ground of direct experimental evidence. The ionisation potential W_0 of helium is known to be about 25 volts[1]. If both electrons were revolving in the same 1_1 orbit, the ionisation potential should be 28·8 volts, which is certainly too large. If either electron was in a 2_k orbit, the ionisation potential would be less than 7 volts and certainly too small. Only one alternative

[1] The optical evidence gives 24·6; but most observers who have measured it directly give values above 25 volts. The difference is not important for our purpose.

TABLE VI

	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	6_1	6_2	6_3	7_1	7_2
H (1)	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
He (2)	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Li (3)	2	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Be (4)	2	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
B (5)	2	2	(1)	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
—	—	—			—			—				—			—			—
Ne (10)	2	4	4	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Na (11)	2	4	4	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Mg (12)	2	4	4	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Al (13)	2	4	4	2	1	...	...	...	...	...	...	...	...	...	...	...	...	...
—	—	—			—			—				—			—			—
Ar (18)	2	4	4	4	4	...	...	...	...	...	...	...	...	...	...	...	...	...
K (19)	2	4	4	4	4	...	1	...	...	...	...	...	...	...	...	...	...	...
Ca (20)	2	4	4	4	4	...	2	...	...	...	...	...	...	...	...	...	...	...
Sc (21)	2	4	4	4	4	1	(2)	...	...	...	...	...	...	...	...	...	...	...
Ti (22)	2	4	4	4	4	2	(2)	...	...	...	...	...	...	...	...	...	...	...
—	—	—			—			—				—			—			—
Cu (29)	2	4	4	6	6	6	1	...	...	...	...	...	...	...	...	...	...	...
Zn (30)	2	4	4	6	6	6	2	...	...	...	...	...	...	...	...	...	...	...
Ga (31)	2	4	4	6	6	6	2	1	...	...	...	...	...	...	...	...	...	...
—	—	—			—			—				—			—			—
Kr (36)	2	4	4	6	6	6	4	4	...	...	...	...	...	...	...	...	...	...
Rb (37)	2	4	4	6	6	6	4	4	...	...	1	...	...	...	...	...	...	...
—	—	—			—			—				—			—			—
X (54)	2	4	4	6	6	6	6	6	6	...	4	4	...	...	...	...	...	...
Cs (55)	2	4	4	6	6	6	6	6	6	...	4	4	...	1	...	...	...	...
Ba (56)	2	4	4	6	6	6	6	6	6	...	4	4	...	2	...	...	...	...
La (57)	2	4	4	6	6	6	6	6	6	...	4	4	1	(2)	...	...	...	...
Ce (58)	2	4	4	6	6	6	6	6	6	1	4	4	1	(2)	...	...	...	...
Pr (59)	2	4	4	6	6	6	6	6	6	2	4	4	1	(2)	...	...	...	...
—	—	—			—			—				—			—			—
Lu (71)	2	4	4	6	6	6	8	8	8	8	4	4	1	(2)	...	...	...	...
Hf (72)	2	4	4	6	6	6	8	8	8	8	4	4	2	(2)	...	...	...	...
—	—	—			—			—				—			—			—
Au (79)	2	4	4	6	6	6	8	8	8	8	6	6	6	1	...	...	...	...
Hg (80)	2	4	4	6	6	6	8	8	8	8	6	6	6	2	...	...	...	...
—	—	—			—			—				—			—			—
Em (86)	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4	...	...	...
? (87)	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4	...	1	...
Ra (88)	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4	...	2	...
Ac (89)	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4	1	(2)	...
Th (90)	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4	2	(2)	...

remains, namely that both electrons are in 1_1 orbits, but that these orbits are independent and 'crossed' in the manner just indicated; this alternative must therefore be adopted. Unfortunately, just as that comfortable conclusion has been set down, Kramers publishes a detailed calculation of the ionisation potential of this alternative, and shows that it should be 20·8 volts, which is certainly too low. None of the alternatives fits the facts; for the first time a numerical prediction of quantum theory is unambiguously in conflict with experiment. It is too early yet to guess what way will be found out of this difficulty; but it will almost certainly lie in some revision of the predicted ionisation of the crossed orbits, not in the acceptance of any other alternative or in the rejection of the whole theory. As an indication of the direction in which a solution may possibly be sought, it may be noted that this first instance in which the quantum theory has given a false numerical result is also the first instance in which the forces determining the orbits to which it has been applied are those between electrons; hitherto in numerical calculations we have always supposed these forces negligible compared with those due to the nucleus. While there is experimental evidence derived from the scattering of rays that the force between a nucleus and an electron varies according to Coulomb's law (beyond a given distance), there is no direct evidence from any source that the same law holds for the forces between electrons. It seems less likely that the solution will be found in a revision of the foundations of quantum theory as suggested on p. 59, for in the closely analogous case of the electron revolving round a single nucleus, theory and experiment agree perfectly.

There the matter must be left for the time being; we have no alternative but to neglect the discrepancy and to proceed as if we could still believe that the ionisation predicted for the crossed orbits was that determined experimentally. If we so proceed, we can discuss a very interesting explanation of some features of the helium spectrum that has been given by Franck and Reiche and by Kemble. (It must be understood that we are now speaking of the arc spectrum of helium and not of the spark spectrum which received so much attention in Ch. XV.) It has long been known that the lines of this spectrum are divisible into two groups; each group forms a typical series spectrum, with a definite set of terms, but

no term is common to the two groups. The spectrum thus resembles that of a mixture of two elements; in fact the spectra are usually known as those of parhelium and orthohelium; but all attempts to separate normal helium into two distinct gases have failed. The largest term of the orthohelium spectrum corresponds to an ionisation potential of 4·78 volts, of which no sign can be detected by the ordinary methods. On the other hand the largest term of the parhelium spectrum corresponds to the measured ionisation potential of helium, namely 25 volts; helium in the normal state must therefore be parhelium; and the highest term of the parhelium spectrum must correspond to "crossed" orbits, *i.e.* orbits that are not in one plane. Franck and Reiche suggest that all the terms of the parhelium spectrum correspond to crossed orbits, the remaining terms corresponding to crossed orbits with n greater than 1; while the terms of the orthohelium spectrum correspond to coplanar orbits which are not represented in the normal state of the atom. The absence of lines representing a difference between a term belonging to parhelium and one belonging to orthohelium must then mean that a transition, accompanied by the emission of radiation, never occurs between a state in which the orbits are crossed, and one in which they are coplanar. This is exactly what we might expect from general quantum theory, which indicates that in such transitions, taking place in the absence of an external electric field, the third quantum number will not change, and that the initial and final orbits of the changing electron will be approximately in the same plane. On the other hand, a change of plane may occur when there is an external electric field; there is such a field when the atom is ionised by a charged particle, and we may expect transitions between orthohelium and parhelium terms during ionisation. We can thus explain why, though the atoms are always normally in a parhelium state, orthohelium states and the orthohelium spectrum may result from ionisation. But to complete the explanation something more is required. If orthohelium states are produced by ionisation and cannot revert to parhelium states in the subsequent recombination accompanied by the emission of radiation, how is it that we do not find some portion of a mass of helium that has been ionised in the orthohelium state and do not find some trace of the low ionisation

potential of 4·78 volts, corresponding to the highest term of that spectrum? Franck replies that the reverse transition can also occur in an external field, which might be produced, for example, by the close approach of two atoms, resulting in incipient chemical combination between them. According to this view the orthohelium 'normal state', with an ionisation potential of 4·78 volts, is metastable; the element in this state is chemically active; it resembles rather the alkali elements, which have similarly low ionisation potentials. The state cannot endure in the presence of the slightest impurity which could give rise to the mutual action between atoms that we call chemical combination; perhaps even there may be chemical action between two active metastable orthohelium atoms, forming a helium molecule which subsequently dissociates into separate parhelium atoms.

Franck adduces evidence for this view, involving the existence of metastable helium, from the resonance spectrum of helium. Some more direct evidence of the existence of such a state for a finite time has recently been found; there can be little doubt of the truth of the explanation. It is especially interesting from our point of view because of the support that it brings to Bohr's assumption of distinct orbits. For the normal orthohelium state cannot be that in which both the electrons are in a single 1_1 orbit; the ionisation potential of 4·78 is far too small. It must be the state in which one electron is in a 1_1 orbit and the other in a coplanar 2_1 orbit. The transition of the second electron to the same 1_1 orbit, if it could occur, would produce a state even more stable and having a higher ionisation potential than the normal parhelium state. But it cannot occur. Even in these exceptionally favourable circumstances, the common orbit is impossible.

So far then our principles work well and give us detailed information concerning the helium atom, and therefore of the two most firmly bound electrons in all atoms. They are always both in 1_1 crossed orbits. We now pass to the next element Li (3). The ionisation potential of lithium, deduced from the spectrum, is 5·3 volts, much lower than that of parhelium, but just higher than that of orthohelium. Now in orbits of the same total quantum number, which are at all analogous to the orbits round a single nucleus, the ionisation potential must increase with Z, as in

equation (82·1). Accordingly we may conclude certainly that the electron, the binding of which is represented by the lithium arc spectrum, is not in a 1_1 orbit, but, as in the normal metastable orthohelium state, in a 2_1 orbit. It is the occurrence of an orbit in the normal state having a higher quantum number which produces the great change in properties which occurs as we pass from helium to lithium. Little is known of the spectra of the next element Be (4), or indeed of any of the remaining elements of the second group in Table VI. Only two of them, O (8) and Ne (10), have been resolved into series[1], and such information as we have derived concerning helium and lithium is not available.

The next certain clue is obtained when the same great change in properties occurs once more as we pass from Ne (10) to Na (11). The similarity of these two changes naturally suggests that they are due to the same cause, namely the entrance of an orbit of higher n. The great stability of helium we have associated with the completion of the orbits for which $n = 1$, and the instability of lithium with the first occurrence of an orbit for which $n = 2$. So clearly we must suppose that the orbits for which $n = 2$ are complete at Ne (10), and that in Na (11) for the first time appears an orbit for which $n = 3$. If this be so, the elements from Li (3) to Ne (10) must differ in the continual addition of 2_k orbits; and there must be eight of these orbits in Ne (10). They will be divided into 2_1 and 2_2 orbits; considerations of spatial symmetry suggest that either group cannot be complete till there are at least four members of the group; we suppose therefore that in Ne (10) there are four 2_1 and four 2_2 orbits, and that in Na (11) there is added a 3_1 orbit. In the elements between Li (3) and Ne (10), there must thus be added three 2_1 and four 2_2 orbits; it is likely that the first 2_2 orbit appears at B (5) and the last at F (9); but this is somewhat speculative.

The sequence from Na (11) to K (19) follows so exactly that from Li (3) to Ne (10) that we may be sure that the development of electronic orbits is similar. Mg (12) will have two 3_1 orbits; the 3_k orbits will be completed when we reach Ar (18), con-

[1] In Ch. XV, p. 8, the oxygen group was erroneously omitted from the list of elements that show typical series spectra. But since the elements on either side of this group do not give such spectra, it is difficult to base on their terms any certain conclusions concerning electronic orbits.

taining four 3_1 and four 3_2 orbits; in K (19) a 4_1 orbit occurs for the first time. Proceeding onwards again, Ca (20) is so similar to Mg (12) in its relation to the preceding element that we may take it to have two 4_1 orbits. But with the next element Sc (21) a change occurs; this element and all that immediately follow it differ markedly from the corresponding elements in the preceding groups of Table VI; the difference becomes more pronounced as the sequence proceeds, until we come to Fe (26); for this element shows no analogy whatever with Ar (18), which is the 8th member of the previous group. The nature of the anomaly in this part of the sequence may be described generally by saying that the change in chemical and other periodic properties which occurs in passing from one member of the sequence to the next is much less than it is in normal parts of the sequence. This feature is especially marked in the curious group Fe (26), Co (27), Ni (28), which hardly differ at all in these properties. After this group, starting with Cu (29), we find a partial return to the normal periodic sequence of the elements. If we compare the elements from Cu (29) to Kr (36) with those from Na (11) to Ar (18), we find a similarity between corresponding members which is appreciable at the start and increases constantly, until the last three members Se (34), Br (35), Kr (36) are precisely analogous to S (16), Cl (17), Ar (18).

These remarkable features, which have always puzzled those who have tried to explain the periodic table, are natural consequences of Bohr's ideas. It will be observed that the 3_k orbits are not really complete at Ar (18); that element contains no 3_3 orbits. Such orbits must be possible; they correspond to the circular orbits of a single electron, and in that case would have greater energy than 4_1 orbits. But the presence of other electrons about the nucleus may make the 4_1 orbits more stable than the 3_3 orbits for reasons we have discussed; part of the former approach much nearer the nucleus, and the effective nuclear charge is therefore greater for them. Such a condition apparently obtains when there are 18 electrons round a nucleus of charge 19 and the 19th electron is added. But it cannot always obtain when the 19th electron is added. If Z is considerably greater than 19 and the nucleus is still surrounded by only 18 electrons, these electrons will be much less effective in counteracting the charge on the nucleus for an

orbit lying wholly outside the 18 electrons; the effective nuclear charge for a 3_s orbit, which so lies outside, will increase relatively to that for a 4_1 orbit, which lies partly inside. As Z is increased we must expect to reach a stage at which the 3_s orbit is more stable than the 4_1 orbit for the 19th electron, just as it would be for a single electron revolving round an unneutralised nucleus.

When that stage is reached the normal rule will break down. Increase of nuclear charge will affect the quantum numbers of orbits already existing in the atom; and if we build up the next element by the successive binding of electrons, the process will follow that of the preceding atom only up to the binding of the 18th electron. Bohr suggests that the stage is reached at Sc (21). In K (19) and Ca (20) the 19th electron enters a 4_1 orbit; the 20th electron in the latter also enters a similar orbit. But in Sc (21) the 19th electron enters a 3_s orbit; one, probably both, of the remaining electrons enters a 4_1 orbit. The rule, hitherto prevailing in the development of the elements, that each additional electron enters an orbit of greater n or an orbit of the same n but greater k, breaks down; and with its failure may be expected an interruption to the normal periodic sequence. For it is the electron last added and least firmly bound which determines the arc spectrum and the other periodic properties of the element. Ca (20) and Sc (21) are exactly the same in respect to this electron; in both cases it enters a 4_1 orbit, one other such orbit being already present. The elements differ only in the orbits of electrons added previously, which are more firmly bound and have comparatively little influence on periodic properties; it is to be expected therefore that the change in periodic properties in passing between these two elements will be considerably less than in passing between the two corresponding elements (Mg (12) and Al (13)) in the previous group of the table. A similar anomaly in connection with the 1_k and 2_k orbits is hardly to be expected; for all sub-groups of these groups of orbits are represented before any 3_k orbits appear. If 2_k orbits were added after the appearance of the 3_k, it would involve the addition of members to already existing sub-groups, and it may be supposed that the number of such members is definitely limited by quantum conditions. The anomaly appears in connection with the 3_k orbits, because the 3_s sub-group is not represented at all.

There is some direct optical evidence that this change in the orbit of the 19th electron does occur at Sc (21), or at least in some element in its immediate neighbourhood. It is based on the allocation of different azimuthal quantum numbers k to the different series of terms in the optical spectrum (cf. p. 80). Both the arc spectrum of K (19) and the spark spectrum of Ca (19) represent states taken up by the 19th electron in the atom; for the spark spectrum represents the states of the atom which has one less electron than in the normal state. According to Sommerfeld's theory, the s-terms represent states n_1, the p-terms states n_2, the d-terms states n_3. The greatest term of each series represents the state with the lowest n and the determination of n for this greatest term is to be made according to the principles discussed on p. 80. n for each series will be the greatest value for the same k that does not occur in the X-ray spectrum, which represents the normal states of the atom, the optical terms representing abnormal states of higher total quantum number. (An exception is made for the greatest s-term which belongs to both X-ray and optical spectra.) Thus in the spectra of K (19) and Ca (19) the greatest s-term must be 4_1. On the other hand the greatest d-term is 3_3; since the 3_3 orbit does not occur in the normal atom. Now in the K (19) spectrum, the greatest s-term is much greater than the greatest d-term; and consequently we have direct evidence for our assumption that, when $Z = 19$, the 4_1 orbit is much more stable for the 19th electron than the 3_3. On the other hand in the spectrum of Ca (19), the greatest d-term is but very little smaller than the greatest s-term: when $Z = 20$ a 3_3 orbit is very nearly as stable for the 19th electron as a 4_1 orbit. We expect then that if Z is increased a very little more, the greatest d-term will become greater than the greatest s-term, and the 3_3 orbit will be more stable for the 19th electron than the 4_1 orbit. That is exactly what has been assumed in our discussion. On the other hand, if we compare in a similar manner the arc spectrum of Na (11) with the spark spectrum of Mg (11), with a view to determining the relative stabilities of the 3_1 and 2_2 orbits for the 11th electron (using for this purpose the p-term, for which $k = 2$, in place of the d-term), we find that in both spectra the 3_1 orbit is much more stable than the 2_2; there is no sign of increasing stability of the latter relative to the former as Z increases. We do not therefore expect, and we do not find,

any further increase in the number of 2_k orbits within the second column of our periodic table.

We now resume the main discussion. Beyond Sc (21) we have no definite evidence derived from spectroscopy of the relative stability of different orbits. But it is natural to suppose that the same anomalous development persists throughout the anomalous elements. Thus in Ti (22) not only the 19th but also the 20th electron enters a 3_3 in place of a 4_1 orbit, and it is again only the last two electrons which enter 4_1 orbits. (It is really quite uncertain that in all these elements the last two electrons do enter 4_1 orbits, but we may retain that assumption for simplicity.) In V (23) the 21st also enters a 3_3; and so on, the addition of electrons resulting in a filling up of the 3_3 orbits and not of the 4_1 or still higher orbits. There is no evidence of a restoration of the normal development and of the appearance of more than two 4_1 orbits until Ga (31) is reached; consequently 10 electrons must be added to 3_k orbits. The ten new 3_k orbits might all be 3_3 orbits, but Bohr makes an alternative and entirely convincing suggestion. He supposes that the introduction of 3_3 orbits into the 3_k group disturbs the spatial symmetry which had previously imposed a limit 4 on the number of orbits in each sub-group 3_1 and 3_2. Complete symmetry could not be obtained with less than four members; but it could equally well be obtained with six or eight. (An indication of this argument can be given by observing that a tetrahedron, a cube and an octahedron are all perfectly regular solids.) If we imagine that in the presence of the 3_3 orbits, complete symmetry is obtained only with six members in each sub-group, the addition of 10 electrons is explained; we have to pass from a condition of four 3_1 and four 3_2 orbits to one of six 3_1, six 3_2, and six 3_3 orbits. Moreover, it is natural to associate with the formation of new 3_1 and 3_2 orbits (which are even more firmly bound to the nucleus than the 3_3 orbits and have even less effect on the electrons added last of all) the appearance of the anomalous iron group, which for this purpose should probably include copper; for in this group the change of periodic properties with addition of electrons is least of all.

Our general view is then that from Sc (21) to Zn (30) the new electrons added go into 3_k orbits lying in the interior of the atom rather than into 4_1 orbits on its surface; in particular from Fe (26)

to Cu (29) they go into 3_1 and 3_2 orbits, which lie deepest of all 3_k orbits. (These geometrical expressions must not be taken too literally; they are intended to indicate closeness of binding rather than geometrical arrangement. For some part of a 4_1 orbit doubtless lies within some part of a 3_3 orbit.) When Zn (30) is reached the 3_k orbits have reached their full complement, with six orbits in each sub-group; the addition of 4_k orbits is resumed in a manner precisely similar to the addition of 2_k orbits in the second column, and with it the normal periodic sequence. Eventually we reach Kr (36) which, with the full 3_k group, has four 4_1 and four 4_2 orbits, precisely analogous to neon, which, with its full 1_k group, has four 2_1 and four 2_2 orbits.

The fifth group of Table VI is precisely similar to the fourth; all that was said of the fourth is true of the fifth, if we substitute 5_k for 4_k and 4_k for 3_k. But when we get to the sixth group we find a yet longer period, and a sequence of elements, namely that of the rare earths, yet longer and changing less rapidly with increasing Z than the iron group of the fourth period or the palladium group of the fifth. And of course we must explain it in the same manner. During the long sequence of rare earths we are completing the 4_k orbits. The completion consists first in the addition of 4_4 orbits which were previously absent, and second in the opening of the 4_1, 4_2, 4_3 sub-groups to receive more members, the total number in each sub-group being raised from six to eight. During this process the number of electrons in 4_k orbits is increased from $3 \times 6 = 18$ to $4 \times 8 = 32$; the process actually requires for its completion the 14 rare earths from Ce (58) to Lu (71)[1]. The completion of the 4_k orbits is followed quickly by, or actually overlaps, the raising of the 5_k orbits from 8 to 18. This last development is represented by the appearance of the platinum group, precisely analogous to the palladium and iron groups. The normal development, consisting of the addition of new 6_k orbits, may start again at Tl (81), but it must be admitted that the elements at the end of this sixth period are not so typically periodic as those at the end of the fourth and fifth periods; it is unfortunate that (85), which

[1] Perhaps La (57) ought to be included among the rare earths, which would then be 15 in number; but it is not a really typical member of the group. On the other hand the recent identification of Hf (72) and the proof that it is *not* a rare earth, are in admirable accordance with the theory—which, indeed, led to its discovery.

ought to be a typical member of the halogen group, is not known. But the period ends with a typical rare gas, Em (86), which doubtless has the typical rare gas structure, namely completed groups of all but the highest n, and four members of each of the sub-groups n_1, n_2 with the highest n.

The final (seventh) period is incomplete; but so far as we have knowledge of it the development proceeds in the normal manner by the addition of 7_k groups followed probably by the partial completion of the 6_3 sub-group. But the instability of the nucleus, of which the universal radioactivity of members of this column is the evidence, finally puts an end to the sequence.

22. **Some consequences of the arrangement.** In the course of our survey we have made little explicit use of data derived from X-ray spectra, though of course the fundamental ideas that underlie the theory and have suggested the principles are derived from such spectra. But we may now inquire how far the very detailed information that arises from this source is in harmony with our conclusions.

The most direct way of testing the theory by means of X-ray spectra would be to determine at what points in the series of elements various terms appear. If we could show, for example, that the term M_1 occurs for the first time in the element to which we assign for the first time a 3_3 orbit, we should have very complete information. Unfortunately direct evidence of that kind is not very easy to obtain; for as a term is traced through elements in the sequence of decreasing Z, the lines in which it is involved always become very faint before they actually disappear. We can say *about* where a term disappears, and the facts are always in accordance with the theory; but we can seldom say exactly where it disappears. We can fix the place quite definitely only in the elements of lowest Z; thus it is quite certain that helium has no L-term. For if it had, the neutral helium atom should have two ionisation potentials, one lower, corresponding to the ejection of the L-electron, and the other higher, corresponding to the K-electron; it is certain that there is only one ionisation potential. On the other hand, Li (3) has two ionisation potentials, as it should have.

But there is abundance of less definite evidence. It has already been noted that Moseley's law is not strictly true. It is very nearly true for the K-term, and also for the L-term except in elements for which Z is less than 10; it is much less nearly true for the M-terms, and for the higher terms it breaks down altogether. If Moseley's law were true, the curves relating $\sqrt{T}$ and Z would be straight lines; they are not straight lines and are not even of continuous curvature; they consist of steeper portions separated at definite kinks from less steep portions.

Now this is precisely what our theory would lead us to expect. The slope of the Moseley line will be constant, only so long as z is constant in (62·1), and the effective charge differs from the true charge by a constant amount. But if we fix our attention on any particular term, representing an orbit A, and consider the relation to A of the orbits appearing in the atom subsequent to the first appearance of A, we shall realise at once that constancy of z is not to be expected. For there are three forms of this relation:—orbits may appear which are (1) in the same group n as A, (2) 'exterior' to A, *i.e.* of higher n, (3) 'interior' to A, *i.e.* of lower n. If all the orbits were circles, and the terms interior and exterior had their full geometrical meaning, it would be obvious that orbits (3) must have a far greater 'screening effect' than orbits (2). For an electron which is always inside the orbit A would be very nearly equivalent to the reduction of the nuclear charge by one unit; the contribution of such an electron to z would be very nearly 1; while such electrons were being added to the atom z would increase as fast as Z, the effective nuclear charge would remain constant, and the Moseley curve consequently should be horizontal. On the other hand, an electron which is always outside the orbit will have comparatively little screening effect; if there were so many of them that they formed a shell of uniform density surrounding the orbit B, they would have no effect on the form of that orbit. Accordingly while such electrons are being added the total screening effect of the electrons is unchanged and we may expect the Moseley curve to be inclined normally, corresponding to z constant. The effect of orbits (1) should be intermediate between these extremes; z should increase while such orbits are added, but not at the same rate as Z.

And this is what we find. The initial portions of the L- and M-

curves, but little inclined to the horizontal, appear exactly where, according to our theory, the $n=2$ and $n=3$ groups, which these terms represent, are being formed; the orbits appearing stand in relation (1) to A. But the feature is shown even more strikingly in the N- and O-terms, the irregular portions of which correspond to the development of the rare earth group. In Fig. 5 the values of $\sqrt{\frac{T}{N}}$ for these terms are plotted against Z. The measurements for the O-terms are not very accurate and the observed points lie

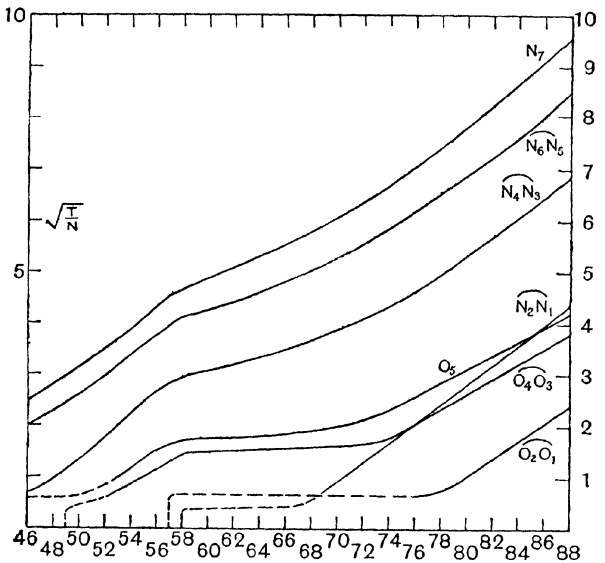


Fig. 5.

sometimes at considerable distances from the lines drawn, but they are sufficient to make the general form clear. In the figure the members of a relativity doublet are not separated, since they are very close together for the smaller values of Z and not very widely separated for the larger. Where measurements are not available the conjectured curve is shown dotted. It will be seen that the first kink in the N-curves, leading to a portion with a small slope, occurs at $Z=57$ or 58, where according to our theory the formation of the 4_k group begins; the second kink, less well marked and restoring the normal slope, occurs between $Z=72$ or

74 where the formation of the group is complete. The marked upward bend in the highest O-term occurs at the end of the sixth period where the anomalous development ends; the previous almost horizontal portion represents the appearance of electrons inside these orbits and standing to it in relation (3). Here we have the clearest possible proof that we have interpreted rightly the significance of the irregularities in the periodic table. Further it will be seen that just before the 4-group is complete, the (N_1N_2) term (the doublet is here hardly separable), which has previously been smaller than the O-terms, becomes greater; the two curves actually cross. At this point, as we expected, the 4_4-group, which is being completed, is actually less stable in the neutral atom than one of the groups already completed (at least for the time being). If the curves for the K-, L-, M-terms are drawn in this region, they are also found to show signs of similar irregularities, most marked in the M-curve and least marked in the K-curve. The electrons being added stand to these orbits in relation (2) and are, in our sense, exterior. But it must be remembered that really they are not wholly exterior, and the reproduction in these other curves of the irregularities on a smaller scale is in perfect accord with our general ideas.

Indeed on the basis of these considerations we may hope to be able to give a rather more detailed account of the screening effect than we have done hitherto. If we divide the quantity γ in (89.1) into two parts, one of which represents the screening effect of the exterior orbits, the other that of the interior orbits (orbits in the same group being included for the present in the latter), then an approximation to the first part can be made with some certainty for the rare gases, in which the arrangement of the orbits in each quantum group is symmetrical and their number known. For such a symmetrical group may be replaced by a spherical shell bearing the same total charge, and its screening effect calculated from the work done by an electron in passing through the shell. By means of such arguments Bohr concludes that the decrease in the effective nuclear charge for any term as we pass from one rare gas to another, due to the addition of an exterior group, should be approximately n^2, where n is the total quantum number characteristic of the term concerned. Thus the effective charge

for the K-term should decrease by 1 as we pass from helium to neon, from neon to argon, and so on; the effective charge for the L-term by 4; for the M-term by 9. The following table shows that this prediction is fulfilled, and that therefore the estimate of the number of electrons in each group is confirmed.

TABLE VII

	γ_K	γ_L	γ_M
Ar (18) ...	2·7	9·6	...
	1	4	
Kr (36) ...	3·7	13·6	27·9
	1	3·2	5·4
X (54) ...	4·7	16·8	33·3
	1	4·8	9·9
Em (86) ...	5·5—6·0	21·6	43·2

Another interesting feature of X-ray spectra which, when it has been investigated more fully, may provide a very complete confirmation of the theory may be mentioned. Among the faint lines (p. 74) that cannot be fitted into the scheme of terms given in Table V are some which appear characteristic of the rare earths; when they appear there are sometimes found also low frequency satellites of the absorption edges. Now our expectation that all X-ray lines in the emission spectrum should be accounted for by the terms of Table V is based on the belief that the transitions representing such lines occur only between levels normally occupied. An electron, if displaced at all, must be ejected completely from the atom (or to one of the abnormal optical orbits lying outside all the normal orbits), and its place must be filled by an electron from one of the other normal orbits; there are no orbits within the atom in which a displaced electron can find a place. But it is quite conceivable that this principle is not strictly true when there is present in the atom a group of electronic orbits in the course of completion; in such circumstances there are potentially possible orbits within the atom that are yet unoccupied; we can readily imagine that an electron displaced from a normal orbit might pass into an orbit belonging to this group and so endeavour to complete it. Thus in the rare earths, when the number of orbits in the 4-group is

being raised from 18 to 32 within the already completed 5- and 6-groups, it is not unlikely that an electron ejected from an inner orbit may pass into a 4-group, endeavouring to complete this group, rather than pass beyond the 6-group. If it does, there will be a new term not included in our scheme, and therefore new lines in the emission spectrum. In the absorption spectrum there will be an edge corresponding in the usual manner to the new term, which will however lie in a region inaccessible to experiment; but there will be also new absorption lines, representing transitions between the normal orbits and this abnormal orbit, which will be accompanied by a smaller change of energy and have a lower frequency than the usual absorption lines corresponding to these orbits. It is not certain yet whether this is the explanation of any of the discrepant lines and low frequency satellites of absorption edges, and still less certain whether in this manner, and that discussed on p. 75, all discrepant lines can be accounted for; but the idea is intrinsically plausible.

23. **The anomalous elements.** In testing the theory, the elements which are anomalous in the periodic table are of peculiar importance, because the theory, unlike all its forerunners, offers a definite explanation of them. Accordingly it will be convenient to notice here some other properties characteristic of these elements which will probably in the near future throw much light upon the details of atomic structure. These properties are the paramagnetism and the coloration of their ions. For though substances not containing any of these elements may be paramagnetic or coloured, the magnetism or coloration of such substances cannot be related to the presence in them of a particular atom or ion. Thus oxygen and ozone are paramagnetic, but other compounds containing this element in large proportion, such as water or hydrogen peroxide, are not; again, mercuric oxide and sulphide are coloured, but mercuric chloride is not. On the other hand, in the elements that we are considering paramagnetism and coloration always appear when the ions of the element are present; thus all ferric and cupric salts are coloured, and all ferric and ferrous salts are magnetic, in solution or in the crystalline state. Paramagnetism and coloration which are in this sense atomic, or rather ionic, properties are not

known outside the elements in the anomalous portions of the periodic table[1].

Coloration, the less interesting of the two properties for our present purpose, may be dealt with first. No quantitative laws of coloration are known; the absorption band characteristic of the cupric ion, *e.g.*, varies with the anion in a manner which at present seems irregular. However, the general explanation of the occurrence of coloration is simple. It is an indication that the frequency of the radiation emitted during transitions between quantum orbits of the most loosely attached electron in the ion lies in the visible spectrum. We shall consider the process of ionisation in solution again in the next section; but it will probably be clear already to the reader that the electrons which are detached in that process from the elements formed in the normal sequence are those of highest total quantum number. Sodium is monovalent, magnesium divalent, because there are present in these elements respectively one and two electrons in 3_k orbits, the remainder being in 2_k or 1_k orbits; the remaining electrons are therefore much more firmly bound than those detached. Now we know that the frequency of the radiation emitted during transitions of the least firmly attached electrons in the normal atom, when it is free from all other disturbance and emits its spectrum, lies in or about the visible spectrum; we therefore expect that the frequencies associated with the more firmly bound electrons, which are left in the ion when these electrons are detached, will lie on the high frequency side of the visible spectrum; we shall expect the absorption bands of metallic ions to lie in the ultraviolet and to produce no coloration. And in general that is what we find. The peculiarity of the anomalous elements that we are considering is that the difference between the binding energies of the electrons in the group of highest n, which are removed in ionisation, and those in the next lowest group is very small, so that when the least firmly bound electrons have been detached, there are still left others of which the binding energy is not much less and with which are associated frequencies in the same region of the spectrum. (We see here also a reason for the association of colora-

[1] It is quite probable that the atoms as well as the ions of these elements possess the properties in question, but since it seems that we never obtain atoms, as distinct from ions, in a condition sufficiently free from external influence to investigate their properties of this kind, experimental evidence is lacking. See Section III.

tion with 'variable valency'; but all matters of valency are purposely postponed for the present.) This difference between the normal and anomalous elements falls in well with our general ideas and with the evidence from X-ray spectra; for we know that in the region of development of these elements, the last bound electron is hesitating, as it were, whether to enter the exterior group and so follow the normal sequence, or the interior group, and so interrupt it; we expect then that the binding energies associated with the two alternatives are not very different.

Paramagnetism is much more interesting. The method by which the magnetic moment of a paramagnetic molecule is determined is sketched in Ch. V, and the formula applicable to experiment is there given in eq. (152), p. 128, which may be written

$$M^2 = \frac{3k'RT}{N_0^2} \quad \text{.....(117.1),}$$

where k' is the magnetic susceptibility of the substance, M is the magnetic moment of the molecule, N_0 the number of molecules in a gram-molecule, R the gas constant for a gram-molecule, and T the absolute temperature. (117.1), which represents Curie's law that the magnetic susceptibility is inversely proportional to the absolute temperature, is known not to be true, especially at low temperatures. According to general quantum theory, it should not be true; for its deduction implies the equipartition of energy, which quantum theory denies. The formula should be corrected according to the ideas which are described briefly in Ch. X, pp. 241–244, and will form the subject of a later chapter. But for many substances a range of temperature can be found over which Curie's law is nearly true, and within this range (117.1) may be used to determine the magnetic moment of a single molecule. It was also explained in Ch. V, p. 128, that Weiss, by the application of this formula to ferromagnetic substances, arrived at the conclusion that the magnetic moment of a molecule was always an integral multiple of a certain fundamental value, which he called a 'magneton'. The value originally given to the magneton has been subsequently corrected to $18{\cdot}54 \times 10^{-52}$ c.g.s. e.m.u. Later work on the salts of the elements of the iron group (*i.e.* Cr (24), Mn (25), Fe (26), Co (27), Ni (28), Cu (29)) seems to have shown that the idea of the magneton is

applicable to them, and that the magnetic moments of these molecules are also multiples of the fundamental unit; but the evidence is not quite conclusive, and some workers in this field reject the magneton as devoid of experimental significance. But whether the magneton exists or not it is certain that in salts of these metals, or at least those in which the metal is present in the ionic form, the magnetic moment is a true atomic property of the metal, being the same whatever the anion. The metals themselves in the uncompounded state fall outside the scheme; those that are magnetic at all are ferromagnetic, displaying the hysteresis characteristic of iron. Here the element is not present in the ionic form or, if it is, the properties of the individual ions are altogether concealed by actions depending on their mutual influence.

The elements of other anomalous groups have been studied far less completely, and apparently the magnetic moments of the ions are not known. But it is known that the palladium, platinum, and rare earth groups are all paramagnetic in the ionic form, some of the rare earth ions being more highly paramagnetic than those of any other element. (Once more, this statement does not mean that the pure elements are more ferromagnetic than iron; they are not.) All this is as it should be, for the rare earths show the anomaly that we are considering in the most marked degree.

But how is our theory to explain the relation of paramagnetism to the periodic anomaly and to the development of interior electronic groups? Until recently the idea still prevailed that a magnetic molecule must owe its peculiar property to Amperean molecular circuits in which permanent currents flow; further these circuits, since the advent of electronic theory, were naturally identified with electronic orbits. With the advent of Bohr's quantum orbits, the theory seemed to receive some support; for an obvious way of explaining the magneton suggested itself. According to Bohr one form of quantum orbit consisted of an electron revolving in a circular orbit with angular momentum $nh/2\pi$. Such an orbit (see Ch. V, p. 122, eqn. (141)) would have a magnetic moment $\frac{n}{2}\frac{\epsilon}{\mu}\frac{h}{2\pi}$, always an integral multiple of a fundamental unit; a magneton might simply be an electron revolving in a quantum orbit.

But there are difficulties. Firstly, the fundamental unit $\frac{1}{2}\frac{\epsilon}{\mu}\frac{h}{2\pi}$

has the numerical value $92{\cdot}2 \times 10^{-22}$, which is about 5 times as great as the experimental unit $18{\cdot}54 \times 10^{-22}$. Secondly, when elliptical orbits, as well as circular, had to be recognised, it was observed that the magnetic moments of these orbits would not be all multiples of a single unit. Thirdly, according to any theory which attributes molecular magnetism to electronic orbits, when a magnetic moment I is induced in a body and the orbits of the revolving electrons orientated in the field, an angular momentum $2\frac{\mu}{e}I$ should be communicated to the body. Such a mechanical action due to magnetisation has been detected experimentally (it is usually called the Einstein-Haas effect, but Richardson had studied it previously), but it is always found to be less than theory predicts; the angular momentum is more nearly $\frac{\mu}{e}I$. Lastly, there is a yet more serious and deeper-seated objection, which has made the identification of Amperean circuits with electronic orbits increasingly difficult to reconcile with any theory of the structure of the atom similar to that considered here. For if there are electronic orbits in all atoms, all atoms should be paramagnetic. The absence of paramagnetism can only be due to a mutual compensation of the magnetic moments of the different orbits, so that the atom as a whole has no magnetic moment. But such a compensation is very difficult to conceive. It is almost impossible in the hydrogen atom which has only one electron—but perhaps it might be urged that we know only hydrogen molecules and not atoms in magnetic measurement. It is almost impossible in the helium atom which has only two orbits; we should have to conceive of the orbits as coplanar and probably similar, an assumption directly contradicted by the evidence we have considered. Moreover, even if compensation was attained in the absence of a magnetic field, it would be expected that in the presence of a field the compensating orbits would move relatively to each other and the structure of the atom be changed; nothing of the kind is observed. So serious had this difficulty become that it was urged as a fatal objection to all theories of atomic structure which involved revolving electrons and adduced as a support for theories, to be mentioned in the next section, in which all the electrons are at rest, or even for theories

in which the ultimate magnetic element was placed within the electron, independent of its motion.

Bohr has once more cut the knot in his own inimitable manner. He simply denies that an electron revolving in a quantum orbit has any magnetic moment at all. And his denial is utterly reasonable. An electron in such an orbit does not radiate, as it should according to classical electrodynamics; the radiation predicted by the classical theory is closely associated with the supposed magnetic field. If we throw over that theory so far as to deny that the electron radiates, what possible ground have we for maintaining in the face of all evidence that it has a magnetic moment? Once more it may be insisted that we must be whole-hearted in this matter. If we are hidebound by tradition, let us by all means stick to Amperean and Maxwellian theory, reject as a pernicious heresy, unsanctioned by the Fathers of the Church, all modern theory of radiation, all modern theory of spectra; let us retire as hermits to the desert of ignorance and refuse to have any dealings with the wicked, bustling world of modern science. If, on the other hand, we believe that progress in science is not impossible, and that the age of discovery did not end abruptly in 1870, let us be confident in our beliefs, and attribute to genius in our own time an authority no less and no greater than that of our intellectual forbears.

But, it may be asked, if in this matter we abandon the traditional view, what is there to put in its place? The theory that we have been considering gives the answer. Paramagnetism appears when a certain kind of instability, probably associated with spatial asymmetry, appears among the electronic orbits, forming a group with the same total quantum number, and renders possible the addition of members to sub-groups which were already complete. Why paramagnetism should be associated with such instability is a question at present as unanswerable as the question why homogeneous radiation should be associated with a transition between quantum orbits. When the reconstruction of classical electrodynamics and mechanics as statistical illustrations of quantum principles has proceeded far enough to answer one question, it will probably also answer the other. For the time being we must accept one proposition as we accept the other, as a fundamental

principle of our science. The cases are precisely analogous. We know that, when the conditions are such that classical rather than quantum theory holds, moving electric charges radiate and give rise to magnetic fields; we know that when quantum theory holds and classical theory is inapplicable, they neither radiate nor give rise to magnetic fields. And there we must leave the matter.

However there is some experimental evidence very definitely in favour of Bohr's idea. According to the principle of the permanence of orbits, the general nature of the orbits round a nucleus, and in particular the number of orbits in each group and sub-group, is determined by the number of electrons present rather than by the nuclear charge; whether the nuclear charge is Z or $Z+1$, the first

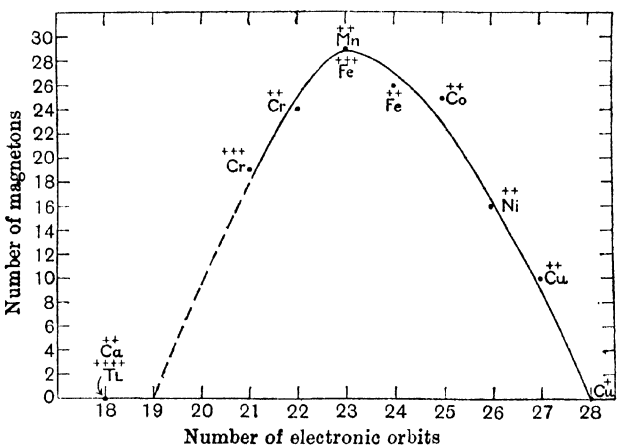


Fig. 6.

Z electrons will be in orbits of the same kind, except in those very exceptional cases where the development of a new sub-group of a temporarily completed group is just beginning. If then paramagnetism depends on the arrangement of the electronic orbits and their spatial relations to each other, it should be the same in atoms with the same number of electrons but different nuclear charges; it should be the same, for example, in an atom of nuclear charge Z, which has formed a doubly charged ion and therefore possesses $Z-2$ remaining electrons, and in an atom of atomic number $Z-1$, which has formed a singly charged ion and therefore also has $Z-2$ remaining electrons. Fig. 6 shows how completely

this expectation is fulfilled. In it the magnetic moments of the ions of the iron group, expressed for convenience as multiples of the magneton, are plotted against the number of extra-nuclear electrons in those ions. It will be seen that the points lie very closely to a smooth curve, and that in one case two points representing different elements coincide; the ferric ion, Fe^{+++}, is the same magnetically as the manganous ion, Mn^{++}, both having 23 electrons. (It is probable that the Co^{+++} ion agrees similarly with the Fe^{++} ion (24 electrons), and Mn^{+++} with Cr^{++} (22 electrons); but since the experimental evidence is not conclusive here, one of these pairs of points is omitted.) Now that attention has been drawn to the matter, further experimental evidence in this and other groups is sure to be forthcoming, and the prediction that the paramagnetic moment is simply a function of the number of electrons definitely confirmed or rejected. If it is confirmed we may hope also to learn by comparison of the different groups of anomalous elements what exactly is the feature of the orbits which gives rise to paramagnetism and why the curve of Fig. 6 has exactly that shape.

SECTION II

THE COMBINATION OF ATOMS

24. Evidence for an atomic theory. Hitherto we have regarded atoms as isolated systems. But we do not often observe an atom completely isolated from all others. Most of the experiments on which our conclusions have been based are made on collections of atoms—'matter' in one of its three classical states—in which we are certain that atoms exert a mutual influence; and our conclusions are justified only in so far as we have reason to believe that the properties of atoms that we have studied would remain unchanged, even if the atoms on which we have made our observations were separated to an infinite distance from each other. To have such reason we must clearly study atoms in combination; both practically and theoretically the most important and the most fundamental properties of atoms are those which they display when they act on each other, and our procedure, though convenient in a book which assumes a knowledge of elementary scientific conceptions, would have been absurd if we had set ourselves the task of developing in a completely logical (and therefore misleading) order the modern doctrine of the atom for the benefit of those who have no previous knowledge of science.

For of course we started on our inquiry in the confident belief that the atomic theory of matter is substantially true and that there are such things as atoms; we have taken for granted all the proofs of that doctrine, now so interwoven into all physical and chemical science that, if these were destroyed, the whole fabric would fall to pieces. When we say that there are atoms or that the atomic theory is true, we mean that there are particles which retain their individuality through all the manifold changes that material bodies undergo, through physical changes—changes of state, electrification, magnetisation and so on—and through the yet more striking changes of chemical compounding. And if they retain their individuality through these changes it is natural to suppose that they would retain them when completely isolated,

and that our procedure, in seeking first to determine these properties in isolation and, from those properties, seeking to explain their properties in combination, is not without justification.

But when a theory is so completely imbedded in our science that doubt is no longer possible, it is always interesting and often profitable to glance back at the state of knowledge in which that theory first arose. We usually find that the evidence on which it was originally based appears ridiculously insufficient; we often find also that it preserves from the embryonic state vestigial relics which play no useful part in full development. That is true, I think, of atomic theory as of most others. If we cast our minds back to the year 1800, or indeed to a very much later date at which some of us, who have no claim to the respectability of age, learnt our elementary chemistry, and if we ask what evidence we had then for asserting that common salt is in any sense composed of sodium and chlorine, we have to admit that the firm structure of our belief had a curiously shallow foundation. For of the properties of sodium and chlorine which we knew then, how many are preserved in sodium chloride? Two and two only, mass and the closely related weight. Some others, such as density, are partially preserved; but the great majority are not preserved at all. Most of the 'periodic' properties are not atomic; it can only be an historical accident that Mendeleef and Dalton do not stand side by side with Newton and Huyghens as the protagonists of mutually irreconcilable theories. Even today we cannot add many to the list. Radioactivity is truly atomic, though very limited, and so must be other nuclear properties; but of these the scattering of α rays alone is open to close investigation. X-ray spectra are very nearly truly atomic, but we have seen that some small reservations must be made; the scattering and absorption of X- and β-rays are less nearly so. And that is about all; the remainder, even if they are partially atomic, are characteristically periodic and are closely associated with typical non-atomic properties.

Now the theory of the atom that we have been developing is curiously unatomic. The conception of atoms as hard elastic spheres has vanished long ago, if indeed it was ever regarded as providing anything but a loose analogy for the elucidation of some of the simpler facts. But the first electronic theories retained something

that was definitely 'the atom'. Thomson's positive sphere was still something comparatively solid and tangible that might lose or gain electrons contained in it and yet retain its individuality. But our atom is a mere cloud of electrons; the nucleus, it is true, is individual, but its function, in almost all the properties we consider, is merely to act as a centre for the cloud. If we were asked, without previous knowledge, what we expected to happen when two such clouds approached each other, we might reasonably answer that they would regroup themselves about the two nuclei in a new manner that need not necessarily preserve any of the salient features of the old. It would strike us, I think, as a surprising rather than a natural discovery that such an answer should be untrue, and that some of the salient features are preserved with only very slight alterations. We know that the orbits which determine the part of the X-ray spectra which is easily accessible to observations are almost unchanged; but while we know that the orbits of low quantum number in atoms of relatively high atomic number are unchanged, optical spectra tell us equally clearly that the orbits of highest n are very profoundly changed. The actions that we are about to consider are determined very largely by these orbits, and in so far as they are concerned, the atomic theory cannot really be true; atoms cannot retain completely their individuality when they enter into mutual action. It is therefore important to realise that there is not, and never has been, any evidence that they do completely retain it. If we find that the view of atomic combination that we are forced to take is rather different from that of the founders of the atomic theory, we must regard that, not as proof of the inadequacy of our theory, but rather of a natural consequence of it. All that we must demand of our theory is that it provides an explanation as good as that which we reject, or at least allows the possibility of such an explanation.

25. **The forms of chemical combination.** In any theory of the mutual actions or the combination of atoms, chemical combination is sure to play an important part; it will be well to plunge directly into the central depths of our problem. How far can the theory that has been developed in the last section explain the facts of chemistry?

Those facts are summarised in the three general laws of constant, reciprocal and multiple proportions and in a vast multitude of particular laws which assign to the various elements the part that they play in phenomena regulated by those general laws. Any theory of chemistry must explain why the general laws are true and why certain compounds obeying those laws are formed, while others are not. The solution of this problem offered by the chemistry of the 19th century was based on the conception of 'valency bonds[1]'. It was supposed that to each atom could be assigned a certain number of bonds, the number of which was its valency; and that atoms could combine to form a molecule if, and only if, their valencies were such that each bond of one atom could be cancelled against one, and only one, bond of another. But it has long been recognised that such a theory is incomplete. If every atom has a fixed valency, the same in all its combinations, then the theory cannot possibly cover all the facts. It covers almost completely a very important range of facts, namely those of organic chemistry; if a few aberrant compounds that are not usually regarded as organic (*e.g.* CO) are excluded, all the compounds of carbon can be interpreted in terms of a set of fixed valencies assigned to carbon and to each of the other elements with which it enters into combination. The success of the theory of valency in this field, which has such a special attraction for chemists, is doubtless one of the main reasons why the modifications of it, which are clearly necessary, have received so little attention in the commoner text-books. But carbon is not the only element, and outside organic chemistry a fixed valency is impossible to reconcile with the facts. On the other hand if valency is variable, the theory can explain anything, facts which are not facts as well as those which are; a system of bonds can be devised to suit any molecule whatever so long as we are under no compulsion to reproduce in another compound the number of bonds

[1] Some writers seem to distinguish between the theory of valency and the theory of bonds. I have never been able to grasp how there can be a theory of valency which involves no bonds; the writers who make this distinction never succeed in making me understand what their theory of valency is. I should add here that I am conscious of my temerity in venturing with a mere smattering of chemistry on such sweeping statements and criticisms as are offered here. But fortunately, since this section comes last, no chemist is likely to penetrate so far.

assigned to each element. The theory of variable valency is reasonable, only if some rule for the limitations for the variability can be devised which are tolerably simple and plausible.

Considerable progress has been made in devising such a rule. Thus variable valency is manifested especially in particular parts of the periodic table. Again there is Abegg's important distinction between 'valency' and 'contravalency'; roughly his rule is that elements on the right of the table have a contravalency as well as a valency, the sum of the valency and the maximum contravalency being 8: thus chlorine has a valency of 1 and a maximum contravalency of 7. And there is Werner's notion of a 'coordination number', designed to explain complex salts, which determines the maximum number of atoms, independent of their valency, with which any other atom can enter into combination; this number is usually 6. By such developments most known compounds can be brought within the range of a generalised theory of valency; though the converse problem of explaining why some compounds, which appear to be consistent with the theory, are not formed is much less completely solved.

All these ideas will require our attention, for they undoubtedly have some validity. On the other hand it is important to realise that the older theory of valency is not so definitely established that any structure that may be suggested for the atom has to satisfy its requirements. A few years ago it would probably have been held that the typical cases of chemical combination were those in which the simplest form of that theory was directly applicable; that it was the business of any theory of the atom to give a straightforward account of that simplest form; and that the facts not fully in accordance with that form were to be regarded as minor exceptions, the full explanation of which could only be expected from a complete and final knowledge of the interior of the atom. But today it is possible to take a precisely contrary view, and to hold that it is the valency compounds that are exceptional, the variants being the normal type. That view has been strongly urged by several of the most eminent representatives of modern chemistry, by Kossel who has played a large part in developing all the ideas presented in this section, and by Lewis to whom is due one of the most purely 'chemical' of atomic theories. Both of these writers, totally

independent of each other but closely allied in their conclusions, insist on two conceptions which are utterly at variance with traditional chemistry.

The first of these is the essential similarity of 'chemical' and 'physical' forces. The theory of valency—unless it is so far developed that it loses all traces of its origin—must deny this identity; the forces which bind together chemically the atoms in a molecule must be different in kind from the physical forces which bind molecules together. For physical combination is not characterised by any of the distinctive laws of chemistry; there is neither constant, reciprocal nor multiple proportions between the masses of the bodies entering into physical combination.

The second is the distinction between polar (or 'heteropolar') and non-polar (or 'homopolar') compounds; of the former KCl may be taken as typical, of the latter CH_4. It is not easy to make an accurate distinction between the two classes on experimental grounds. All compounds that are electrolytes in the liquid form are polar, but the oxides of the true metals are polar, though they are not electrolytes. Again polar compounds are generally formed from elements remote in the periodic table, non-polar from near neighbours; but this criterion can only be applied to binary compounds. Polar compounds can also be recognised by their readiness to enter into chemical reactions (which is not the same thing as chemical instability), and by their physical stability, indicated by high melting and boiling points. The division between the two classes is really drawn on theoretical grounds, guidance being derived from similarity to typical members; but since we shall only be concerned with general principles, we can confine ourselves to these typical members; the minutiae of the distinction will not concern us. It should be observed that the same compound can be in different portions typically polar and typically non-polar; thus K_2SO_4 is non-polar in the combination of the $-SO_4$, polar in the combination of this part with the metal. This division of compounds into two classes is again inconsistent with the older conceptions of valency, which aspired to interpret in the same sense all combination satisfying the fundamental chemical laws. The division is not that between compounds which display simple valency and those which do not; for though most of the discrepant features that we have

noticed are characteristic of polar rather than of non-polar compounds, some typically non-polar compounds (*e.g.* CO or NO) offer serious stumbling-blocks to any theory of valency.

26. **Polar compounds.** Now let us regard the matter from another point of view and inquire in what manner atoms may be expected to enter into combination if they are constructed in accordance with our theory.

A simple explanation of one form of chemical combination, which is now seen to be that characteristic of polar compounds, was one of the most attractive features of the earliest electronic theories of the atom. Berzelius had long ago suggested that the chemical forces binding the atoms together were electrical, and such theories showed how the necessary electrical forces could arise. It was known that the alkali metals and other electropositive elements lose electrons easily in some circumstances, and it was suspected (it is known now) that electronegative elements tend to take them up; the former process is apparent in the photoelectric effect, the latter in the formation of negative ions in ionised gases. What more simple than to suppose that, when sodium and chlorine are brought into contact, each sodium atom gives an electron to a chlorine atom, leaving the atoms charged with opposite signs and ready to adhere by electrostatic attraction? If the electrons so transferred, the 'valency electrons', are those concerned in the emission of spectra, in the conductivity of metals and in other periodic properties, the great change in these properties consequent on chemical combination is explained at once.

But there are some difficulties. The first and not the least serious, although it did not originally receive much attention, arises from the existence of atoms that are permanently multivalent. If the chemical combination of calcium, for example, is due to a loss of electrons, the familiar arguments of elementary chemistry would show that it must always lose two electrons and never one; similarly oxygen must always take up two and never one. Nothing of this kind is found when such atoms lose or gain electrons in other circumstances; there is then no sign of more than one 'valency electron'. The loss of two electrons in ionisation by charged particles or other rays is a very rare event, and even when it occurs

it is certain that the second electron is more difficult to detach than the first; similarly when atoms take up electrons to form gaseous ions, it is very rare that they should take up more than one. Further it is remarkable that the atoms which are required by the theory to lose many electrons are those which less easily lose electrons at all; thus potassium loses electrons more easily than calcium, but in chemical combination it only loses one while calcium loses two; how can a reaction with a chlorine atom which causes a potassium atom to part with only one electron cause a calcium atom to part with two? We shall return to this question later.

The second difficulty is that mere electrostatic attraction seems quite unable to account for the formation of molecules containing definite and constant numbers of atoms. Let us grant that by the interaction of potassium and chlorine atoms all the former acquire a single positive charge, all the latter a single negative charge; there is still no reason to believe that each negative atom will combine with one positive and leave the remainder unaffected. Unless the opposite charges can coincide and so neutralise each other completely, the union of a positive and negative charge will form an electrical doublet, which will still have a positive end attracting negatives and a negative end attracting positives. We might well expect, as has been insisted already, that the atoms could interpenetrate each other and lose their identity; and if that happened, a complex of two oppositely charged atoms, exerting no appreciable external electrostatic force might be formed. But such an hypothesis, fatal to atomic theory even if favourable to molecular theory, is contradicted by the preservation of X-ray spectra. If the oppositely charged atoms retain their identity, we cannot explain the formation of molecular pairs independent of each other; we should expect according to the principles of electrostatics that all the atoms would agglomerate into a single swarm, just as do a collection of magnets if brought into sufficiently close proximity. How are we to reconcile this theory with the formation of molecules which is the basis of chemical theory?

Today the answer is simple. We do not reconcile it: we reject molecular theory applied to polar compounds (with certain exceptions); they do not form chemical molecules. And this step is not so very startling, for the molecular theory has long been abandoned

(except by a few fanatics) as applied to polar compounds in the liquid state. Such compounds are always electrolytes, and unless we deny that the current in such bodies is conveyed by the motion of charged atoms (which may or may not be attached to other systems bearing no resultant charge) we cannot possibly conceive of each atom being permanently attached to another; things are not attached if they can be separated without the expenditure of energy to an infinite distance. If independent polar molecules exist at all it can only be in the gaseous or solid state. Now the only gaseous polar compounds we know anything about contain hydrogen as one part of the compound; all those in which it is not present are volatile only at very high temperatures, and there is more than a suspicion that they are then largely 'dissociated'. Now hydrogen polar compounds are peculiar because the positive hydrogen ion is not an 'atom' at all; it is a mere nucleus without attached electrons; such a nucleus, bearing only a single electronic charge, may be so completely merged in another atom that the combination exerts very little external force. Even if it is proved—and the experimental evidence is by no means strong—that in the gaseous state polar hydrogen compounds form molecules as permanent and as distinct as those of non-polar compounds, there is still no evidence that other polar compounds also form such molecules, and no objection therefore to the view that the 'chemical force' in such compounds is the electrostatic attraction between atoms bearing resultant charges of opposite sign.

In the solid state our information is much more satisfactory. We know with perfect definiteness that in solid polar compounds (which are always and necessarily crystalline) there are no chemical molecules at all. Our knowledge is derived, of course, from the analysis of crystal structure by means of X-rays. It is quite certain that in NaCl (*e.g.*) each sodium ion is equally spaced from and equally related to 6 chlorine ions and each chlorine atom is equally related to 6 sodium ions. There is no sign whatever of a special relation between one sodium atom and one chlorine atom; the whole crystal is one big molecule and no smaller portion of it is individually complete[1]. So far from there being a difficulty in

[1] A curious point which often puzzles those who come fresh to the subject may be mentioned here. If we take what crystallographers regard as a 'unit cell' of the

reconciling the electrostatic theory of polar combination with the structure of solids, that structure is precisely what the theory suggests. The general laws of chemical combination tell us here nothing whatever about the relations of individual atoms. They are due to two features, one belonging to the individual atoms and independent of their combination, the other belonging to the whole crystal. The first feature is that the charge which an atom acquires in forming a polar compound is independent of the element with which it combines. The second that the crystal as a whole is very nearly electrically neutral; and it must be electrically neutral because, if there were any appreciable preponderance of ions of one sign, even though it amounted only to one in a million, the total charge and the resultant electrostatic forces would be so great as to make it impossible to preserve or observe such a system experimentally.

If this view is correct, the distinction between chemical and physical forces in polar compounds vanishes entirely. Chemical combination and cohesion are not merely due to forces of the same nature; they are the very same thing; and any theory which will account completely for one should account equally for the other. In recent years great progress has been made towards such a theory, chiefly by Born, Landé and Madelung. The problem to be solved may be stated thus. We are presented with a collection of oppositely charged ions, bearing positive and negative electronic charges, the numbers of the two kinds present in the collection being such that the total charge is zero. We have to determine what arrangement these particles will take up under the influence of electrostatic forces; what energy will be liberated as they assume that arrangement starting from infinite dispersion (this energy will be that of chemical combination); and what will be the forces opposing distortion of the arrangement (these forces will represent the

crystal lattice, the number of atoms of each kind in it is never representative of the crystal as a whole. Thus in the unit cell of NaCl as usually described there are either 14 sodium atoms and 13 chlorine, or 14 chlorine and 13 sodium. How then can the crystal be built up of these unit cells? The answer is that no finite crystal can be really complete; a perfect lattice structure must imply infinite extension. A finite crystal, such as we actually examine, must be incomplete and distorted near the boundaries; and this distortion must affect, with an ever increasing degree of minuteness, the interior layers. In the boundary layer where the lattice structure is distorted and incomplete there may well be arrangements more nearly representing the chemical molecule.

mechanical properties of the system). But before we proceed it is well to ask whether any direct evidence can be adduced for the fundamental assumption that the points of the crystal lattice are ions and not atoms. X-ray analysis on the lines indicated on p. 57 could decide the matter by determining how many electrons are associated with each atom, if the theory of X-ray reflection were sufficiently complete. An attempt has been made to settle the question in this direct manner by inquiring whether, in LiF, the points are Li (3) and F (9) or Li (2) and F (10). The evidence favours the second alternative but is not conclusive.

At the outset of our inquiry we are met with a difficulty that has been mentioned in another connection. If the forces are purely electrostatic no arrangement that the particles can assume will be statically stable, except that in which the particles coincide and neutralise each other's charges completely. The fact that they do not coincide and that the final system has a finite volume indicates that the forces are not purely electrostatic; that, when the atoms approach sufficiently closely, forces not varying as the inverse square come into play; or, in other words, that the atoms have a finite volume. But it is profitable to start by leaving stability out of consideration and to inquire what arrangements of infinitely small particles would be in equilibrium even though this equilibrium may be unstable. It is found, as might be expected, that an infinite number of arrangements is possible; to decide which of these we are to discuss, further evidence has to be drawn from the known facts of crystal structure as elucidated by X-ray analysis. We know, for example, that both the sodium and chlorine atoms in a crystal of sodium chloride are arranged in a face-centred cubic lattice; it appears that such an arrangement is in equilibrium, although not stable, if the forces are electrostatic; we may proceed to inquire into the properties of such an arrangement.

Let δ_0 be the length of the side of the elementary cube, which represents a complete crystallographic unit of NaCl. This cube contains effectively four ions of each sign or four chemical 'molecules'; δ_0 is the distance parallel to the cubic axis of successive similar ions. Very simple considerations will show that if such an elementary cube is supposed to form part of an infinitely extended repetition of the same arrangement, Φ_0, its potential energy or the

work required to disperse completely its component particles, is given by

$$\Phi_0 = \frac{a(p\epsilon)^2}{\delta_0} \quad \text{.....(134.1),}$$

where $p\epsilon$ is the charge on the ions. But the calculation of a is a very complicated matter. Madelung arrives at the value $a = 13{\cdot}94$. (134.1) with this value of a applies to all crystals with similar lattices. In particular it applies to all the alkaline halides which differ only in δ_0; to them we shall apply it particularly, but it would also apply to crystals such as ZnS, for which $p = 2$. But if the opposite charges on the ions are not equal, a different a is required, for the lattice is not strictly similar; thus for CaF_2, if p is put equal to 1, $a = 38{\cdot}655$.

There must now be taken into account the forces, not purely electrostatic, which must be operative if the arrangement is to be stable. Born and Landé propose to represent these forces by an additional term in (134.1), and write

$$\Phi = (p\epsilon)^2 \left\{\frac{a}{\delta} - \frac{b}{\delta^n}\right\} \quad \text{.....(134.2),}$$

where n has to be determined experimentally. Since the arrangement characterised by (134.2) is supposed to be stable if disturbed and, in particular, if the whole lattice is expanded we must have, when $\delta = \delta_0$,

$$\frac{d\Phi}{d\delta} = (p\epsilon)^2 \left\{-\frac{a}{\delta^2} + \frac{nb}{\delta^{n+1}}\right\} = 0 \quad \text{.....(134.3),}$$

or

$$\Phi_0 = \frac{a(p\epsilon)^2}{\delta_0} \cdot \frac{n-1}{n} \quad \text{.....(134.4).}$$

The value of n Born and Landé propose to determine from the compressibility of the crystal which has been carefully determined by Richards, who has long maintained that there must be an intimate connection between this and chemical properties. If $\Delta = \delta^3$ is the volume of the elementary cube, the pressure p opposing a change of volume must be given by

$$p = -\frac{d\Phi}{d\Delta} \quad \text{.....(134.5).}$$

On the other hand the compressibility is given by

$$K = -\frac{1}{\Delta}\cdot\frac{d\Delta}{dp} \quad \text{.....(135.1),}$$

so that

$$\left(\Delta\frac{d^2\Phi}{d\Delta^2}\right)_{\delta=\delta_0} = \frac{a(n-1)}{9\delta_0^4} \quad \text{.....(135.2).}$$

Since the cube of edge δ_0 contains four ions of either sign and of masses m_+ and m_-, we have, if ρ is the density and N_0 the number of molecules in one gram-molecule ($6{\cdot}2\times10^{23}$),

$$\delta_0 = 1{\cdot}86\times10^{-8}\left(\frac{m_+ + m_-}{\rho}\right)^{\frac{1}{3}} \quad \text{.....(135.3),}$$

$$n = 1 + 4{\cdot}75\times10^{-12}\cdot\frac{1}{a}\cdot\frac{1}{K}\cdot\left(\frac{m_+ + m_-}{\rho}\right)^{\frac{4}{3}} \quad \text{.....(135.4).}$$

If the calculated value of a is taken, n can be determined by (135.4) from the compressibility, density and ionic weight. The following are typical results given by Born and Landé:

Compound	NaCl	NaBr	NaI	KCl	KBr	KI
n	7·75	8·41	8·33	9·62	9·56	9·10.

From such results Born and Landé at first drew the conclusion that $n = 9$ for all the alkaline and alkaline earth halides, with the exception of those containing lithium, for which $n = 5$; they attributed divergences to errors of experiment. It now appears certain that this conclusion is not perfectly correct, and that n estimated in this manner is not constant and is not necessarily an integer. This is not surprising; for there is no reason to believe that it is possible to represent the departure of the field surrounding an ion from that surrounding a point charge by a single term varying as an integral negative power of the distance; (134.2) must be regarded as a mere approximation. Nevertheless it must be a good approximation; and from the constancy of n for different compounds, it is legitimate to derive support for the theory that the compressibility (which determines many other mechanical properties) can be accounted for by the electric field surrounding the ions arranged in the crystal lattice. The first part of our problem is solved, and it remains to be determined whether we can account for the 'chemical' forces between the atoms by means of the same field.

For this purpose we return to (134.4), using the value $n = 5$ for lithium compounds and $n = 9$ for the remainder of those we consider. Φ as given there refers to the elementary cube; to obtain U, the work required to disperse completely a gram-molecule of the compound, we have to write $U = \frac{1}{4} N_0 \Phi$. If the chemical and physical forces are identical, U should be the heat of formation of the compound from its ions. The heat of formation of a gram-molecule Q, estimated by thermochemical methods, is that evolved in the formation of the compound from its neutral atoms in the solid state; the difference between U and Q should represent (1) the work required to vaporise the solids, D_+ and D_-, and (2) the work required to ionise the atoms I_+ and I_-, the suffixes referring to the positive and negative ions. We thus have

$$U = Q + D_+ + D_- + I_+ + I_- \quad \text{.....(136.1).}$$

D_+ and D_- can be estimated from the vapour pressures of the elements; they are small compared with I_+ and I_-. I_+ can be determined from the ionisation potential, which can be measured conveniently by means of the largest term in the optical spectrum; but I_- is not so easily measured. For the spectra of the halogens have not been resolved into terms, while direct measurements by the impact of electrons give only the energy required to ionise the molecule; this differs from the energy required to ionise the atom by the unknown energy required to dissociate the molecule. Accordingly in order to compare our theory with experiment it is necessary to consider the differences between compounds containing the same positive but different negative ions; the values so obtained are shown in the following table, where the second column gives $\Delta(U - Q)$, the difference between $(U - Q)$ for the pair of elements shown in the first column, this difference being usually a mean of several concordant values derived from their compounds with the various halogens; the third column gives $\Delta(D_+ + I_+)$, the corresponding difference between $(D_+ + I_+)$. There is a general agreement which is quite as good as can be expected in view of the uncertainty of some of the experimental data and known inadequacy of the approximation represented by the second term in (134.2). In fact the agreement is very striking when it is realised how various is the material from which the values are derived; U involves the

density, compressibility and molecular weight, D the vapour pressure, I the spectrum and Q the thermochemical heat of formation. A theory which correlates all these varying data is obviously near the truth.

TABLE VIII

Elements	$\Delta(U-Q)$	$\Delta(D_+ + I_+)$
Li – K	+28	+24
Na – K	+24	+18
Rb – K	−19	− 4
Cs – K	−11	−13

Fajans has obtained even better agreement between chemical data and those derived by means of the Born and Landé theory from physical properties; he uses for the former the heats of solution which are well known and avoid the uncertainty of D in the earlier comparison. But his results need not be set out in detail; the conclusion which they support is already sufficiently established.

The 'dynamics of the crystal lattice', studied from the point of view we have been considering, has now a very considerable literature. Two chief aims are kept in view; first, to determine as many properties of simple lattices as possible from the known arrangement of the ions bearing known charges, and in particular all the mechanical and thermal properties which are so closely associated; second, to extend the theory to more complicated lattices which we have left wholly out of account, and in particular to calculate in terms of the ionic charges the quantity or quantities corresponding to α. But though this is directly relevant to our inquiry concerning how atoms combine, it does not lead us to further knowledge of the structure of the atom or to bridging the gulf between the theories of chemistry and physics; accordingly we may leave these matters for a future discussion. On the other hand the general ideas underlying the study suggest a simple explanation of some serious difficulties that have beset all chemical theories, namely the formation of complex salts, which cannot be fitted in with the conception of valency bonds. Most of these represent a further combination of molecules which, according to

that conception, should be already complete with all the bonds satisfied. For, if the formation of a polar 'compound' requires nothing more than that the sum of all the charges on the combining ions should be zero, it is clear that any two compounds in which that condition is fulfilled should be able to combine with each other to form a more complicated compound. Thus suppose that KCl and $PtCl_4$ are both polar compounds (the supposition is probably untrue for the second of these); the ions of which each of them is composed will then be able to arrange themselves in a crystal lattice in the solid state. But if the ions of the two salts are mingled together they may once more be able to arrange themselves in a more complicated lattice; and if they can, then, since the lattice arrangement must be regular, there will be some fixed proportion between the amounts of the two simple salts occurring in the complex lattice. In this particular case, it appears that the new arrangement is possible when there are equal amounts of the two simple salts, and the compound K_2PtCl_6 is formed; but in any case the law of constant proportions, which is often regarded as the test of a 'chemical' compound, will be obeyed. When the lattice is broken up once more, the disintegration need not be complete, nor need it follow the original lines of division; it is possible that the K-ions are separated from the remainder, leaving the $PtCl_6$ as a negative ion united by non-polar combination.

How far this view of the matter is correct for complex salts of this type is still uncertain, but it is doubtless right when applied to water of crystallisation. When a crystal such as $Na_2SO_4.10H_2O$ is formed, the ions of the sulphate and the ions of the water have rearranged themselves on some crystal lattice more complicated than that of either the anhydrous salt or of ice[1]. In such cases the 'compound' is formed only in the solid state, and is inseparable from the crystalline form. A further step in the same direction, leading us away from chemical combination to mere physical mixture, is represented by mixed crystals, which are often formed in all proportions by isomorphous salts. Here Vegard has shown

[1] The absence of a correspondingly hydrated crystal of the other alkaline sulphates is doubtless due to the fact that in these very complicated crystal lattices the possibility of a given arrangement is largely determined by the relative sizes of the ions. The size of the sodium ion happens to be such that a regular arrangement is possible; it ceases to be possible if that size is slightly altered.

by X-ray analysis that in the mixed crystal the two simple compounds are definitely entangled in the same lattice; thus in a mixed crystal of KBr and KCl, the chlorine and bromine ions occur indifferently at corresponding points of the lattice, the whole structure being slightly distorted, owing to the difference in volume of the two anions, and different from that characteristic of either of the simple salts.

27. **Non-polar combination.** We conclude then that, if chemical combination involves the formation of molecules of fixed size, there is no such thing as polar chemical combination. The formation of aggregates obeying the law of constant proportions is due to the production of ions by the loss or gain of electrons, and the gathering of the ions so produced into masses that are on the whole electrically neutral. It is only in the solid state that the ions are permanently arranged in any definite configuration, and then that configuration is determined simply by the electric field surrounding the ions. There are no isolated bonds; every ion reacts to some extent with every other and the final arrangement is determined by forces extending throughout the whole aggregate. But we left on one side two difficulties which were noted at the outset. We must explain how the ions come to be formed, and in particular why some atoms lose or gain several electrons, and we must explain also why the ions retain their individuality to so large an extent. The explanation that we shall offer is so intimately connected with the discussion of the second type of chemical combination that we had better proceed directly to it.

Non-polar combination has always been one of the stumbling-blocks of electronic theories of the atom, and their inability to explain the structure of organic compounds, which are so important in chemistry, was the reason why they had little attraction for chemists. In an organic compound a strongly electronegative element can replace a metal without any fundamental change in the structure (*e.g.* ether and zinc ethyl). It is here just possible the combination is of the type we have considered; that in one compound the carbon atom loses two electrons and in the other gains them. But what are we to say of $CHCl_3$ in which the atoms attached to the carbon are partly electropositive and partly electro-

negative; and what of compounds, such as H_2, N_2, O_2, between atoms of the same kind? Moreover there is clear evidence of the existence of molecules in the gaseous state; and the facts of stereo- and tauto-isomerism seem imperatively to demand that within the molecule forces are stronger and the spatial relations more definite than they are without it. Nowadays these objections have been reinforced by crystal analysis; for Bragg has recently proved that in some ring compounds the crystallographic 'point' is indeed the chemical molecule, or something very like it[1]. This conclusion had already been foreshadowed by the analysis of the non-polar part of polar compounds; thus in $CaCO_3$, though there is no unique relation between a single Ca atom and a single CO_3 group, the CO_3 group does form a crystallographic point, the atoms within which are related to each other as they are to no others outside the group.

Nevertheless, even before the nuclear atom was proposed, an explanation of non-polar combination had been suggested by Thomson and elaborated in some detail by Stark, which probably contains the germ of truth. It is that, in non-polar combination, electrons are not transferred from one atom to another, but are shared between atoms. But it was a little difficult to describe the suggestion in greater detail; if two atoms are near enough to attract and thus 'share' the same electron, they must be near enough to attract (or repel) each other, as they do in polar compounds; the difference between polar and non-polar could only be one of degree, while experiment indicates strongly that it is one of kind.

A great advance, though at one time it seemed to be along a by-path rather than along the main track, was made by Lewis, whose ideas have been developed further by Langmuir. Stated generally, Lewis' suggestion was that there were certain specially stable configurations of electrons about nuclei. In all chemically reactive atoms these configurations were not attained, because there were too few electrons to make up the entire stable pattern; but when two or more atoms, each with a relatively incomplete and unstable configuration of electrons, came into sufficiently close

[1] The carbon rings in naphthalene, *e.g.*, are joined to each other through certain of the hydrogen atoms. It is not certain that at the contact between two molecules all the hydrogens can be definitely divided into two classes, one of which belongs to one molecule and the other to the other.

touch, the electrons might rearrange themselves round the nuclei; the electrons of one might fit into the incomplete configuration of another, so that complete, and therefore more stable, configurations were formed by the sharing of electrons. A simple illustration will make the matter clearer. Suppose that a cube with an electron at each corner is one of the special stable configurations, and two atoms each having six electrons come into contact. Neither of the atoms has enough electrons to form the stable cube, but between them they have enough to form two cubes which have a common face and therefore 'share' four electrons; according to Lewis' theory they will then share these electrons; the resulting complex is a non-polar chemical compound.

Except in a detail, unessential for our immediate purpose, this is actually the way in which Langmuir, working with Lewis' ideas, proposed to picture the formation of the compound O_2, typically non-polar, as all compounds involving only one kind of atom must be. (The detail omitted is the presence of two other pairs of electrons inside the cubes. The true stable configuration is that of the 8-point cube surrounding a pair, together with the nucleus.) The essential difference between this theory and that of Thomson or Stark is the complete divorce of 'sharing' from mutual attraction. If the forces holding the electrons in the stable configuration are electrostatic or vary in any simple way with the distance, then not only four electrons are shared; all of them are shared. There must be attractions of the same order of magnitude between the parts of one atom and the electrons which it does not share with the other and between those parts and the electrons which it does share; there is no real difference between electrons which are shared and those that are not; the atoms are really merged in one another. But Lewis does not attempt to explain non-polar combination in terms of forces at all. He takes as fundamental the assumptions that there are certain stable configurations and that electrons are shared; how these configurations arise, why they are stable, and what compels the sharing of electrons to complete the configurations, these are questions that he does not consider at all. To a chemist such an attitude is natural; he is concerned to explain chemical facts, and so long as any assumption he makes is able to coordinate the facts in which he is interested

he has no reason to inquire further. But the attitude of the physicist is different; he is concerned, not so much to explain the dreary waste of structural chemistry (I speak, of course, as an unrepentant physicist) as to elucidate the reactions of charged particles. To him the question which the chemist leaves on one side is the most interesting of all. Accordingly before we can consider the theory seriously at all, we must see that there is some chance of reconciling it with the conclusions at which we have arrived already.

In their earlier work both Lewis and Langmuir pronounced that such a reconciliation was impossible[1]. Two main reasons were given why a dynamic atom (such as that of Bohr) was incapable of satisfying the demands of chemistry. The first was that dynamic atoms (or at least Bohr's atom) was two-dimensional, while stereochemistry and other branches of the science demanded a three-dimensional atom. The second was that 'structures in which atoms are not able to shift their relative position except when acted on by strong external forces are inconceivable if atoms contain only electrons revolving in orbits about the nuclei' (Langmuir). The first objection has vanished; Bohr's new atomic model is definitely three-dimensional. Indeed it was probably never seriously maintained that all orbits were coplanar rings; the possibilities of that form of orbit were explored first merely for the sake of mathematical simplicity. The second objection overlooks the essential principles of quantum dynamics—and it is only quantum dynamics that need be considered seriously in connection with atomic theories. If orbits were continuously transformable one into another, then it might be hard to believe that they could determine fixed relative positions of the atoms. But they are not continuously transformable; the orbits that can exist are separated finitely in space as well as in energy. This point has already been discussed in connection with the third quantum number on p. 95; orbits can exist only in definite spatial relations to each other and with definite angles between their planes (if indeed they are accurately plane). And if orbits must thus exist in definite spatial relation, it is not difficult

[1] Since the main text was written, Lewis and others who have developed his theory have admitted the possibility of reconciling it with a dynamic atom. They propose to retain its main ideas, but to re-interpret them in a manner similar to that suggested here, so that the sharing of electrons means the sharing of orbits.

to understand that atoms must also take up a definite configuration, which is not merely 'unalterable except by strong forces', but unalterable at all. If that configuration is not assumed, then the structure cannot exist at all; it must be replaced by some other structure. A structure cannot be deformed; it must either remain or be totally destroyed.

Having removed these preliminary objections, we have yet to inquire whether a definite meaning can be assigned to the sharing of electrons, which distinguishes it clearly from a general attraction between two atoms. An obvious suggestion at once occurs; 'sharing an electron' may mean sharing an orbit. In an isolated atom (whether neutral or not) the orbits of the exterior electrons are determined by the forces due to the nucleus of that atom and by the interior electrons associated with it. If such an atom is brought under external forces, such as those due to another similar system, the orbits are slightly altered; but if the disturbance is sufficiently small the orbits will still be characterised by the same quantum numbers and will still approximate closely to central orbits about a single nucleus, which has an effective charge somewhat different from that of the actual nucleus and the forces due to which are not strictly those of the inverse square law. The atom has retained its individuality, although there may be forces between it and an external atom. But if the contact between the two atoms is made more intimate, a second alternative becomes possible. The orbits may be so greatly disturbed that they change their nature; in place of orbits round a single nucleus approximating closely to central orbits, there may arise orbits round both nuclei and determined by one as much as by the other. If we still distinguish between the two atoms, we must regard these orbits as belonging equally to both: their geometrical relations to the nucleus of both atoms may be much the same; they may for instance be such that both nuclei lie definitely inside them and both play an equally important part in determining the groups and sub-groups of the other orbits in both atoms. Such an orbit, and the electron in it, can be said very appropriately to be shared between the atoms.

If then there are such orbits, we may tentatively translate the conclusions of the Lewis-Langmuir theory into the language of the Bohr theory and proceed to inquire whether we can account for

chemical combination by the sharing of this kind which the principles of Bohr's theory suggest or show to be possible. In one case there does appear to be evidence, wholly distinct from any chemical theory, of orbits shared between nuclei and belonging equally to both; this case, as might be expected, is the simplest possible case, for in no other can we hope at present to apply quantum principles in sufficient detail to decide the matter. In his earliest work, Bohr suggested that the hydrogen molecule might consist of an orbit, in which revolve two electrons, with its plane perpendicular to the line joining the nuclei and its centre at the middle of that line. The characteristics of such an orbit can be calculated. If a is the radius of the circular orbit, ω the angular velocity of the electrons, b the distance between the nuclei, a simple calculation shows that we must have

$$a = b\sqrt{3}, \quad 4\mu a^3\omega^2 = \epsilon^2(3\sqrt{3}-1) \quad \text{.....(144.1).}$$

Further, by quantum theory, the angular momentum of each electron[1] must be a multiple of h: hence

$$2\pi\mu a^2\omega = nh \quad \text{.....(144.2).}$$

We assume further that the normal orbit is that for which $n = 1$, and that consequently only circular orbits need be considered. It follows directly that the work required to disperse the system to infinity is given by

$$W_2 = \frac{4\pi^2\mu\epsilon^4}{h^2}\left(\frac{3\sqrt{3}-1}{4}\right)^2 = 2{\cdot}20Nh. \quad \text{.....(144.3).}$$

We can make an immediate deduction. Let the system be so dispersed and the components be then allowed to reassemble into two neutral hydrogen atoms. The work gained in the reassembling is, by (82.1), $2Nh$; and the net loss is

$$W_1 = 0{\cdot}20Nh = 2{\cdot}7 \text{ volts.}$$

Consequently the formation of hydrogen molecules out of hydrogen atoms should be an exothermic reaction, yielding $0{\cdot}20Nh$ ergs per molecule or $6{\cdot}1 \times 10^4$ cal. per gram-molecule. The 'heat of reaction' of this change is not easy to determine experimentally, but it has been estimated by Langmuir to be $8{\cdot}4 \times 10^4$ cal. Since

[1] It is not certain whether we ought to put equal to h the moment of each electron or the sum of both. Quantum theory has not yet been elaborated for these multiple orbits; but our assumption is at least plausible.

the mode of estimation, though ingenious, is very indirect, the agreement with prediction is probably sufficiently satisfactory.

We may also calculate the ionisation potential; though here the matter is more complicated, because it is not certain what precisely is the change occurring in ionisation. The work required to take one electron away leaving the other attached to the two nuclei is 17·8 volts, but it is unlikely that a positively charged hydrogen molecule is the normal result of ionisation. If the result is one ionised and one unionised atom, then the work is

$$W_2 - Nh = 16{\cdot}2 \text{ volts.}$$

On the other hand the latest experimentally determined critical potentials are 10·8, 13·4, 15·9 volts; but it is not certain that they are all ionisation potentials; some may be radiation potentials at which electrons are displaced to abnormal orbits without being ejected completely. The 15·9 potential (which other workers place between 16 and 17 volts) certainly represents ionisation and is very strongly marked; it agrees sufficiently with the 16·2 which we have calculated. The 13·4 potential ought to be the ionisation potential of the hydrogen atoms, the formation of which is associated with the ionisation of the molecule; but according to some workers it is a radiation potential. Again the 10·8 potential does not fit in either with the model of the atom (which *must* be right) or with that of the molecule. It has been definitely established since Ch. XV was written that ionisation may take place in two stages, an electron being first displaced and then ejected at a subsequent encounter either with a charged particle or with radiation; and this possibility makes the interpretation of all experiments on ionisation potentials rather less simple than appears at first sight. The matter, interesting as it is, cannot be discussed here incidentally; but we may conclude that there is nothing definitely inconsistent with the model in these experiments. In particular it may be noticed that the difference between successive critical voltages agrees well with our estimate of the energy required to dissociate the molecule into neutral atoms.

Support for the model has also been based by Debye and others on the study of the refractive index and dispersion of hydrogen. But unfortunately the development of quantum theory has thrown

doubt on the older theory of dispersion sketched in Ch. II; for that theory is based on the classical theory of light emission, which involved a coincidence between the periods of electronic vibrations and that of the radiation they emit. Considerable progress is being made with a quantum theory of dispersion, but this again is a matter with which we cannot deal here, Once more the evidence of dispersion, and of some allied optical properties is favourable but not conclusive. On the other hand there are some definite objections to the model. One which has been frequently urged has now lost its force; we see now (p. 120) that the absence of paramagnetism is only to be expected. Quantum orbits are not paramagnetic except in very exceptional circumstances and when their mutual relations are very complicated; and a single orbit such as we are considering is the least likely of all to be paramagnetic. More serious is the disagreement between predicted and calculated molespecific heats. An extension of the theory of this property along the lines indicated in Ch. X, pp. 240–244, Ch. XII, pp. 308–312 and Ch. XV, pp. 106, 107 enables us to calculate from the variation of the specific heat the moment of inertia of the molecule of a gas; the value so determined is considerably greater than that given by the model. The position of the model is therefore uncertain, and some authorities, in general favourable to Bohr's atomic theory, definitely reject it. The study of the 'many-lined' spectrum of the hydrogen molecule, which will no doubt ultimately decide the matter, is as yet little advanced.

But whether Bohr's model of the hydrogen molecule is right or wrong, it can hardly give much information about non-polar compounds in general; for hydrogen is an altogether exceptional element. The orbits of other elements are so complicated that it is unlikely that in the near future we shall be able to deduce directly from the principles of quantum theory what form the sharing of orbits between nuclei must take, or even to decide whether any proposed form is actually possible. Langmuir is doubtless right when he urges that we had better examine the chemical facts and guess from them some plausible rule distinguishing stable configurations and some general meaning to be attributed to electron sharing. If we can find such a rule and such a meaning which covers completely all the facts, then we shall have a certain guide by which to direct the further development of our fundamental principles.

The idea which underlies the theories of Lewis and Langmuir is one that formed the basis of Thomson's first explanation of (polar) chemical combination, and indeed follows almost inevitably from the view that succeeding elements in the periodic sequence differ from each other by the addition of an electron. The rare gases, lying between the highly electropositive halogens and the highly electronegative alkali metals, are the most chemically stable of all elements; if chemical combination means change of configuration they show no tendency to such change. The elements on either side of them, after taking up or losing electrons in the formation of a polar compound, contain the same number of electrons as the intermediate rare gas. It is natural to suppose that the configuration of the electrons is determined by their number; and we may conclude that the transference of electrons in polar combination represents a passage of both the elements concerned into a state in which their electrons take up the very stable configuration characteristic of the rare gases. The extension of the idea to non-polar compounds is obvious; they are formed by the sharing of electrons in such a way that the configuration of electrons surrounding each nucleus is that characteristic of the rare gases.

But what is this configuration? Langmuir, in the first expression of his theory, attributed to He(2) a pair of electrons closely associated; to Ne(10) such a pair surrounded by a cube with 8 electrons each at one corner; to Ar(18) the structure of neon with yet another cube of 8 electrons outside it. To Kr(36) he assigned a further outer cube or shell with 18 electrons; to Xe(54) yet another 18-electron shell; while Em(86) had a shell surrounding all these with 32 electrons. He supposed that in the formation of the elements lying between successive rare gases the new cube or shell distinguishing the second rare gas from the first was gradually filled up by the addition of one electron as we pass from element to element. The formation of non-polar compounds he attributed to the fitting of the exterior shells of the combining elements into each other in such a way that both these shells were complete and contained the number of electrons characteristic of the rare gas next higher in the sequence than the element concerned. From a consideration of typical cases of combination between elements of low atomic number it then appears that the single bond of

chemistry must represent the sharing of a pair of electrons, forming one edge of an 8-electron cube, or 'octet'; a double bond the sharing of four electrons or one face of the octet; a triple bond the sharing of six electrons (an arrangement not so easy to interpret geometrically). The theory has been applied mainly to elements of low atomic number; and it is unnecessary therefore to consider more precisely what the bonds must mean in an 18- or 32-electron shell.

On the other hand, according to Bohr, the distinguishing feature of the rare gases is the presence of an outer group of highest quantum number which contains 8 orbits and is either permanently or temporarily complete, the arrangement of these orbits being highly symmetrical. Helium is exceptional, since there are no inner groups and only two orbits in the outer; but it resembles the other rare gases in the fact that this group is complete. It is obvious at once that the two theories are closely similar, at any rate up to Ar (18); and Ladenburg had suggested before the publication of Bohr's theory a modification which would remove the divergence beyond that point; he had already conceived that in the long periods an inner, not an outer, shell might be in course of completion. Indeed we have only to give a suitable meaning to the sharing of electrons according to Bohr's theory to make it possible to translate conclusions derived from one theory directly into the language of the other. Suppose we say, for example, that the sharing of an electron in Langmuir's language is to mean in Bohr's the presence of an orbit which surrounds both nuclei and forms effectively a member of the group of highest quantum number about each of them. If then we attribute the formation of non-polar compounds to the re-grouping of the orbits in such a way that the number of orbits shared in this sense is sufficient to complete the group of highest quantum number about the nuclei of all the elements concerned; then our conclusions as to what compounds are possible, as to the similarities and dissimilarities between different compounds, and as to the distinction between various kinds of bonds will be precisely the same whichever mode of expression we choose to adopt.

It seems therefore that in order to adapt Bohr's theory to the purposes of chemistry as interpreted by Lewis and Langmuir, all that need be added is the assumption that such shared orbits can

be formed and are actually formed in non-polar compounds. If Langmuir's theory does give a sufficient account of chemical facts so complete as to leave no doubt of its truth in this region, then we must conclude that this assumption is true. Such a conclusion would throw grave doubt on Bohr's hydrogen model; it would suggest that in the hydrogen molecule the orbits of the two electrons are independent; both surround both nuclei and are related to them both as are the 'crossed' orbits of normal helium. On the other hand, as has been said already, hydrogen is clearly exceptional and the stable configuration may here be altogether different; but for our purpose it will be convenient to apply the new conception even to hydrogen, and to suppose that even here the single bond represents the sharing of two orbits and not (as in Bohr's model) the sharing of two electrons in a single orbit. A slight modification of the theory would, however, enable us to retain the Bohr model—but since the whole matter is so speculative, it is not proposed to discuss it further.

But now we must face the question whether this theory of non-polar combination explains the facts so completely that we can use it as a guide to the determination of stable configurations and thus to a further development of the principles underlying atomic structure. The inquiry involves of course a survey of all the facts of chemistry in the light of the theory; such a survey is far beyond the scope of this volume, and any partial examination would be misleading. We can only attempt to summarise and to review the conclusions that others have reached. The conclusion which seems to have been reached by chemists is that the theory gives a better account of the facts than any which has been proposed hitherto. It is definitely better than the old theory of valency bonds; for the compounds explained by that theory appear as particular cases of a more general type of combination which includes that of the complex salts to which Werner's conception of a 'coordination number' alone was applicable. But it does not cover all the facts. The mystery of NO, for example, is as great as ever. Moreover, even its successes are not wholly of the type we desire. Just as the theory of valency would explain anything if we were allowed to attribute to the same atom different valencies in different combinations, so the theory of the sharing of electrons in stable con-

figurations will explain anything if we are allowed to choose the stable configuration to meet the needs of the particular compound. The theory will give us the guidance we require only if we can lay down a general principle, applicable to all cases, and find that it covers all the facts; we need not assume that the stable configuration is the same in every molecule, but we must have some clear rule by which to decide whether a proposed configuration will or will not be stable.

Now such a rule does not seem to have been found. Lewis and his pupils, so far as I can make out, do not propose a definite rule at all. They hold that in all compounds there is a sharing of pairs of electrons, but the configurations in which they suppose that these pairs are shared in different compounds do not seem to present any obvious common feature; and if they have no common feature, the theory can explain anything; if all the facts of chemistry were utterly different from what they are, a new set of configurations could be invented which would account for the new facts as well as for the old. Langmuir on the other hand in the first statement of his theory, did lay down a definite rule applicable to all elements up to Ar (18); it is that the stable configuration is an octet, probably an eight-cornered cube, but at least the same in all compounds. But it is now generally recognised that this suggestion is too narrow; most important of all, it will not explain the stereochemistry of carbon, which seems imperatively to demand a tetrahedral configuration, or at least a quartet rather than an octet. Of course the necessary emendation is easily made, but then we find ourselves once more in the position of having no general rule concerning stable configurations.

At present then it seems to me (with all respect to the many chemists engaged in the task) that speculation on the precise constitution of individual chemical compounds is not likely to lead to any considerable advance. We need some further guiding principle, which is already dimly foreshadowed by the suggestive indications of the theory of quantum orbits. If a stable configuration is one in which a quantum group, or perhaps even a quantum sub-group is completed by the sharing of orbits, it may be possible to define a limited number of possible geometrical arrangements. But for the time being support for Lewis' ideas must come from

their intrinsic plausibility rather than from their concordance with the facts. They offer for the first time a definite conception of non-polar combination which is not obviously discordant with physical principles, and is indeed a natural development of them.

Nevertheless some of the more detailed conclusions which have attracted much attention should be noticed. One natural consequence of the theory of stable configurations is that molecules containing the same number of electrons and the same number of nuclei should be very similar, although the charges on the nuclei may differ somewhat. The properties of an isolated atom depend greatly on the nuclear charge, because that charge determines to what extent the last group of quantum orbits is complete; all our discussion in the last chapter indicates how closely properties are determined by the degree of completion of this group. But in a molecule the last groups about all nuclei are completed by the sharing of orbits; the groups will be precisely similar if the number of electrons and the number of nuclei (and therefore of groups) is the same; the charges on the nuclei will affect the external reactions of the molecule only through the distribution of the same total charge among the nuclei, lying within the atom. Now this prediction is fulfilled in the only two instances which can be cited; CO_2 and N_2O (2 nuclei and 22 electrons) satisfy the conditions; and so do N_2 and CO (2 nuclei and 14 electrons). Each of these pairs of compounds are very closely similar in all reactions which do not involve the resolution of the molecule, *e.g.* in vapour pressure, in viscosity, and in all properties depending on the 'size' of the molecule. Here is notable support for the theory.

However, there has been some tendency to exaggerate it, because the attention was first called to the facts by Langmuir; any reasonable nuclear theory must predict considerable resemblances between such atoms. It is well, therefore, to point out that no support is offered for the particular constitution assigned to these molecules as against any other showing the same features. This warning is especially important in connection with the N_2 and CO molecule. If the rule of the sharing of pairs of electrons is to be maintained, this molecule cannot be pictured as composed of two octets, one about each nucleus; for that would involve the sharing of three electrons and both Lewis and Langmuir insist on the sharing of

pairs. Accordingly Langmuir suggests that it is formed of a single octet, both nuclei lying within this octet and being almost equivalent to a single nucleus. This arrangement would represent an even closer type of combination, and one more completely destructive of the individuality of atoms, than those we have considered hitherto; if it can really be justified, it is highly important. Langmuir cites in support of his view the low boiling point of nitrogen as compared with the high boiling point of carbon, preceding it in the periodic sequence, and suggests that this difference indicates a peculiarly close form of combination and a small external field. But the boiling point of nitrogen is very near that of oxygen which succeeds it, and to which the normal double octet structure is assigned. Other explanations are not impossible which might at the same time give some account of the unique chemical properties of carbon.

28. **Miscellaneous evidence.** Hitherto we have made as sharp as possible the distinction between polar and non-polar combination. But there must be some connection between them, and it is probably clear already to the reader that by establishing such a connection we can remove to a great extent the outstanding difficulties of our view of polar combination, namely the occurrence of multivalency and the retention of their individuality by the combining atoms.

Polar combination probably takes place in two stages, of which non-polar combination is the first. Thus when calcium and oxygen combine, the oxygen does not drag directly two electrons out of the calcium; the two combine to form a non-polar compound in which the two exterior (4_1) orbits of the calcium atom surround the oxygen nucleus, raise its exterior (2_k) group from two to eight and thus complete it. We may suppose next that when the non-polar compound which is thus formed by the sharing of orbits comes under the influence of similar molecules (or, in solution, of the molecules of the solvent), the non-polar molecule is resolved, leaving the two shared orbits surrounding the oxygen nucleus but not the calcium nucleus, and thus giving rise to a calcium atom with two positive charges, and an oxygen atom with two negative charges, in both of which the exterior group is complete and similar to that of argon in one case and of neon in the other. The great stability

of these exterior groups prevents any further reaction between the atomic orbits, and the atoms, though exerting forces on each other, retain their individuality.

However, it should be observed that this process is not exactly in accordance with Langmuir's theory, which would demand that in a non-polar compound between calcium and oxygen the exterior shells of both atoms should be completed; the outer shell of calcium ought to be completed by the sharing of six electrons from the oxygen as well as that of the oxygen by the sharing of two electrons from the calcium. But there is no reason why we should follow Langmuir's theory too closely in this matter; indeed it may be urged that the recognition of a form of combination in which the exterior shells of some of the combining atoms are completed by the sharing of electrons while those of others remain incomplete is not only in better accordance with the suggestion of Bohr's theory, but also allows of a more complete explanation of chemical facts. For instance some of the peculiarities of carbon can be explained if it is supposed that it sometimes retains its configuration of four exterior orbits and sometimes increases that number to eight. Again, perhaps we may see how complex anions, such as SO_4, come to be formed. In SO_3 we may imagine that the six exterior orbits of S (16) fill up the two missing places in the exterior orbits of each of the three atoms of O (8). When this complex group receives two extra electrons, these complete the exterior group of the sulphur atom and at the same time can bind to it another oxygen atom by completing its exterior group as well. But there is no end to these speculations, which are rather to be deprecated in the present state of knowledge. I have no doubt that the reader interested in chemistry will pursue them for himself and find out the various developments of the idea that best account for the different classes of combination. Scientifically the next step must be to discover from quantum theory that this imagined process of electron sharing, leading to the completion of exterior groups of orbits, is indeed possible.

But some facts which support generally our view of the relation between polar and non-polar combination may be mentioned. Kossel has drawn attention to the remarkable change in the properties of the series of halogen compounds of the elements as we pass across

the periodic table. Thus in the series NaF, MgF_2, AlF_3, SiF_4, PF_5, SF_6 the first three are typically polar, the last three typically non-polar; the first three are extremely non-volatile and stable, the stability increasing from member to member; the last three are volatile and increasingly unstable. We suppose that the first stage in the formation of each of these compounds is a non-polar compound in which electrons are shared between the atoms. In the first three compounds the number of halogen atoms surrounding the metal is insufficient to shield the metal atom entirely from the influence of others similar to it in the neighbourhood. Under this influence the non-polar group breaks up into ions of opposite sign and the attraction between these ions is the greater, and the stability of the crystal lattice formed from them the greater, the greater the charge on the multivalent metal ion. On the other hand when there are four halogen atoms surrounding, and in non-polar combination with, the metal atom, this atom is completely shielded from others; the non-polar combination does not break up. The residual attraction between the combined groups is merely that between the similar halogen atoms which alone come into 'contact'; there can be no attraction between the halogen atoms of one group and the metal atom of another such as confers on polar compounds their great physical stability. The compound therefore is volatile exactly as the halogen itself is volatile; indeed Kossel points out that there is a very simple relation between the boiling points of these non-polar compounds and those of the halogens themselves.

Other support comes from determination of the sizes of the atoms in polar combination. Of course we must not expect a nuclear atom with its surrounding cloud of electrons to have a perfectly definite size, the same in all its reactions; and we find that the size to be attributed to atoms actually differs considerably according to the property from which we estimate it. But there are certain striking and instructive features which appear whatever method of estimation is adopted. W. L. Bragg and others following him have shown that throughout a large range of compounds definite sizes can be attributed to atoms forming crystal lattices; if the atoms are supposed to be spheres of definite radius, the dimensions of the lattice are determined by the condition that these spheres touch

one another. Another estimate can be based on the recent work of Rankine on the viscosity of gases interpreted according to the theory of gases due to Sutherland and Chapman. Yet a third from the infra-red absorption bands which are determined, according to Bjerrum's theory, by the moment of inertia of the molecule, which again is determined by the distance apart of the nuclei. (See Ch. XV, p. 106.) All these estimates lead to the result that the diameters of the atoms in a group of Table VI decrease asymptotically downwards, so that those of the halogens are very nearly the same as that of the rare gases which follow them immediately; and that, as we pass from one group of the table to the next, the radii increase by regular and nearly equal steps. The following are some of their results.

TABLE IX

Diameters in Å from crystal analysis.

Na	Mg	Al	Si	P	S	Cl	Ar (extrapolated)
3·55	2·85	2·70	2·35	?	2·05	2·10	2·05

Diameter from	Crystals	Viscosity	Absorption band
He ...	...	1·89	...
		0·46	
Ne ...	1·30	2·35	1·86
	0·75	0·52	0·70
Ar ...	2·05	2·87	2·56
	0·30	0·32	0·30
Kr ...	2·35	3·19	2·86
	0·35	0·32	
Xe ...	2·70	3·51	...

These conclusions accord with expectation in so far as the diameters of the ions agree with or approach those of the atoms of the rare gases; for according to our view the electrons in the ions are in the configuration characteristic of those gases. But the large diameters of the electropositive elements and the decrease rather than increase of the diameters as we pass to the electronegative is not in accordance; for our view would suggest that the diameter of Na (10) should be very nearly the same as that of Ne (10) and not, as we find, larger than that of Ar (18). But it must be remembered that the diameters of these ions are determined wholly

by crystal analysis; the other two methods are not available; the conception of the crystal as built up of spheres, in contact but not close-packed, on which the estimate is based, does not really represent the truth.

Again, we find as we should expect that in non-polar compounds the molecular volume is not strictly an atomic property, but depends considerably on the mode of chemical combination. Thus, though the molecular volume of the paraffin hydrocarbons increases regularly with each addition of $-CH_2$, this addition cannot be represented as the sum of two parts, one due to the C and the other to the H; the contribution of both these elements to the molecular volume differs widely according to the form of attachment. On the other hand, Rankine has shown that in compounds, such as SO_2, which are on the border-line between polar and non-polar combination, the molecular volume, as displayed in viscosity, can be represented by the sum of the atomic volumes, if certain reasonable assumptions are made concerning the arrangement of the atoms and consequently concerning the relation between volume and effective cross-section. But the most definite evidence concerning molecular volume and atomic arrangement in non-polar compounds is likely to come in the future from the work which W. H. Bragg has just begun on the crystal structure of organic compounds. He has shown, for example, that the benzene ring really exists in aromatic compounds (though not exactly in any of the forms imagined by chemists), the carbon atoms composing it having a definite spatial arrangement and a definite volume. With such knowledge the determination of the electronic orbits which, according to our theory, are shared by these atoms should be greatly facilitated.

Here too bare mention may be made of some recent work of great interest by Shearer which seems likely to throw light in the same direction. He compares the degree of symmetry shown by an actual crystal with that which would be displayed if the atoms in the elementary cell, the number and arrangement of which is known, were perfectly symmetrical or perfectly asymmetrical. He finds that the actual symmetry is always greater than that consistent with perfect asymmetry, but less than that which would appear if the atoms were perfectly symmetrical. He concludes that the

atoms must have a symmetry which is not perfectly spherical; and from the degree of symmetry in the atom necessary to account for the crystal symmetry he can sometimes make a plausible guess at the shape of the ion (if the combination is polar) or the shape of the orbits connecting it to other atoms (if the combination is non-polar). But this work is only beginning.

Finally we may inquire concerning the relation between the similar atoms of elementary substances. When these are in the gaseous state the older conception of individual molecules is valid, and these molecules are clearly in non-polar combination. Of such combination the Lewis-Langmuir theory (at any rate as modified in accordance with Bohr's conceptions) gives an entirely adequate account. When the atoms are similar, the possibilities of the completion of electronic groups by the sharing of orbits are especially obvious; we understand why the rare gases, in the atoms of which the groups are complete, are all monatomic. Perhaps we see also why the gaseous molecules of metallic elements are monatomic; for here the number of 'valency' electrons, outside the completed groups, is so small that they are insufficient to complete another group; if at least four electrons are necessary to complete a group, completion is impossible in the combination of two sodium atoms which can each contribute only one valency electron.

The liquid state we have to leave on one side; for our knowledge of this state is still very fragmentary. But when we pass to the solid state and can seek aid from crystal analysis information again becomes available. Of the non-metals carbon is far the most completely studied. Here we find the carbon atoms arranged in a lattice, the element of which is closely similar to the benzene ring. The combination between these atoms is doubtless non-polar and due to the sharing of electronic orbits between neighbouring atoms so as to form a single molecule embracing the whole of the crystal. The peculiar physical properties of the diamond, its density and its hardness, can thus be related to its peculiar chemical properties that are the basis of organic chemistry.

In metals on the other hand the lattices are almost always cubic, usually of the face-centred type, or approach cubical form very nearly. Here we must expect the combination to be rather of the polar type; and a suggestion made by many writers indicates

how such combination can arise. The structure is essentially similar to that of a typical polar compound, such as KCl; the metallic atoms, having lost a valency electron, are the positive ions, the electrons themselves are the negative ions. Crystal analysis, at present at least, can only place the positive ions definitely, but it seems certain that the forces which hold these positive ions in the lattice are those between these ions and the electrons. We can then understand why solid metals are conductors of electricity and possess 'free' electrons, according to the older theory (see Chap. III). The electrons that take part in conduction are not free in the sense that they are subject to no forces, but they are free in the sense that they can be displaced without any permanent disarrangement of the solid structure. Metallic conduction is another aspect of the 'slip-planes' to which metals owe their special physical property, ductility. Owing to the small size of the electrons, the crystal planes containing them can slip between the atomic planes, and the atomic planes can slip relatively to each other. At ordinary temperatures the atomic planes are not perfectly definite owing to the motion of thermal agitation of the atomic ions; the slip of the electrons in their planes is not therefore quite unopposed. But at sufficiently low temperatures the thermal agitation ceases, perfect slip is possible, and the 'super-conductivity' of Kammerlingh-Onnes makes its appearance. The exact interpretation of these ideas according to the later developments of quantum theory belongs to another chapter.

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