

Emission Spectra and Atomic Structure.

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THE invitation of the Council of the Chemical Society to take part in a series of three lectures during the present session is peculiarly acceptable to me, in that it gives me an opportunity to draw attention to certain problems of atomic structure in which further progress can scarcely be hoped for without a more complete co-operation between the physicist and chemist than has hitherto been customary.

The chemist appeals frequently to the physicist, or even to the mathematician, for guidance. I wish to emphasise, and I hope that my remarks will serve to do so, that it is even more a necessity that the real aid to be invoked in the problem which we share in common—that of the elucidation of the nature of the elementary atom—is that of the chemist. It is my belief that this problem will not proceed further towards a satisfactory solution without the joint action of the physicist and the chemist, who have hitherto tended to work in separate channels, without a complete knowledge of their mutual activities. Some of the problems in which co-operation is desirable I hope to indicate, perhaps vaguely, but sufficiently clearly for those of us who have really common interests.

Prof. Soddy has relieved my task very much. One of the pioneers on the chemical side, he gave an account of the bearing of chemistry on the problem of atomic structure which is beyond criticism, and to which nothing further can really be added from that point of view. Some questions were raised on which more could perhaps be said—for instance, the spectra of isotopes, to which I may refer again. As regards his address, I should like to say at the outset that the views therein expressed cannot be contested seriously by the physicist or the mathematician who has worked at the problem of atomic structure.

My own object is to consider this problem from the point of view of spectra. I will endeavour to confine my remarks to the more immediate issues, for the subject of spectra is at present so vast as to transcend any delimitation as a branch of chemistry or of physics. I must consider it only from the point of view of atomic structure, which I have already described as the ultimate aim of both physics and chemistry, an aim only to be achieved by

co-operative effort, and preferably by the existence at the same time of strong chemical and physical schools at one of our leading universities. Prof. Soddy began at the "heavy" end of the periodic table of the elements. I shall, in effect, begin at the "light" end—with hydrogen and helium and possible lighter elements. Before I so begin, however, a few words regarding the nature of spectra are necessary—and my remarks are confined to emission spectra, and not absorption spectra, which, although of supreme importance to the chemist, are less interesting as bearing on the structure of the atom.

Any complete account of the nature of spectral series, as elucidated by experiment, would be quite outside the limits of time of a single lecture. I must perforce neglect various matters, such as satellites of spectrum lines, as of secondary importance. The account of spectra which I give must be accepted as an ideal simplification of existing spectra, to which, nevertheless, theories of atomic structure must conform. Moreover, it is not to be understood that such an account is valid for the heavier elements, the spectra of which exhibit a more complex scheme of relations, but since atomic theories must in practice be illustrated or even confirmed from the lighter and more chemically simple elements, showing the simpler types of spectra, no disadvantage is thereby involved.

Series of spectrum lines will then be regarded as falling into three mutually related sets—the so-called diffuse, sharp, and principal series. The existence of any one of these implies that of the other two, and the lines constituting any one of these series may be single, double, or triple. An element may emit two distinct sets of series, perhaps more. For instance, helium gives three series of single lines and three of doublets. It is a great advantage to work with wave numbers, or numbers of complete wave-lengths in a centimetre, rather than wave-lengths themselves, in the discussion of series, for this procedure enables the relations of the three types of series to be stated very simply. If we proceed along a spectrum series towards the violet, the lines are seen to become closer and closer together until a limit is reached at which two successive members coincide. Lines are never, in fact, visible in the laboratory near this limit, although their convergence towards it can be seen readily enough, the actual limit being a matter of calculation. The diffuse and sharp series tend to the same limit in all cases, and from this limit we can calculate, and thereby predict, the wave-number intervals between the lines of the principal series. The Rydberg-Schuster law gives also the limit of the principal series.

In regard to double lines, the series relations are even more interesting. The wave-number interval between the two members of a doublet is constant along the diffuse and sharp series—the two members form separate series tending to different limits. In a principal series, on the other hand, they tend to the same limit, and the doublets rapidly become narrower towards the violet end of the spectrum.

Our present interest in these questions is mainly confined to the discovery of a chemical atom which can produce a set of ethereal waves the frequencies of which are related in this curious manner.

I will endeavour to summarise some of the more extreme difficulties met at the outset. In the first place, a series contains an infinite number of lines, and if the spectra are in any sense dynamical vibrations of the atom, the frequencies of which are transmitted to our instruments by the ether, the atom must have an infinite number of degrees of freedom. This is not consistent with the very finite number of possible vibrating parts which, from many converging lines of evidence, we are now compelled to assume for its structure—the positive nucleus and some electrons in rotation round it. The only way to surmount this difficulty is, in fact, to postulate that series spectra are derived from the nucleus, and are not a question of the outer electrons. This nucleus must then be endowed with an extremely complex structure. In this way, we might hope to preserve the conception of spectra as dynamical vibrations, and all the lines of the three series might then arise simultaneously from the same atom. We cannot altogether reject this possibility, but if it were more than a possibility, we should be driven to a very disappointing conclusion. For nuclear structure is a thing we may, and often do, speculate about, but it is at the same time practically beyond the power of our experiments. We know, for instance, that α - and β -particles in radioactive phenomena are shot from the nucleus, but nothing we can do appears to have any retarding or accelerating effect on such phenomena or to give a clue to the arrangement of the particles before their emission. We cannot, in fact, influence the nucleus in any effective way, but only its surrounding electrons. Speculative theories of spectra as arising from a nucleus may then be constructed in the future, but there would remain the fundamental difficulty of testing them experimentally. Many phenomena, however, for instance, the Zeeman and Stark effects, and the curious variations shown in the spectra of mixed gases, seem to indicate that the surrounding electrons are vitally concerned and that the nucleus gives us no mode of escape.

Since we cannot have the infinite number of degrees of freedom,

the conception of an infinite number of states of an atom arises with a finite number of spectrum lines—perhaps only one—corresponding with each state. Two lines of the same series are then never given simultaneously from the same atom. This underlies the two theories of production of spectra which have achieved some success, namely, the theories of Ritz and Bohr, on which more will be said later.

The second difficulty to which I shall refer is that all the formulæ which give a useful expression for the series relations of spectral lines serve to show quite conclusively that the frequencies of the lines are simple functions of a quantity to which we can assign any whole-number value we please, each value corresponding with a definite line. Dynamical theory always leads to an expression for the *square* of the frequency, and the frequency itself is a square root which ordinarily does not work out into a simple form. This difficulty is of a type which I do not wish to expound at length now, but it is sufficient to say that a satisfactory theory of spectra as atomic vibrations must lead to an equation giving the frequency itself, and not its square, in the first instance. There is only one known case in which this occurs, namely, the case in which the forces which regulate the vibrations of the atomic electrons are mainly *magnetic*. This is the manner in which Ritz overcomes the difficulty. He found it necessary to postulate the existence of a specific magnetic moment—the *magneton*, in fact—which was invariable, like the electric charge of an electron, from atom to atom. An atom could contain various numbers of magnetons, each corresponding with one of its “states,” and each state gave a spectrum line when the electrons of the atom vibrated under the influence of the elementary contained magnets.

This theory of spectra was extraordinarily successful. Its prophecies were verified at every turn, and it was the instrument which, more than any other, has directed the experimental work of spectroscopists into fruitful channels and led to a consolidation of the phenomena of spectra into great generalisations which are now fully established. It led, in fact, to the well-known *combination principle* of spectra on which Bohr’s theory was subsequently founded. The defects which are regarded as fatal to it are derived from other considerations than those of spectra. Such problems as the scattering of α - and β -particles by atoms, treated experimentally and compared with the theory developed by Darwin, Bohr, and others, do not appear to be consistent with such fields of magnetic type, although Hicks has had some success in the contrary direction in interpreting the deflections of these particles by a magnetic core of the atom.

I do not propose to say more regarding the existence of magnetic forces within the atom or as regards the existence or non-existence of the magneton itself. There is a vast amount of literature on the subject, which only, in fact, comes into the scope of existing theories of spectra in the manner already briefly indicated. The other theory which has had some success in explaining series spectra is of quite another type, and does not admit such magnetic forces. We shall discuss it later, but shall proceed at present to consider some spectra which do not form ordinary series.

It is difficult to think of an atom as a nucleus of positive electricity with satellite electrons without imagining that the atom is capable of vibrations of a periodic type, and that these vibrations must show themselves in the form of optical wave-lengths. These should, from general considerations, have a frequency which brings many at least into the visible spectrum. The argument is founded merely on the accepted—from many well-established facts—values of the radii, electronic velocities, and so forth. I will proceed to give a short account of some of my own work in this connexion, the data on which it is founded being mainly those of spectroscopic astronomy.

In the first place, one very general result must be stated. It is so frequently ignored in the construction of theoretical atoms that too much emphasis can scarcely be given. Under the inverse square law of attraction or repulsion of elements of electricity, or, indeed, any inverse law at all, coplanar rings of electrons are not possible, in the sense that even an undisturbed atom cannot preserve its configuration. The conclusion may probably be extended to non-coplanar rings.

Rutherford has shown that the nucleus apparently continues to act on electrons with this law at distances less than the atomic radius, and there is much evidence that the electrons continue so to act on each other. If this is confirmed further, the explanations of the phenomena of Röntgen radiation, based on transfer of an electron from one ring to another, will fall to the ground. The subject has many ramifications, and the following statements, capable of logical demonstration, show the chaos in which the physics of the atom is now involved:—

(1) Experiments on scattering of α - and β -particles by atoms indicate that the usual laws of electrical action are valid *inside* the atom. This precludes comparable forces of magnetic origin.

(2) Separate rings of electrons are impossible if (1) is true, and this would annihilate attempts hitherto made to interpret the characteristic X-radiation of atoms, which then can only be a property of the nucleus.

(3) The now accepted dimensions of this nucleus are not consistent with (2). They are also not consistent with the fact that it is capable of sending out β -particles during a radioactive change, for a single β -particle is much larger than a nucleus.

It would be possible to continue such a table of contradictions for a considerable time, and if the quantum theory is invoked, the situation is little better. I do not wish to do more than indicate the position, for more could not be done in a sufficient space. What I wish to make clear is that whilst those who, like Prof. Soddy, discuss radioactive phenomena, proceed from the "heavy" end of the periodic table, any constructive account of spectra must begin at the "light" end.

For the simplest possible elements, there can only be a question of one ring, whatever view is adopted. My own procedure was as follows. Taking the ordinary laws of electrical action, it is possible to work out the frequencies of dynamical vibration of an atom with, say, any number of electrons up to six, in one ring, rotating round a nucleus of any defined strength. The ratios of these frequencies are pure numbers in most cases, although for certain defined vibrations there is a small correction involving the ratio of mass of the electron and nucleus. We may search for vibrations, falling into groups with the prescribed ratios among individual members, in any spectrum that is known to emanate from matter of the simplest form—determined by the fact that no known element heavier than helium, for instance, is indicated as being present—and if such a spectrum is found which falls completely into such groups there is an a priori case for the conclusion that we have given a theory of the spectrum which is satisfactory, and of necessity settles many points of atomic structure.

The nebulae and the solar corona have been generally believed to consist of the simplest forms of matter. They have always been invoked by speculators on the periodic table and its possible "early" elements, and with much reason. The spectrum of a nebula, for instance, contains only lines of hydrogen and helium, and others which cannot be produced in the laboratory after every possible mode of deriving them from likely elements has been tried. The spectrum of the corona, whilst rich in lines, contains nothing that can be produced in the laboratory. Naturally, in a search for the groups in specified numerical ratios, derived from precisely described atoms, we began with these spectra. The results were startling. The coronal spectrum consists entirely of lines—in number about thirty-six—which all fit precisely into the scheme of ratios for elementary atoms in which the nucleus has a charge $5e$ or $7e$, and five or seven electrons rotating round it, as the case

may be, in its normal state, and smaller or greater numbers in its charged states. The chemical identity of the atom must be regarded as determined by the charge of its nucleus—or its atomic number. The whole coronal spectrum can thus be linked up as the superposed spectra of two chemical substances, and represented by simple formulæ. It was found, moreover, that these formulæ would go further and predict the existence of new and unobserved spectrum lines. A notable instance was the coronium line $\lambda 6374$ found by MM. Deslandres and Carrasco some time after the publication of the formula which predicted it, and similar predictions in the case of the spectra of planetary nebulæ have been verified. The corresponding substances in the nebulæ which are invoked as hypothetical entities are the same in kind as those for the solar corona, differing only in nuclear charge or atomic number. It is curious to note that the atomic numbers of the necessary hypothetical atoms for nebulæ are the even numbers 2, 4, 6, and for the corona they are odd numbers, 5, 7. The coronal spectrum appears to come in the main from these hypothetical atoms endowed with strong negative charges, for instance, the atom $7e$ with 9 revolving electrons. This points to an abundance of negative electrons in the corona, unattached to atoms and readily capable of attachment. There is much evidence, at the same time, that the atoms themselves are endowed with very high velocities, and may be a new form of α -particle.

To return to our main argument. What all these atoms share in common is the fact that their angular momenta are simple multiples of a constant unit. Armed with this generalisation, we can calculate the spectrum of any of these hypothetical elements—say one in the nebulæ—from that of another of different chemical nature—say one in the corona. I ventured to put forward the suggestion that this was the real basis of the quantum theory, and that the angular momenta of the electrons in all atoms were related in this simple way to a universal constant of nature, which, being an angular momentum, had the proper dimensions, and even the proper numerical value, as calculation showed, of Planck's unit.

Dr. Bohr, in the theory of series spectra which he subsequently put forward, adopted this generalisation. Prof. Jeans is to address you on the subject the fringe of which we are now touching, so that I will proceed no further, but turn aside to another aspect of importance to chemists. We have seen already that in certain spectrum lines calculated in the way outlined above, there will be a small discrepancy of wave-length due to the fact that the nucleus itself oscillates, as well as the electrons, in the types of vibration producing these lines. Its mass must therefore enter into the

question in these special cases, and it enters as a small term of order m/M , where m is the mass of the electron and M that of the nucleus. From the discrepancies, we can calculate M/m , which, with our practical knowledge of H/m , where H is the mass of the hydrogen atom, gives us M/H , the *atomic weight* of the hypothetical atom. Very concordant results are obtained from these calculations. The atomic weight of coronium, the name given to the hypothetical atom causing the most striking line $\lambda 5303$ in the coronal spectrum, is 4.0, suggesting that it may be a helium atom radiating in an unusual manner in an unusual environment; but the atomic weight of the other element there required is 2.0, which corresponds with no known terrestrial element. Again, in the nebulae, the two most important atoms required give atomic weights 1.3, 3.0, again with no known terrestrial equivalent. Yet, nevertheless, MM. Buisson and Fabry, by their method of determining the mass of a radiating atom from the interference of its radiation, experimentally confirmed the value 3.0, and showed that the element for which our value is 1.3 had an atomic weight greater than, but not much greater than, that of hydrogen. It seems necessary to presume the existence, in circumstances which we perhaps are unable to produce at present in the laboratory—and maintain for a length of time—of such atoms which may not be chemical elements in the sense ordinarily understood by that term.

We have, in fact, two alternatives. Either the atoms in question have not an existence or have not been produced terrestrially, or we have not yet excited them in the laboratory in the appropriate manner to produce such spectra. The latter alternative seems more probable. There is reason to believe that the coronal spectrum at least consists of a somewhat scattered "negative band" spectrum, produced in the presence of an excess of electrons by a very mild form of excitation. However that may be, these spectra, although without doubt the first spectra to receive a strict theoretical basis which is satisfactory, are not *series* spectra as known to us, being in the nature of their relations very analogous to, and without doubt a special case of, band spectra. Series spectra themselves, as defined above, cannot, as we have seen, be ascribed to dynamical vibrations about an atomic condition of steady motion.

Before we proceed to series spectra, we should perhaps state the assumptions involved in the above work. They are, in effect, identical with the conclusions derived by Sir Ernest Rutherford on experimental grounds about six months after the publication of the first paper in which some of these results were obtained. In fact, they can all be included in the statement that the nucleus is at least as small as an electron, and that the law of force between

electric charges is *strictly*—to an extreme order of approximation—that of the inverse square. It is not necessary at this point to emphasise the very definite atomic structure which these results imply. The law of inverse square, the small nucleus, the existence of Planck's constant as a universal angular momentum, are simple examples of what can be deduced. The law of at least some negative spectra of atoms, previously unknown, is another corollary. Many of these deductions have been confirmed by the later experimental work, on quite other ground, of Rutherford and of his colleagues, and have to a large extent become part of the essential basis of Bohr's theory of spectra and its extraordinary consequences, recently worked out by Paschen and others, in regard to the fine structure of lines in the spectrum of hydrogen.

The spectra which we have just described are not series spectra in the ordinary sense of the term. They are in all essentials band spectra. Their production in the laboratory from known materials involves a new type of experiment—an experiment in which a gas of extreme tenuity must be excited by an electric force insufficient to ionise the gas and thus detach an electron, but sufficient to show a “dynamical vibration” spectrum after an exposure of many hours. No such form of excitation has yet been tried in any experimental production of spectra, but it is now being tried by Dr. Merton. It appears to be the only hope of producing some of these elusive astronomical spectra in the laboratory, and thus reaching one of the goals of the astronomical spectroscopist.

It is already clear that series spectra cannot be “dynamical vibration” spectra from the reasons cited above. What are they? The only suggestion which has met with any considerable success is that of Dr. Bohr. Proceeding from the point of view outlined above, he supposes, for instance, that an atom of hydrogen can have one electron rotating with an angular momentum which is any multiple of $h/2\pi$, where h is Planck's constant. He calculates the energy in any such state of rotation—a *stationary state*—and assumes that radiation is emitted in the passage between two such stationary states of amount equal to the loss of energy between the states, and also of amount $h\nu$, where, in accordance with Planck's law, ν is the frequency of the emitted vibration. He thus deduces the hydrogen spectrum as containing the frequencies

$$\nu = B\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where m and n are any integers and B is a universal constant dependent on Planck's constant, the calculated value of which approximates in a remarkable way to Rydberg's universal constant of spectra. The theory does, in fact, reproduce the hydrogen

spectrum, although, of course, that of Ritz, founded on the magneton, did the same, and is too frequently ignored. I wish at this point to make a remark which seems to me essential, and relates to a matter not previously dealt with effectively by theoretical physicists intent upon constructing models of a hydrogen atom which can give the Balmer series spectrum. This spectrum consists of about six lines in the laboratory. The actual spectrum of the hydrogen *atom* contains more than a thousand lines, the rest being the so-called "secondary spectrum." At least six theories of a hydrogen atom have now been given, leading to the Balmer series as its spectrum. But none gives any clue to the origin of the secondary spectrum of hydrogen, which is the real key to the problem of atomic structure, for it is known to be due in the main to the hydrogen *atom*, and not the molecule. I regard the disentanglement of this spectrum into its component bands and series as the most fundamental problem of modern spectroscopy. It is the great simplicity of the formula for the Balmer series which renders it so easy to construct physical theories to account for it. These theories are, nevertheless, unable to carry conviction if they do not provide for a much more extensive spectrum of the hydrogen atom, and no theory has yet even begun this task, which is one of great difficulty in the case of an atom believed to contain only one electron.

I have naturally confined my attention mainly to the more fundamental matters which relate to the simplest chemical atoms. Time is too short to enter into many other interesting points, such, for instance, as the fine structure of the hydrogen lines, which Dr. Merton and I have been elucidating recently. It is now known, for instance, that the Balmer series is a principal series, and not a diffuse series, as hitherto assumed. This result alone has an important bearing on the mechanism of production of this series from an assigned atom. If we were to discuss the spectra of mixed gases or of molecules, a host of problems remains to be solved, and can only be solved by co-operation of the physicist and chemist. To give only one instance, we may ask a question. In a mixture of calcium and barium molecules, with perhaps a temporary association CaBa , what relation would the spectrum of such a molecule have to those of the calcium and barium molecules? The whole question of the spectra of the temporary associations found in vacuum tubes, and analysed by Sir J. J. Thomson's method of "positive rays," remains for solution. All such work will bear on the problem of atomic structure, for an atom is not satisfactory unless it also forms molecules the spectra of which are deducible from that of the atom. No present model of a hydrogen atom appears as yet to have succeeded.