LETTERS TO THE EDITOR.

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The Spectra of Hydrogen and Helium.

IN a letter to NATURE of February 11, Prof. J. W. Nicholson discusses the recent interesting experiments of Mr. Evans on the spectrum emitted from a vacuum tube containing highly purified helium and subject to a heavy discharge. Evans found that the 4686 series and the Pickering series can be obtained in a helium spectrum showing no trace of the ordinary hydrogen lines. These series were observed a few years ago by Prof. Fowler by sending a heavy discharge through a mixture of hydrogen and helium; previously they had been observed only in star spectra. In addition, Evans observed that under the same conditions as the 4686 series and the Pickering series a new series of lines appeared, which, with regard to position and intensity, could be united with the Pickering series into a single series of the same type as the 4686 series. The lines of the new series have wave-lengths very close to the hydrogen lines of the Balmer series. In his letter Prof. Nicholson expresses the opinion that Evans's results cannot be used to discriminate between the different theoretical interpretations of the spectra in question, since the new series as well as the Pickering series can be deduced from the 4686 series on the general principle of combination of spectral lines. I cannot agree with this view, and should like here to state my reasons.

According to the theory proposed by Rydberg, and generally accepted for a long time, all the lines in question are ascribed to hydrogen. This theory is based on a supposed analogy between the hydrogen spectrum and the spectra of the alkalies. The Balmer series, the Pickering series, and every second member of the 4686 series are considered as diffuse series, sharp series, and principal series.

According to the theory proposed by the writer, the series spectrum of hydrogen is simply represented by the formula

$$\nu = K\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad \ldots \ldots \quad (1)$$

including only the Balmer series, the Ritz series in the ultra-red, and the series in the ultra-violet recently observed by Lyman. The other series are all ascribed to helium and represented by the formula:

$$\nu = 4K'\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad \ldots \ldots \quad (2)$$

including the 4686 series, the Pickering series, and Evans's new series. K' is not exactly equal to K, though very nearly so, the theoretical value for the ratio K'/K being 1.00041. The theory rests upon a certain application of the quantum theory to the energy of the nucleus atom, and essentially involves the combination principle. While the ordinary helium spectrum is supposed to be emitted from a helium atom which has lost a single electron, spectrum (2) is emitted, according to the theory, from a helium atom which has lost both its electrons. If spark spectra result from the removal of two electrons from the atom, formula (2) should correspond to the spark spectrum of helium, while hydrogen, which is supposed to have only one electron in the atom, cannot give a spark spectrum.

Since the numerical relations between the different series claimed by the two theories are not exactly the same, it would be possible at once, as mentioned by Prof. Nicholson, to discriminate between the theories if the wave-lengths of the lines were exactly known. It seems that both the measurements of Fowler and Evans are in close agreement with formula (2), but that it would be difficult to reconcile Evans's redetermination of the wave-length of the Pickering lines with Rydberg's assumption that the Balmer series and the Pickering series have the same limit. Quite apart, however, from the question of the exact numerical relationship between the series, it seems that fundamental difficulties in Rydberg's view are brought to light by the experiments of Fowler and Evans. Fowler's observation that the 4686 series contains twice as many members as the series predicted by Rydberg, and Evans's observation of the new series accompanying the Pickering series, destroy completely the simple analogy with the alkali spectra which forms the basis of Rydberg's theory. If, as Prof. Nicholson proposes, we look upon the Pickering series and the Evans series as a simple combination series deduced from the 4686 series, the contrast with the alkali spectra seems even more striking, since then apparently no sharp series is observed. On the other hand, it will be noticed that this simple relation between the series is an immediate consequence of formula (2), and that Evans's observation makes the representation of this formula more complete than before since only every second member of the series corresponding to $n_1 = 4$ was previously observed.

I must confess, however, that perhaps the strongest objection to Rydberg's view seems to be the entirely different chemical conditions for the appearance of the Balmer series and the other series, so clearly shown by Evans's experiments. This difference has no analogy in the appearance of the diffuse series in the alkali spectra. I am afraid that it may not seem reasonable to emphasise this objection so strongly, since it, of course, has been contemplated by spectroscopists ever since the theory was proposed, but it appears that the basis for the consideration of this question recently has entirely changed. Rydberg's theory of the hydrogen spectrum offered not only an adequate representation of the evidence at hand at that time, but it was apparently the only way to bring the Pickering series into line with Rydberg's own fundamental investigations on the general relations between spectral series. However, Fowler's recent important work on series in spark spectra has shown that these spectra obey laws of exactly the same character as the ordinary arc spectra, with the only exception that the Rydberg constant is replaced by a constant four times as large. Consequently formula (2) corresponds to the general formula for series in spark spectra exactly as formula (1) corresponds to the general formula for series in arc spectra. It would therefore appear that at present there is scarcely sufficient theoretical evidence to justify us in disregarding the direct evidence as to the chemical origin of the lines given by Evans's experiments.

It may be of interest in this connection to mention that the above conclusions seem to be supported by spectroscopic evidence of an entirely different character. Recently Dr. Rau (*Sitz. Ber. d. Phys. med. Ges. Würzburg,* 1914) has made some interesting experiments on the minimum voltage necessary to produce spectral lines. He finds that about 30 volts are necessary to produce the lines of the ordinary helium spectrum, and that the voltage necessary to produce the different lines and series in this spectrum differ only by a few volts. On the other hand, he finds that the lines of the Balmer series appear with

a voltage of only about 13 volts, while about 80 volts are necessary to produce the lines of the 4686 series and the Pickering series. According to the theory of the writer, the energy necessary to remove the electron from the hydrogen atom corresponds to a fall of an electron through a potential difference of 13·6 volts, while the energy to be used in removing one electron from the helium atom corresponds to a fall of 29·0 volts, and in removing both electrons to a fall of 83·4 volts.   N. BOHR.

Physical Laboratory, University of
    Manchester, February 21.

X-Ray Fluorescence and the Quantum Theory.

THE experimental conclusions which I briefly outlined in a letter to NATURE of February 18 point directly to a theory of X-ray fluorescence and of the emission of radiation in quanta, which certainly bears a resemblance to Bohr's theory of line spectra. The experimental evidence obtained is, however, so direct that there seems little possibility of escape from the conclusions given below. Indeed, the theory was forced upon the writer directly by the experimental results, and it was only afterwards that he was reminded of some similarity with the theory of Bohr based on the Rutherford atom.

It is an experimental fact that in the case carefully investigated (and obviously in many, if not in all, other cases), the ejection from an atom of an electron associated with a fluorescent X-radiation of frequency n necessitates an absorption of energy greater than the kinetic energy carried away by the electron by approximately the energy (hn) of one quantum of radiation of frequency n. Thus :—

(1) Total absorption per electron emitted $= \frac{1}{2}mv^2 + hn$ (approximately)—that is, the energy required to separate the electron (a K electron, say) from the parent atom, is approximately equal to the energy of a quantum of the fluorescent radiation of series K associated with that electron.

The energy of a quantum of radiation may therefore be regarded as the mutual potential energy of the separated atom and electron, measured from the zero given by the electron in its normal position and state. When the displaced or any other electron falls back into the position of the displaced electron, the energy is re-emitted as a radiation characteristic of the atom, and this, of course, in definite quantity. So much may be claimed as at any rate giving a first approximation to the truth. The results of experiments, however, suggest the possibility of the necessity for some modification of this theory in detail, though not in principle. For in the one case thoroughly investigated we get a nearer approximation to the experimental results by writing

(2) Total absorption per electron emitted $= \frac{1}{2}mv^2 + hn_K + hn_L$, where n_K and n_L are the frequencies of the K and L fluorescent radiations respectively. As the third term (hn_L) is at its maximum value only about 7 per cent. of the whole, it is impossible at this stage to say definitely whether or not it expresses a physical fact. This term was, however, suggested by a consideration of the probable process following the ejection of a K electron. The relation indicates that *possibly* the energy required to free a K electron is equal to the sum of the energies of quanta of K, L, and any other fluorescent radiation of lower series M, N, etc.—presumably originating in vibrations in the outer rings of the atom.

If we accept this provisionally it means that the energy of a quantum of K radiation is that required to displace a K electron into the position of an L electron, while the energy of a quantum of L radiation

is that required to displace an L electron into the position of an M electron, and so on. Such a process may never occur; it is, however, a convenient way of expressing the energy required completely to eject the electron in terms of steps which can only be regarded as extremely probable in the inverse process involving radiation.

Thus the energy of a quantum of K radiation is left in the atom from which a K electron is hurled; or *possibly* the energies of one quantum of each of the fluorescent radiations, K, L, M, etc., are left in the atom. This energy must, of course, be radiated while the atom is regaining its original configuration by the absorption of an electron into the K position. It seems probable, however, that the readjustment of the atom and the principal radiation take place even before the atom as a whole regains an electron, by an L electron falling into the position of a displaced K electron, an M electron replacing an L electron, and so on; only the final stage of the readjustment being completed by the absorption of an electron into an outer depleted ring.

It is obvious in this case—unlike that studied by Bohr—when and why an electron falls into an inner ring; it is simply subsequent to and due to the removal of an inner ring electron. No new principle of radiation is involved, yet it accounts for radiation taking place in quanta. We should thus expect L radiation to be associated with the emission of K electrons as well as with L electrons. Search for such a radiation is at present being made. Pointing to the probability of such an associated radiation is the fact that when hn_L becomes a smaller fraction of the whole absorption, the discrepancy found when it is omitted, as in equation (1), diminishes. Not only is this so, but the energy of the corpuscular radiation and of the K fluorescent radiation actually emitted, do not quite fully account for the whole energy absorbed. The discovery of the L radiation in calculated intensity would give almost perfect agreement.

In spite of these indications the writer hesitates to make a definite statement about the physical reality of the third term concerned with L radiation; experiments will very soon decide the point.

In either case we have the direct evidence that the energy of a quantum is simply energy absorbed in removing the corresponding electron from its normal orbit; it is the energy afterwards set free, presumably when the electron returns.

It is hoped that experiments now being undertaken will determine also if X-ray fluorescence—that arising from the vibration of inner ring electrons—can be appreciably delayed by retarding the return of the ejected or other electrons from outside the atom. It is more probable that X-ray *phosphorescence* will not be detected, the readjustment of the interior of the atom taking place immediately after the ejection of an inner electron, and the final absorption of an electron into a surface ring being the only part of the process susceptible to external conditions. The subject can, however, only receive adequate treatment in communications to other journals.   C. G. BARKLA.

University of Edinburgh, February 27.

The Physical Properties of Isotopes.

PROF. SODDY's letter in NATURE of February 4 would seem to lead to certain interesting conclusions about the structure of the atom. It is easy to show that two elements of different atomic weight must differ either in their chemical or in their physical properties. If elements are inseparable chemically their affinity A must be equal. Now $A = -T\int_0^T \frac{U}{T^2} dT$ if T is the tem-