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Bakerian Lecture: On X-Rays and the Theory of Radiation

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IX. Bakerian Lecture.—*On X-rays and the Theory of Radiation.*

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INTRODUCTION.

Of the various possible methods of approaching present day problems of electromagnetic radiation—particularly the problem of reconciling with the older electromagnetic theory those experimental facts which have led to the formulation of the Quantum Theory—the most profitable is probably to be found in the study of the phenomena of Röntgen radiation.

Primarily this is due not to the accuracy which may be attained in measurements upon radiation of this type, though this is an important factor, but to the fundamental nature of the phenomena themselves. The result of this is shown both in the simplicity and in the generality of the laws observed.

My purpose in this lecture is to call attention to some of the most significant experimental facts bearing on the nature of the processes resulting in the emission of X-rays—dwelling especially on the work I have been able to do in the last few years. Some of this I indicated in short notices appearing in 'Nature'* at the beginning of last year, but the communications were too brief, perhaps, to be fully intelligible. Although the war has naturally retarded the work since then, certain facts have been established sufficiently conclusively, and, what is important, are sufficiently simple in themselves, to justify a further and more complete announcement. And though the theory put forward will provide subjects for investigation for some years to come, much might be lost by waiting for more complete evidence.

I therefore propose to give in outline the experimental basis for this theory. (A detailed description of the experiments themselves may be left for publication elsewhere.) In addition, the results of earlier work which has a direct bearing on recent problems of radiation will be incorporated. The significance of much of this work has probably been overlooked in discussions on the theory of radiation.

The known processes resulting in the emission of X-rays will be considered under

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* "Problems of Radiation," 'Nature,' February 18, 1915, and "X-ray Fluorescence and the Quantum Theory," 'Nature,' March 4, 1915.

[Published, August 29, 1917.

three heads, the names we apply to the radiations produced :—(1) scattered X-rays; (2) fluorescent (characteristic) X-rays ; (3) primary X-rays. This order has been chosen as probably leading to the greatest simplicity of treatment.

SCATTERED X-RADIATION.

When X-rays traverse matter of any kind, that matter becomes the source of a radiation of X-rays indistinguishable in kind from the primary radiation exciting it.* What in many ways appears to be simply a re-directed or scattered primary beam is, however, more truly a new radiation. The similarity between the primary radiation and the secondary radiation of this type, while perhaps tending rather to mask the full importance of the phenomenon in reality enhances the value of the results obtained. The simplicity of necessity permits of less ambiguity in the interpretation of the experimental results.

The established facts which have an obvious bearing on the theory of radiation may be briefly stated.

1. Slight polarization of the primary radiation—as shown by the variation in intensity of radiation scattered around such a primary beam,†
2. Polarization of the scattered X-radiation, proceeding in a direction perpendicular to that of propagation of the primary radiation‡ (such as is shown in light scattered from the sky), and
3. The close agreement between wide limits, of the theoretical and experimental distribution of radiation scattered in a plane containing the direction of propagation of the primary beam,§

are inexplicable except on the transverse wave theory.

These experimental results were, in fact, looked for as necessarily following from such a theory. Similar results may, however, be obtained by transverse waves along strings or flexible tubes. An arrangement of flexible tubes may be used in lecture demonstrations illustrating mechanical phenomena exactly analogous to the three above-mentioned X-radiation phenomena.

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* BARKLA, 'Phil. Mag.,' June, 1903; May, 1904; June, 1906; February, 1908.

† BARKLA, 'Nature,' March 17, 1904; 'Phil. Trans. Roy. Soc.,' vol. 204, 1905; 'Phil. Mag.,' June, 1906.

‡ BARKLA, 'Roy. Soc. Proc.,' A, vol. 77, 1906.

§ BARKLA, 'Phil. Mag.,' February, 1908; BARKLA and AYRES, 'Phil. Mag.,' February, 1911. When the secondary radiation experimented upon is *purely scattered radiation*, the distribution experimentally determined agrees with the theoretical distribution remarkably closely between the limits of 180° and about 30° for θ. On the other hand the discrepancy between the two becomes very marked for small values of θ, indicating either the necessity for some modification of the simple theory in this direction, or possibly the superposition of other effects. Various possibilities might be suggested, but they could not at present be regarded as more than speculations.

Difficult as the first two results would be to explain on any entity or quantum theory—that is, any theory assuming radiation itself to exist in definite indivisible bundles or quanta—perhaps the strongest evidence against this is provided by the third fact stated above. The distribution calculated and given by the expression $I_\theta = I_{\pi/2}(1+\cos^2\theta)$ where I_θ is the intensity of radiation scattered in a direction making an angle θ with that of propagation of the primary beam depends essentially on a steady variation with direction, not of a number of indivisible entities, but of the energy density around a single radiating charge—an electron in this case.

4. Further, measurements of the energy of radiation scattered* have furnished one of the most searching and critical of tests that could be applied to any theory.

In the early experiments it was found that the intensity of the radiation scattered from light elements was simply proportional to the mass of scattering substance traversed.† That is, the intensity of scattering per atom or molecule of scattering substance was proportional to its atomic or molecular weight—independent of density, chemical combination, or state of ionization of the substance. It thus became evident that neither atoms, molecules, nor gaseous ions were the scattering units, but that the scattering particles were the constituent electrons, and that in general, for light atoms, the number per atom was proportional to the atomic weight.

Using the result of a calculation given by Sir J. J. THOMSON, for the fraction of a beam lost by scattering per centimetre of its path,

$$f = \frac{8\pi}{3} N \frac{e^4}{m^2} \mu^2 ,$$

where N is the number per cubic centimetre of particles of charge e and mass m, it was calculated that the number of electrons per atom was several times the atomic weight. With the much more accurate data available for N, $\frac{e}{m}$, e, a few years ago I showed that the intensity is such as on the old spreading wave theory would be given by 1 electron per atom of H, 6 per atom of C, 7 per atom of N, 8 for O, 15 or 16 for S, &c.

These results concerning the constitution of the atom have been confirmed by independent evidence and are becoming generally accepted. Thus RUTHERFORD,‡ from experiments on the scattering of α particles, arrived approximately at the complementary conclusion—that the central nucleus charge of an atom is $\frac{we}{2}$ where w

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* BARKLA, 'Phil. Mag.,' May, 1904; 'Jahrb. d. Radioaktivität u. Elektronik,' 1908; 'Phil. Mag.,' May, 1911.

† Hydrogen scattered about twice as much as the other elements, mass for mass. This at the time was thought to be due to impurity. CROWTHER, however, later obtained a value only slightly lower than this.

‡ 'Phil. Mag.,' May, 1911.

is the atomic weight and e the electronic charge. (This nucleus, together with the number of electrons found from the scattering of X-rays, constitutes a neutral atom.)

BOHR[*] on certain assumptions has shown that such an atom is capable of forming the basis of an explanation of the line spectra of hydrogen and helium, agreeing in a most remarkable way with experimental fact.

MOSELEY,[†] too, has given further evidence in support of the conclusion as to the number of electrons per atom. His "atomic numbers" are identical with the values given above.

This agreement is probably much more remarkable and significant than it at first sight appears. For apart from the orthodox electromagnetic theory of radiation, the intensity of the scattered radiation might have been anything between say $\frac{1}{1000}$ part and 1000 times what was experimentally observed; yet the value experimentally determined twelve years ago—long before the precise significance of the results could be realized—agrees within a very small fraction with that to be expected on the modern conception of the atom and the old electromagnetic theory of radiation. Originally, while assuming this theory to hold, I used it to determine the number of electrons per atom. It is, however, perfectly legitimate now that the conclusions have been confirmed as indicated above, to use this agreement as evidence in support of this theory of radiation. The chances of such an agreement being accidental are almost infinitesimal.

Looking at the result in a somewhat different way, if for instance we imagined the gaseous ions to be the scattering units and calculated the number necessary in order to produce the scattering experimentally observed, we should find a number some millions of times the total number of molecules present in the scattering substance, that is, a number probably trillions of times too many. Yet applied to determine the number of electrons, the theory gives the number now accepted, certainly within a possible 5 to 10 per cent. error.

The theory on which this is based is the spreading wave theory. It assumes that the scattered radiation is the radiation resulting from the disturbance in electrons while under the influence of—in fact while controlled by[‡]—the primary radiation. Thus every electron in the matter traversed is influenced by every wave in the primary radiation passing over it, and receives a definite acceleration, f say, which is proportional to the electric intensity in the primary beam. The rate of radiation of energy from an electron with charge e and acceleration f is $\frac{2}{3}\mu e^2 f^2/\mathrm{V}$—as first shown by LARMOR. This summed up for all electrons gives the rate of emission of scattered radiation by those electrons; and this is readily expressed in terms of the rate of transmission of energy of primary radiation through the substance, for the acceleration

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[*] 'Phil. Mag.,' November, 1913.

[†] 'Phil. Mag.,' December, 1913.

[‡] At least the motion of the electrons resulting in radiation is not appreciably affected by atomic forces.

f is simply $\frac{Xe}{m}$ where X is the electric intensity in the primary wave producing the disturbance. (See Sir J. J. THOMSON'S 'Conduction through Gases.')

Thus the theory assumes that radiation can take place from these electrons in any quantity whatever, and is not confined to units or quanta; that radiation is a continuous process not depending on any limiting or critical condition.

5. Again, in perfect agreement with this theory, I have found that the intensity of the radiation scattered from light elements varies little with the wave-length of the primary radiation. This indeed is also indicated by the above equation, the derivation of which was based on the assumption of independent action of the electrons.

6. And more recently* it has been found that the intensity from the heavier atoms in which the constituent electrons are more closely packed, increases rapidly and continuously with the wave-length of the radiation unless this is very small. Such a result is to be expected on the wave theory when the wave-length becomes comparable with the size of the atom; ultimately a group of electrons and not an individual electron moves as a whole and becomes the scattering unit.† Further experimental results support this conclusion, and indicate that the radiation is emitted not in quanta but in any quantity, and that the process is a continuous process.

There is thus in the phenomena of scattering not only no suggestion of a quantum or entity in radiation, or of any discontinuity in the process of radiation involved, but there is some of the strongest positive evidence against any such theory. The tests which have been applied are the most searching and sensitive; the results appear conclusive. The phenomena observed become meaningless on any quantum or entity theory.

Absorption.

As in the transmission of X-rays (particularly of short wave-length) through matter consisting of light elements only, the energy absorbed is practically all re-emitted as scattered X-radiation, the quantities *radiated* by each electron are identical with those *absorbed.* When there is little other absorption, viz., that associated with the emission of corpuscular and fluorescent X-radiation, the total absorption may be approximately calculated from the number of electrons in the matter traversed. It follows that this process of *absorption* is also a process which takes place in any quantity whatever, and is unlimited by any critical condition.

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* BARKLA and J. DUNLOP, 'Phil. Mag.,' March, 1916.

† When the group comprises all the electrons in the atom, the scattering per atom becomes on this theory proportional to the (atomic number)^2, instead of to the atomic number, when the electrons scatter independently.

FLUORESCENT (CHARACTERISTIC) X-RADIATION.

Each element when traversed by X-rays emits X-radiations characteristic of the element;* each characteristic radiation is unaffected by changes in the physical condition or state of chemical combination of the radiating element, and its quality is independent of that of the exciting primary radiation. But only primary radiations of shorter wave-length are able to excite the characteristic X-radiation (an extension of STOKES'S law).†

All radiations hitherto definitely observed have fallen into two series—the K and L series.‡ (Experiments made within the last year, and briefly described in this paper, have established the existence of a third, a higher frequency series, which will be called the J series).§

The absorption method of analysing a radiation showed radiation of the K series from a particular element to be so homogeneous that it was regarded as giving a spectral line—the K spectral line; but the possibility of the L radiation consisting of more than one line was suggested by an obvious heterogeneity in the L radiation.

Interference experiments,‖ however, have shown that both the K and the L radiations give spectra consisting of a number of neighbouring lines. In the greater portion of what follows these radiations of neighbouring wave-length will, however, be classed together as K or L radiations simply.

A characteristic radiation, unlike the scattered radiation, is uniformly distributed around a polarized primary beam¶ and also in a plane containing the direction of propagation of primary radiation.

The intensity of a characteristic radiation** varies in a definite regular way with a variation in the wave-length of the exciting primary beam, rising rapidly and afterwards falling more gradually as the wave-length of the primary diminishes.

The uniformity in the distribution of the characteristic radiation around the radiating substance shows that in contrast with the process of emission of scattered radiation, the emission of a characteristic radiation is absolutely uncontrolled by the primary radiation exciting it. The phenomenon of emission is not an immediate

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* BARKLA, 'Nature,' March 9, 1905; 'Phil. Trans. Roy. Soc.,' January, 1905; 'Roy. Soc. Proc.,' January, 1906; 'Nature,' February 15, 1906; 'Phil. Mag.,' June, 1906; 'Jahrb. der Radioaktivität u. Elektronik,' April, 1908. BARKLA and SADLER, 'Phil. Mag.,' September, 1907; 'Nature,' February 13, 1908.

† BARKLA, 'Jahr. der Rad. u. Elek.,' April, 1908; 'Proc. Phil. Soc. Camb.,' May, 1909.

‡ BARKLA, 'Proc. Phil. Soc. Camb.,' May, 1909; 'Phil. Mag.,' September, 1911; BARKLA and NICOL, 'Nature,' August 4, 1910; 'Proc. Phys. Soc. Lond.,' December, 1911.

§ An M series has recently been observed by SIEGBAHN and others.

‖ BRAGG, 'Roy. Soc. Proc.,' 1914; DE BROGLIE, 'Comptes Rendus,' 1914–16; MOSELEY, 'Phil. Mag.,' 1913–14; SIEGBAHN, 'Jahrbuch der Radioaktivität u. Elektronik,' 1916.

¶ BARKLA, 'Phil. Mag.,' February, 1908; BARKLA and AYRES, 'Phil. Mag.,' February, 1911.

** BARKLA and SADLER, 'Phil. Mag.,' May, 1909.

result of the passage of the primary beam, but arises only indirectly from it; the process is dependent on some critical condition, as evidenced by STOKES's law. Here at once we see the possibility of the applicability of some kind of quantum theory.

The most significant evidence as to the origin of the characteristic radiation comes from a study of the accompanying phenomena of (1) absorption of the exciting primary radiation; and (2) emission of electrons by the radiating substance, in the form of a corpuscular radiation. It is necessary here to introduce a brief account of these phenomena.

Absorption.—The absorption of a primary radiation is due to various causes which can be quite readily distinguished;* they are distinct and apparently independent absorptions. Thus the total absorption in a particular element of radiations of various wave-lengths may be represented by a curve of the form shown in fig. 1, the ordinates in which indicate the absorptions of radiations whose wave-lengths are given by the abscissæ. The curve is of simpler form however, if instead of wave-lengths we plot as abscissæ the absorbabilities in some standard substance which has no spectral lines in the part of the spectrum considered.† Then the absorption curve takes the form of fig. 2. This, however, for the sake of clearness is not drawn to scale. The lower portion of the figure gives the spectral lines of the substance traversed.‡ Proceeding

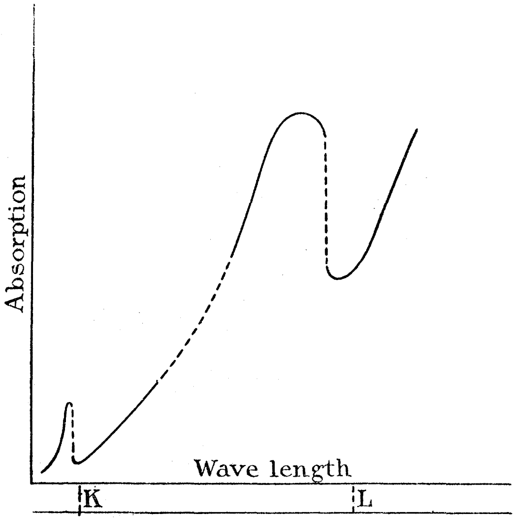

Fig. 1.

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* BARKLA and SADLER, 'Phil. Mag.,' May, 1909; BARKLA and COLLIER, 'Phil. Mag.,' June, 1912; BARKLA, 'Proc. Phil. Soc. Camb.,' May, 1909; BARKLA and SADLER, 'Nature,' July 16, 1908, and March 11, 1909.

† Or the (wave-length)^3 approximately, as HULL and RICE have shown.

‡ These curves do not show the exact relation in the regions of very rapid change, as the radiations used were not perfectly homogeneous.

from right to left, *i.e.*, from long to short waves, we see that sudden increases in absorption occur when the primary radiation becomes of shorter wave-length than the radiations characteristic of the absorbing substance—that is, when the characteristic radiations begin to be excited in the absorbing substance—and that the absorption afterwards gradually approaches proportionality with the absorption in the standard substance—as shown by the approximation to a straight line through the origin. Thus the line ABB′ shows what would be the absorption of radiations of various wave-lengths if there were no L characteristic radiation excited in the absorbing substance. The rise as shown by the portion BCD is associated with the emission by the absorbing substance of the fluorescent X-radiation of series L. The difference between the ordinates of the curve BCD and BB′ gives the absorption associated with the emission of L radiation, or what we shall call the "L" absorption (E_L). In a similar fashion we can get the "K" absorption E_K. The lower portion of fig. 2 indicates the various independent absorptions S, E_K, E_L, $E_{M,N\ldots}$ in separate curves where S = energy absorbed and re-emitted as scattered radiation, E_K, E_L, $E_{M,N\ldots}$ = energy absorbed in association with the emission of characteristic radiations of series K, L, and M, N, ... respectively. The absorption S due to the process of scattering is approximately independent of wave-length, so is represented by a horizontal line. It however rises considerably at the long wave-length end if the wave-length be sufficiently great.

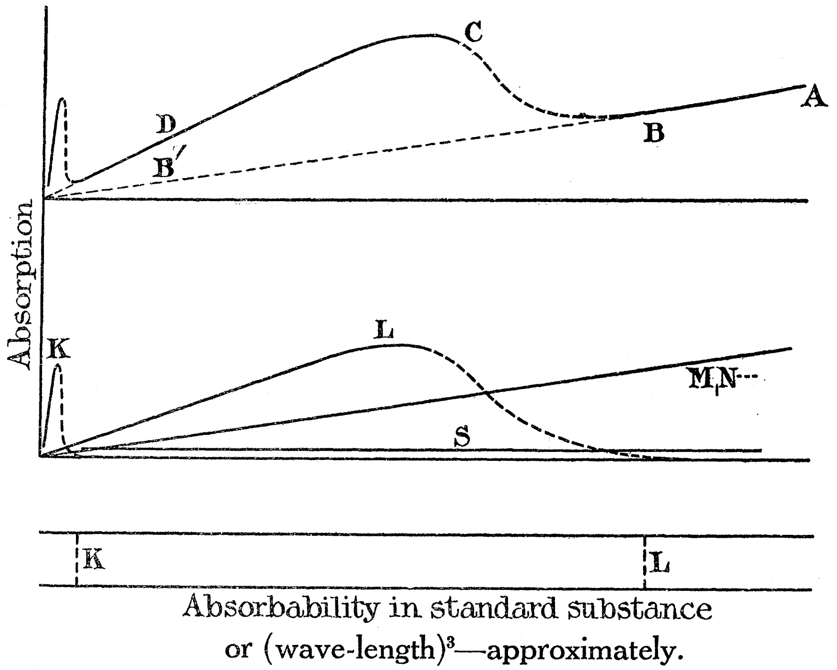

Fig. 2.

Thus the total absorption E may be written

$$E = S + E_J + E_K + E_L + \ldots\ldots$$

in which all the right-hand terms appear to be independent quantities.

Corpuscular Electronic Radiation.—In addition it may be shown that the corpuscular radiation (*i.e.* the radiation consisting of high speed electrons emitted from substances exposed to X-rays) may be divided into several distinct groups, each associated with the emission of a fluorescent X-radiation of a particular series; thus the total corpuscular radiation $C = C_J + C_K + C_L + \ldots$ where C_J, C_K, C_L, are corpuscular radiations definitely associated with the emission of J, K, and L characteristic radiations respectively. This we shall proceed to show.

C. T. R. Wilson's condensation experiments* show that X-ray ionization is due to the corpuscular radiation which the X-rays excite in the gaseous substance ionized. (All other investigations of less direct nature which at first appeared to indicate this only to a partial extent may now be shown to confirm this conclusion as accurately as the possible errors of experiment allow.)† Wilson's experiments indicate, too, that there is little or no variation in the velocity of the electrons ejected by X-radiation of one wave-length. For the length of path of an electron was shown by Whiddington to vary as the fourth power of the velocity; consequently an electron with half the maximum velocity of ejection would have a path only one-sixteenth that of the other. If then the velocities of ejection ranged from zero to the maximum, Wilson's experiments would show a very large number of short paths. Simple observation of the photographs showing the trails of the ejected electrons is sufficient to convince one that little variation of initial velocity exists, and that such variation as is observable in the lengths of the trails is probably due either to the heterogeneity of the primary beam, or to fore-shortening of the trails. Ionization of air by homogeneous X-rays is therefore through the agency of electrons emitted with one velocity, approximately, if not accurately.

From experiments on ionization it may readily be shown that the corpuscular radiation consists of several independent groups each associated with the emission of a particular fluorescent X-radiation. For the ionization of a substance by X-rays of varying wave-length varies with the wave-length of these rays in a manner similar to that of the absorption. Thus the ionization in a substance R say, is proportional to the ionization in a second substance for a range of wave-lengths not near to a spectral line of either on its shorter wave-length side. As the wave-length of the primary X-radiation is diminished beyond that of a spectral line of R, there is a sudden rise in the ratio of ionizations, and the ratio gradually approaches a constant

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* 'Roy. Soc. Proc.,' 1912.

† This refers to the investigations of Barkla, Bragg, Beatty, Barkla and Philpot. Bragg was the first to insist that ionization was *entirely* due to the high speed corpuscles.

but higher value until another series of spectral lines in one of the substances is passed when a further change occurs. This is shown in fig. 3, in which the upper portion shows the ratio of ionizations plotted against wave-length of the X-rays used. In the figure the horizontal broken line indicates the relation that would have existed if there had been no radiation characteristic of R within the range of wave-lengths used, and no corresponding increase in the corpuscular radiation from the substance R. The rise of the curve above the broken line gives the increase in ionization associated with the emission of the fluorescent X-radiation of series K, say. As ionization is due to the emission of high speed electrons by the substance, the difference between the two curves is due to additional electrons emitted in association with the fluorescent characteristic X-radiation of series K. We thus see and are able to measure accurately the effect of what will be called the K corpuscular radiation, to distinguish it from the L, M, N corpuscular radiations which are emitted in association with the similarly named fluorescent (characteristic) X-radiations.

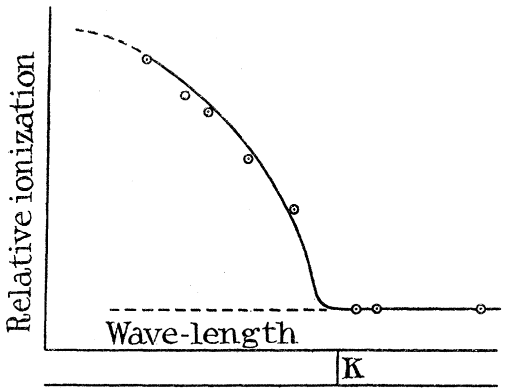

Fig. 3.

As it has recently been shown* that there is no appreciable difference between the velocities of these electrons of different groups K, L, &c., it follows that ionization experiments give us accurate data for determining the relative numbers of electrons in the various groups emitted by a substance when exposed to X-rays. This method has been used in some preliminary determinations which are described later.

Energy Relations between the Corpuscular and the Fluorescent Radiations, and the Exciting Primary Radiations.

In investigating the process of emission of the characteristic X-radiation when this is excited by another shorter wave-length radiation, a study of the relation between the energies of primary radiation absorbed and the associated corpuscular and fluorescent radiations emitted, is of fundamental importance. It is, however, necessary first

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* Barkla and Shearer, 'Phil. Mag.,' December, 1915.

of all to analyse the absorption of the primary radiation into J, K, L, M, ... and S absorptions, the secondary corpuscular radiation into J, K, L, M corpuscular radiations, and the secondary X-radiations into J, K, L, M ... and S radiations, and observe only the relations between the corresponding quantities, or at any rate to do this for one particular series, say the K series, with primary radiations of various wave-lengths.

Energy of Fluorescent (*Characteristic* X-*radiation*).

The energy of the fluorescent X-radiation was first measured and expressed in terms of the energy of the absorbed primary X-radiation by BARKLA and SADLER.* In this as in all similar measurements the energies of radiations of different wave-lengths were compared by their total ionizing powers. With a primary radiation of wave-length considerably shorter than that of copper K radiation, the energy of the X-radiation emitted was about 33 per cent. of the energy absorbed, or about 40 per cent. of the K absorption; with a primary of shortening wave-length the fraction diminished.† For other substances the transformation fraction was of the same order of magnitude.

SADLER,‡ working with approximately homogeneous primary radiations, made a much more systematic and accurate investigation of the energy in the fluorescent characteristic radiations from several substances, and expressed this in terms of the primary energy absorption obtained by BARKLA and SADLER. The results obtained are given in Tables I. and II. Table I. shows the fraction of the *total energy absorbed*

TABLE I.—Giving Fraction (F_K/E) of Total Primary Energy Absorbed transformed into Fluorescent X-radiation of Series K.

Primary radiation.	Wave-length (α_1).	Substance exposed to primary radiation.					
		Cr.	Fe.	Co.	Ni.	Cu.	Zn.
	cm.						
Fe X-radiation (series K)	$1\cdot93\times10^{-8}$	0·151					
Co " (")	$1\cdot78\times10^{-8}$	0·132	(0·098)				
Ni " (")	$1\cdot65\times10^{-8}$	0·125	0·216	0·066			
Cu " (")	$1\cdot54\times10^{-8}$	0·110	0·194	0·262	0·080		
Zn " (")	$1\cdot43\times10^{-8}$	0·095	0·179	0·243	0·289	0·086	
As " (")	$1\cdot17\times10^{-8}$	0·067	0·132	0·170	0·203	0·248	0·281
Se " (")	$1\cdot10\times10^{-8}$	0·055	0·106	0·130	0·163	0·199	0·239
Ag " (")	$0\cdot56\times10^{-8}$		0·058			(0·105)	(0·113)

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* 'Phil. Mag.,' October, 1908.

† At the same rate as the fraction $\frac{\text{absorption in air}}{\text{absorption in Cu}}$. The range of wave-lengths, however, was short.

‡ 'Phil. Mag.,' July, 1909.

which was transformed into K fluorescent (characteristic) radiation; Table II. the fraction of energy of K absorption which re-appeared as K fluorescent radiation. Before generalising from these results, we must eliminate all those which are obviously unreliable. Thus when the primary radiation was of just shorter wave-length than the fluorescent radiation which it was exciting, the latter appeared in only small intensity accounting for from 2 to 10 per cent. of the total absorption (Table I.). Owing to this and to the admixture of scattered radiation, the possible percentage error was extremely high; these results expressed in terms of the special K absorption, which also being a difference effect is difficult to measure with any accuracy in this region, are seen to be irregular and of no value. We must therefore reject these.*

TABLE II.—Giving Fraction (F_K/E_K) of Primary Energy Specially Absorbed—"K Absorption"—transformed into Fluorescent X-radiation of Series K.

Primary radiation.	Wave-length (α_1).	Substance exposed to primary radiation.					
		Cr.	Fe.	Co.	Ni.	Cu.	Zn.
	cm.						
Fe X-radiation (series K)	$1 \cdot 93 \times 10^{-8}$	0·176					
Co ,, (,,)	$1 \cdot 78 \times 10^{-8}$	0·154	(0·504)?				
Ni ,, (,,)	$1 \cdot 65 \times 10^{-8}$	0·145	0·252	0·287 ?			
Cu ,, (,,)	$1 \cdot 54 \times 10^{-8}$	0·127	0·225	0·305	0·288 ?		
Zn ,, (,,)	$1 \cdot 43 \times 10^{-8}$	0·109	0·207	0·282	0·340	0·358 ?	
As ,, (,,)	$1 \cdot 17 \times 10^{-8}$	0·0757	0·150	0·195	0·233	0·288	0·327
Se ,, (,,)	$1 \cdot 10 \times 10^{-8}$	0·0624	0·120	0·149	0·187	0·231	0·278
Ag ,, (,,)	$0 \cdot 56 \times 10^{-8}$		0·062			(0·118)	(0·132)

By plotting the fraction $\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}$ against wave-length of the primary radiation it is seen that the other results are perfectly regular (fig. 4). Of the energy of primary radiation absorbed in association with the emission of K radiation, the greatest fraction is transformed into K fluorescent radiation when the wave-length of the primary radiation differs least from that of the fluorescent radiation. As the wave-length of the primary radiation diminishes the fraction so

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* A note of interrogation indicates these in Table II. Reference to the corresponding values in Table I. shows them to be based on the experimental determination of small quantities. Their irregularity, where all else is regular, is evidence of their unreliability except as indicating orders of magnitude: the reason is obvious. If these values could be experimentally determined with accuracy, they would probably be quite different from those obtained by the use of a perfectly homogeneous radiation of wave-length given in column II. Still, this fact would not appreciably affect the conclusions drawn below, because the values are compared with corresponding absorptions—that is, with the absorptions of identical radiations.

transformed diminishes also, the relation being almost a linear one within the range of these experiments.

[Originally the writer determined the wave-length of a primary radiation from the speed of the electrons it ejects, *i.e.*, from the equation $\frac{1}{2}mv^2 = hn$, where h is PLANCK'S constants, —v being obtained from WHIDDINGTON'S law. These results are plotted in fig. 4A as they are somewhat more regular than those in fig. 4.]

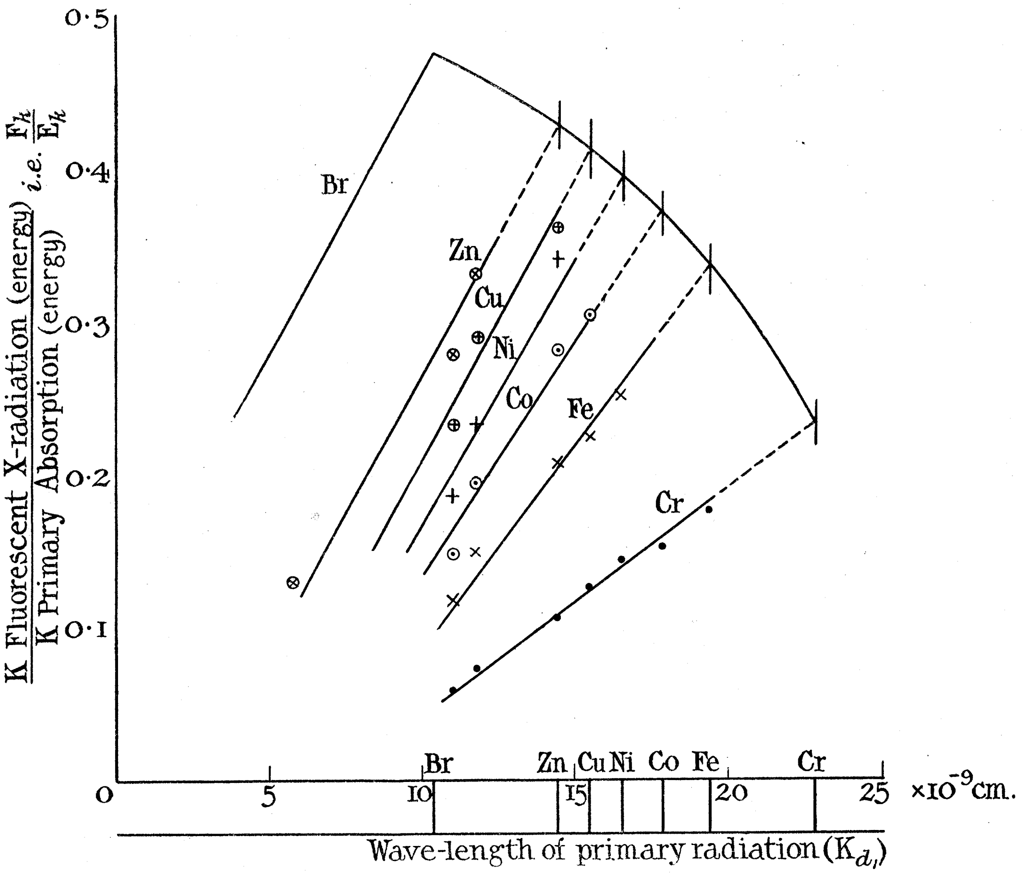

Fig. 4. Showing the fraction of the energy of primary radiation absorbed—K absorption—which is transformed into fluorescent (characteristic) X-radiation of series K, in elements Cr, Fe, Co, Ni, Cu, Zn.

It will be noticed that by producing these lines backward so as to get the transformation fraction when the primary has a wave-length *just* shorter than the fluorescent (characteristic) radiation, this fraction approaches 0·5 for the heavier elements; there is evidence, too, that from the heaviest substances the maximum transformation coefficient does not exceed about 0·5. This is seen by plotting the maximum transformation coefficient for various elements against their atomic weight or by continuing the curve in fig. 4 to the left; the value found by extrapolation is evidently very near to 0·5.

In arriving at these results the energies of primary and fluorescent radiations have been compared by their total ionizing powers. Now the only possible error arising from this assumption occurs when primary and fluorescent radiations differ considerably in wave-length; when the primary is of just shorter wave-length than the characteristic radiation, the error becomes vanishingly small, consequently cannot affect the accuracy of the determination of the maximum transformation coefficients. As will be seen later, there is also strong evidence that even when the primary and fluorescent radiations are widely different in wave-length, the error is certainly not large, if it is of appreciable magnitude.

The substances Cr, Fe, Ni, Co, Cu, Zn in which the transformation coefficients have been determined are not suitable for accurate experimental determination of the energy of the *corpuscular* radiation—nor if they were, would they be the most suitable for the purpose of the present investigation. There is, however, little or no disadvantage in obtaining the transformation coefficients in the substance bromine by extrapolation from the above results, for the results experimentally obtained with elements of lower atomic weight are so regular as to leave little room for error in the results so determined.

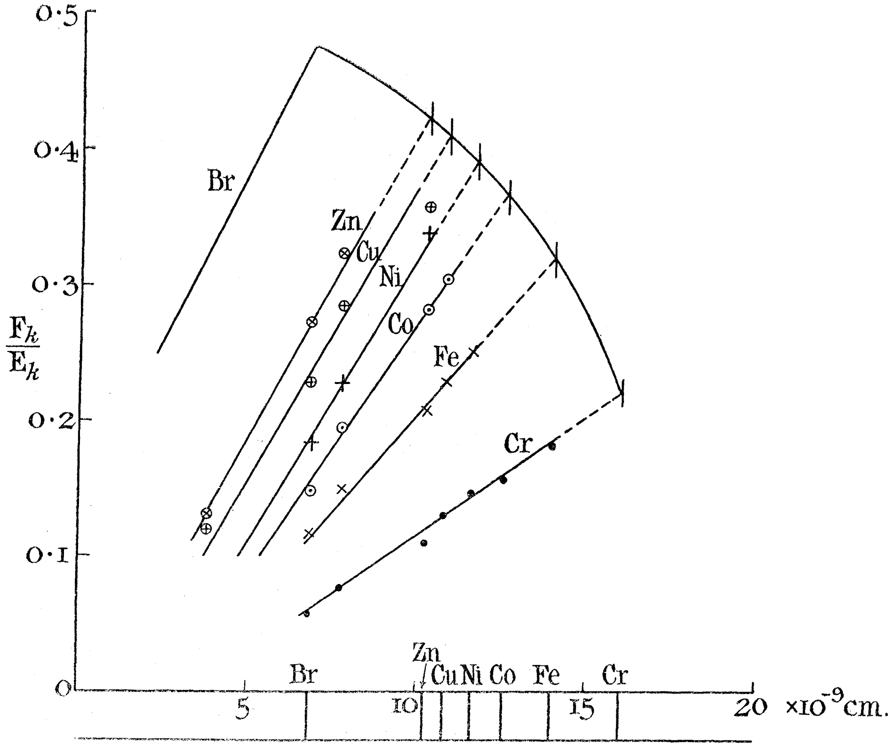

Fig. 4A.

The advantages in the choice of bromine as the experimental substance are (1) it can be obtained in the gaseous state alone or in combination with light elements, so that ionizations may readily be obtained and the energy of corpuscular radiation accurately measured; (2) its K spectral lines are of about the most suitable wave-length for observation of the energy transformations of an exciting primary radiation through a long range of wave-lengths; (3) the energy of fluorescent radiation from bromine is not far removed from the limiting value observed; the behaviour of bromine is thus probably typical of the greatest number of elements, and for this reason the experimental results are the least open to question.

The relation between $\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}$ and wave-length of primary radiation, when bromine is the fluorescent substance, is given in fig. 4, along with the position of the bromine spectral lines of series K, and is reproduced on a different scale in fig. 5, curve F. The continuous portion of the curve we may thus regard as obtained by direct experiment. It should be pointed out that the wave-length of the K_{α_1} line has been adopted throughout.

There is much evidence, too, that the curve must turn through the origin as indicated by the broken line (fig. 5). This represents a small, decreasing, and ultimately vanishing amount of fluorescent X-radiation emitted by a substance exposed to a primary radiation of small and decreasing wave-length.

Thus (1) BARKLA and PHILPOT* showed that when a primary radiation is of much shorter wave-length than any characteristic radiation it excites, its absorption results in the emission of approximately the same number of electrons, whatever the absorbing substance; it follows from the complementary property of the characteristic (fluorescent) X-radiation† that there cannot be varying amounts of fluorescent radiation unless this is so weak that variations would not be observable. This means that all the curves must pass through the same point; the only point through which all the lines in fig. 4 can turn consistently with the experimentally observed results is the origin, or a point near to it.

(2) There is little doubt that air like other substances emits a K radiation which is of very long wave-length compared with an ordinary primary beam of X-rays; yet C. T. R. WILSON'S cloud experiments show few, if any, very short tracks such as would be produced by the re-absorption of such a radiation if emitted in appreciable intensity. We conclude that with a primary radiation of comparatively short wave-length, the fraction of energy transformed into fluorescent X-radiation becomes very small.

(3) Again, in the most accurate measurements by BEATTY and by BRAGG of the corpuscular radiation from metal sheets, the possibilty of the existence of such soft fluorescent radiations in any large quantity has been entirely neglected; yet the results show sufficient consistency to indicate that the characteristic radiations of longer wave-length must account for only a small portion of the energy of primary radiation absorbed.

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* 'Phil. Mag.,' June, 1913.

† See p. 336.

(4) Support for the general conclusion given above can also be obtained from some results incidentally got by BRAGG and PORTER.* I have used these experimental results to determine the fractions as given in Table II., with the results given below:—

Primary radiation.	F_K/E_K.			
	Fe.	Ni.	Cu.	Zn.
Zn X-rays	0·236	0·322	—	—
As X-rays	0·227	0·336	0·394	0·432
Sn X-rays	0·17	0·29	0·34	0·39

All these values are a little higher than SADLER'S and indicate a smaller change with the wave-length of the primary radiation, that is, a smaller slope in the curves of fig. 4;† but the important features to be observed in the results of Table II. are in evidence here. They are so consistent, especially in the case of the radiators of higher atomic weight, that little error in these seems possible.

Briefly and approximately the results of experiments on the heavier elements are these:—When the wave-length (μ) of the primary radiation is just less than that (μ_K) of the fluorescent (characteristic) radiation, of the energy specially absorbed in association with the emission of the fluorescent radiation, nearly 0·5 is re-emitted as fluorescent radiation. As μ becomes less, the fraction diminishes almost proportionately, until for a primary radiation of very small wave-length, the energy of the fluorescent radiation becomes a very small fraction of the energy of the primary radiation (E_K) specially absorbed.

Energy of Corpuscular (Electronic) Radiation.

Though measurements of the energy of the corpuscular radiation emitted by substances exposed to X-rays have been made by a number of investigators, the changes taking place as the wave-length of the exciting radiation passes from one side of a spectral line to the other have not been studied. In addition the results obtained by different investigators have been by no means consistent. It seemed probable that much more reliable results could be obtained by experimenting on substances in the gaseous state, and estimating the energy of corpuscular radiation by the ionization it produced on complete absorption in the gas itself. The method

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* 'Roy. Soc. Proc.,' May, 1911.

† These results from experiments with lighter elements agree more closely with theory than do those of SADLER.

can be most clearly explained by reference to the results obtained in one particular substance, ethyl bromide.

Experiments were commenced by the writer and Mr. M. THOMAS* on the ionization produced in ethyl bromide vapour by a number of approximately homogeneous X-radiations of various wave-lengths. One series of these experiments was made in a very large ionization chamber cylindrical in shape, of length 68 cm., diameter 44 cm., and with an axial electrode connected through a side tube to an external electroscope. Ionization-pressure curves were obtained in the usual way and with great care, both with air and with ethyl bromide in the chamber, all other conditions being similar. After the usual correction for absorption in the gases themselves, the relative ionizations given in Table III. were obtained. Column I.

TABLE III.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Source of X-rays.	Approximate wave-length (K_{α_1}).	Absorbability $\left(\frac{\lambda}{\rho}\right)_{\text{Al.}}$	$\frac{\text{Ionization coefficient in } C_2H_5Br}{\text{Ionization coefficient in air (K, L ...)}}$.	$\frac{\text{"K" ionization coefficient in } C_2H_5Br}{\text{Ionization coefficient in air (K, L ...)}}$.	$\frac{\text{Absorption in } C_2H_5Br}{\text{Absorption in air (K, L, M, \&c.)}}$.	$\frac{\text{"K" absorption in } C_2H_5Br}{\text{Absorption in air (K, L, M, \&c.)}}$.	$\frac{\text{Ionization in } C_2H_5Br \text{ (L, M, N, \&c.)}}{\text{Ionization in air (K, L, M, \&c.)}}$ for equal absorptions of primary radiation.	$\frac{\text{Ionization in } C_2H_5Br \text{ (K)}}{\text{Ionization in air (K, L, M, \&c.)}}$ for equal absorptions of primary radiation.
	cm.							
Cu	$1\cdot54\times10^{-8}$	47·7	50		24·4		2·05	
As	$1\cdot17\times10^{-8}$	22·5	49·3		25·3		1·94	
Se	$1\cdot10\times10^{-8}$	18·9	50·5		26·2		1·93	
Sr	$0\cdot871\times10^{-8}$	9·40	165	115	159	133		0·865
Mo	$0\cdot710\times10^{-8}$	4·70	221	171	190	164		1·04
Ag	$0\cdot562\times10^{-8}$	2·50	279	229	210	184		1·255
Sn	$0\cdot487\times10^{-8}$	1·57	298 × 1·32 = (393)	343	267	241		1·42
Ce	$0\cdot355\times10^{-8}$	0·6	342 × 1·39 = (475)	425	321	295		1·44

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* Shortly after the outbreak of war, Mr. THOMAS was given a commission in the army, so was unable to complete the work he commenced so successfully. He was killed in action on December 31, 1915.

gives the source of the homogeneous rays used to ionize the gases; column II. the approximate wave-length of the radiation; column III. the mass coefficient of absorption of the radiation in aluminium; column IV. the ratio of ionization coefficients in ethyl bromide and in air. Thus when two similar beams of radiation traverse two equally thin layers of ethyl bromide and air at the same pressure and temperature, and in each case the gas absorbs its own corpuscular radiation completely, and all fluorescent radiations of no greater penetrating power than this corpuscular radiation, the ionization in ethyl bromide varies from 50 to about 342 times that in air as the wave-length of the radiation diminishes, or from 50 to 475 times that in air by K, L, M ... corpuscles (electrons) alone, as we shall see later. Of course the ratio of the absorption in ethyl bromide to that in air is also high, and it varies with the wave-length of the radiation used. It should be pointed out, however, that the K characteristic radiation from bromine when excited was allowed to escape without adding its effect to the total ionization measured in ethyl bromide.

Thus when Cu, As and Se "K" radiations were used as ionizing agents, the ionization in ethyl bromide (produced by L, M, N electrons) was about 50 times that in air. But when Sr, Mo, Ag, &c., radiations were used, the "K" corpuscular radiation was emitted by the bromine in ethyl bromide and produced an increase in the relative ionization. Subtracting 50 from the values in column IV. we get the effect of the additional (K) electrons, *i.e.*,

$$\frac{\text{ionization in } C_2H_5Br \textit{ due to K electrons alone}}{\text{ionization in air by K, L ... electrons}},$$

as given in column V. Column VI. gives the relative absorptions of the ionizing radiations in ethyl bromide and air at the same pressure and temperature. Here again there is a large increase when the particular radiation is of sufficiently high frequency to excite the K radiation in bromine. Subtracting the ratio obtained when no K fluorescent radiation was excited from that obtained when it was excited, we get the values in column VII. which consequently represent the

$$\frac{\text{K absorption in } C_2H_5Br}{\text{absorption in air (K, L, M, ...)}}.$$

Dividing values in column IV. by the corresponding values in column VI. we get

$$\frac{\text{ionization in } C_2H_5Br}{\text{absorption in } C_2H_5Br} \div \frac{\text{ionization in air (K, L, ...)}}{\text{absorption in air (K, L, ...)}},$$

which is
$$\frac{\text{ionization in } C_2H_5Br}{\text{ionization in air } (K, L, \ldots)}$$
for equal absorptions of the ionizing radiations (column VIII.).

Similarly dividing the values in column V. by the corresponding values in column VII. we get $\frac{\text{ionization in } C_2H_5Br \text{ due to K electrons}}{\text{ionization in air } (K, L, \ldots)}$ for equal absorptions of the ionizing radiations (see column IX.).

Thus column VIII. gives ionization in ethyl bromide due to L, M, N, &c., electrons, relative to ionization in air due to K, L, M, N, &c., electrons, produced by equal absorptions in the two gases. Column IX. gives ionization in ethyl bromide due to K electrons alone, relative to ionization in air due to K, L, M, N, &c., electrons, for equal absorptions of the ionizing radiation in the two gases. As ionization produced in a given gas by a given homogeneous X-radiation is proportional to the number of electrons in the corpuscular radiation producing that ionization, we see from columns VIII. and IX. that when the exciting primary radiation is of just shorter wave-length than the bromine K radiation, the K absorption is accompanied by the emission of a much smaller number of electrons than is the L, M, N absorption. For instead of 205, 194, 193, L, M, and N electrons, there are emitted 87, 104, 125, 142, 144, K electrons for primary radiations of higher frequency; or for equal absorptions of energy there are only about half as many K electrons emitted as L, M, … electrons, when the primary radiation is of just shorter wave-length than the K characteristic radiation. As primary radiations of shorter and shorter wave-length are used, the number of K electrons emitted more closely approaches the number of L, M, … electrons emitted for an equal absorption of energy of primary radiation. At first sight it appears from column VIII. as though twice as many electrons are emitted from C_2H_5Br as from air when equal absorptions of Cu, As and Se radiations take place. This, however, is due to the fact that more ions are produced by a high speed electron moving through C_2H_5Br than through air. The former is more easily ionized. The factor by which the numbers 2·05, 1·94, 1·93, &c., in columns VIII. and IX. must be divided to give the relative numbers of electrons emitted by C_2H_5Br and air is approximately 1·75.* Thus $\frac{\text{number of L, M, N, \ldots electrons emitted by Br}}{\text{number of K, L, M, \ldots electrons emitted by air}}$ and $\frac{\text{number of K electrons emitted by Br}}{\text{number of K, L, M, \ldots electrons emitted by air}}$ for equal absorptions of energy are given in Table IV., columns II. and III., for primary radiations of wave-length indicated in column I.

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* The value given by BARKLA and PHILPOT ('Phil. Mag.,' June, 1913) as a first approximation was 1·6. This, however, needed a small correction, the magnitude of which was unknown at the time, but has since been found from experiments by CARSE to raise the value to about 1·75. The correction was necessary on account of the appreciable reflexion or return through the face of incidence of corpuscles on entering the substance ethyl bromide.

Table IV.

Approximate wave-length of primary radiation.	Number of L, M, … electrons emitted by Br / Number of K, L, M, … electrons emitted by air for equal absorptions of primary radiation.	Number of K electrons from Br / Number of K, L, M, … electrons from air for equal absorptions of primary energy.
cm.		
$1\cdot54 \times 10^{-8}$	$1\cdot17$	
$1\cdot17 \times 10^{-8}$	$1\cdot11$	
$1\cdot10 \times 10^{-8}$	$1\cdot10$	
$0\cdot87 \times 10^{-8}$		$0\cdot49$
$0\cdot71 \times 10^{-8}$		$0\cdot59$
$0\cdot56 \times 10^{-8}$		$0\cdot72$
$0\cdot49 \times 10^{-8}$		$0\cdot81$
$0\cdot355 \times 10^{-8}$		$0\cdot82$

This shows the numbers of electrons emitted by ethyl bromide and by air to be about equal when the primary radiation is of longer wave-length than that characteristic of bromine ($K_{\alpha_1} = 1\cdot035 \times 10^{-8}$ cm.).[*]

First Approximation.

The significance of these results is most easily understood if at first we express them approximately.

Let the wave-length of the primary radiation be μ, and that of the K fluorescent (characteristic) radiation of the substance bromine be μ_K. Then when μ is greater than μ_K, for a given absorption of the primary radiation, the same number of electrons is emitted by ethyl bromide (L, M, N, &c., electrons) as by air (K, L, M, N, &c., electrons), as shown in Table IV., column II.

When μ is just less than μ_K, the additional (K) absorption in ethyl bromide is accompanied by the emission of only half as many electrons—that is, only half the K energy absorbed is re-emitted as energy of K corpuscular radiation (column III.).[†]

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[*] It might be suggested that the sudden decrease in ionization is possibly due to a sudden decrease not of the number of electrons emitted, but of the total ionizing power of each electron when its velocity is increased beyond a critical value—that necessary to excite the K fluorescent radiation. There is, however, plenty of evidence against this—(*a*) theoretically it is highly improbable; (*b*) such changes in relative ionizing power with velocity have not been observed; and conclusively (*c*) the decrease above described in this case is true when the electrons are absorbed not in the substance itself, but in another gas (see p. 336).

[†] We here assume that the energy of an X-radiation is approximately equal to that of the full corpuscular radiation which it excites in a substance completely absorbing it, when the conditions are such that little energy is re-emitted in the form of either scattered or fluorescent (characteristic) X-radiation. The evidence for this is very weighty and may be summarized as follows :—

When during the transmission of a primary radiation through matter there is very little transformation into corpuscular radiation, practically the whole of the loss of energy is accounted for by the process of

But as μ becomes smaller, an increasing fraction of the energy absorbed (K absorption) goes into the K corpuscular radiation. And the rate of change indicates that with a primary radiation of very small wave-length, practically the whole of the K absorption would be accounted for by the K corpuscular radiation alone. There is, in addition, very strong indirect evidence that when μ is very small, nearly all the energy absorbed is re-emitted as corpuscular radiation, for, as already pointed out, whatever the absorbing substance under these conditions, the energy of this corpuscular radiation is approximately a constant.

Similar measurements have been made of the energy of corpuscular radiation emitted from iodine from observations of the ionization in methyl iodide. Owing to complications—the causes of which need not be discussed—difficulty was found in determining accurate values by extrapolation, and such as were obtained only indicated the energy of corpuscular radiation when the wave-length of the primary radiation was slightly less than that of the K fluorescent radiation. They show that when the K radiation from barium ($\mu_{K\alpha} = 0{\cdot}39 \times 10^{-8}$ cm.) is incident on iodine ($\mu_{K\alpha} = 0{\cdot}44 \times 10^{-8}$ cm.) nearly 0·5 of the K absorption is accounted for by the K corpuscular radiation from iodine. This is in as close agreement with the corresponding value for bromine given above as could be expected.

scattering, showing there is little energy truly absorbed except as the accompaniment of the emission of corpuscular radiation.

When absorption is accompanied by the emission of only very little fluorescent (characteristic) X-radiation and a negligible amount of scattered radiation, the number of high speed electrons emitted by the absorbing substance is approximately independent of the substance; so for a radiation of a particular frequency absorbed, the number of high speed electrons emitted is proportional to the energy absorbed.

Even when a considerable amount of fluorescent radiation is emitted—about half of the total energy absorbed—the number of high speed electrons emitted by certain substances is still approximately proportional to the energy absorbed minus that re-emitted as fluorescent radiation. Thus, in many cases, energy of high speed electrons emitted by an absorbing substance $= k(E - S - F)$ where k is a constant, E is energy of primary radiation absorbed, S the amount of energy scattered, and F the amount re-emitted as fluorescent radiation.

This has been shown to be true (approximately) in C_2H_5Br when S is small and $F = \frac{1}{2}E$. And if we assume that the energy of X-radiations differing in wave-length may be measured by their total ionizing power in a given gas, it is true in C_2H_5Br as the wave-length of the primary diminishes and the proportions of fluorescent and corpuscular radiations change.

This is strong evidence both that the equation holds in ethyl bromide while the wave-length of the primary radiation changes considerably, and at the same time that the energy of X-radiation of various wave-lengths may be compared at least approximately by their ionizing powers.

As the equation holds under such a variety of conditions, and through various transformations, we conclude that under these conditions the energy of the corpuscular radiation is not only proportional to, but *equals* that of the energy of X-rays disappearing, or that $k = 1$. (Under other conditions, probably in lighter elements, there appears to be appreciably less corpuscular radiation than would be expected from this relation. The energy disappearing may not be re-emitted in radiation of any recognisable form.)

As the energy of a corpuscle, too, has been found to be approximately that of a quantum of radiation measured by other methods, we conclude that in the cases given above the number of quanta of X-radiation absorbed, when not re-emitted as X-radiation, is measured by the number of high speed corpuscles emitted.

Again, in the light of the results obtained from these experiments on bromine, the results of experiments on corpuscular radiation from metal plates by Beatty and Bragg, though somewhat irregular and decidedly fragmentary for the purpose of this investigation, may be seen to point to the generality of the above laws—at least in general features if not in detail.

Further experiments on the corpuscular radiation from substances in the form of plates indicate, though with a greater possible error, that when μ is slightly less than μ_K the K corpuscular radiation accounts for about 0·4 of the K absorption. Such measurements can however, be regarded as giving only the order of magnitude of these quantities.

Thus direct and indirect experiments indicate that when the wave-length of the primary radiation μ is just less than that (μ_K) of a fluorescent radiation, of the energy specially absorbed in association with the K fluorescent radiation, nearly 0·5 is re-emitted as energy of corpuscular radiation. As μ becomes less, the fraction increases, until for primary radiation of very small wave-length, nearly all the energy absorbed (K absorption) is re-emitted as K corpuscular radiation. The values actually obtained for the K energy emitted by ethyl bromide as K corpuscular radiation are plotted in fig. 5, Curve C, for various wave-lengths shown by the abscissæ.

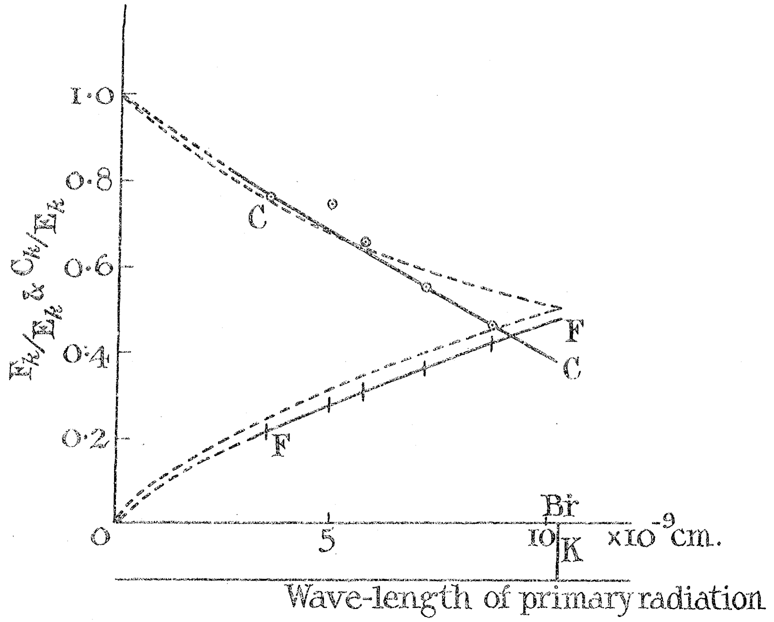

Fig. 5. Showing fraction of energy of primary beam absorbed—K absorption—transformed into K fluorescent (characteristic) radiation, and into K corpuscular radiation (lines FF and CC respectively).

It is evident at once that the energy of K corpuscular radiation from bromine is approximately complementary to that of the K fluorescent X-radiation. A full discussion is, however, given later.

THEORY OF FLUORESCENT X-RADIATION.

The conditions essential to the emission of a fluorescent X-radiation show that it originates in some exceptional disturbance of an atomic system. In the phenomena considered, the most violent disturbance of the atom of which we have any knowledge is that accompanying the ejection of a high speed electron. It is natural to regard this as the probable source, direct or indirect, of the characteristic X-radiation. Investigation completely confirms this view.

Independence of Electron after Expulsion.

There is considerable and apparently conclusive evidence that the electrons after expulsion take no part in the process of radiation*—that is, the process of emission of the characteristic radiation as ordinarily detected. They must, of course, on encountering other atoms, give rise to some radiation—this, however, is not the fluorescent radiation which is emitted in such intensity as that observed. That this is so follows from the following considerations:—

As the exciting primary radiation becomes more penetrating (of shorter wave-length), the speed with which electrons are emitted from a substance exposed to this primary radiation becomes greater, whereas the fluorescent radiation remains homogeneous and unchanged in character. Now all experiments on the production of X-rays show that as the speed of the generating cathode rays increases, although an intense homogeneous X-radiation may be emitted, there is emitted also a heterogeneous radiation of comparable intensity, which becomes more penetrating. No such heterogeneity or change in penetrating power is observable in the fluorescent radiation.

Again, the ionizing power of the fluorescent radiation is comparable with—in limiting cases it is equal to—that of the secondary corpuscular radiation. This corpuscular radiation cannot then produce the fluorescent X-radiation by any process subsequent to expulsion, for all experiments on the relation between the ionizing power of cathode rays and of the X-rays they produce show that only a small fraction of the ionizing power goes into the resulting X-radiation.

Again, if the fluorescent X-radiation was produced by electrons subsequent to their expulsion from the parent atoms, there could be no distinction between the effectiveness of various groups of electrons provided they had the same velocity. Yet the intensity of the fluorescent X-radiation is most distinctly related not to the whole number but only to a particular group of electrons in the corpuscular radiation.

Direct experiments made by CHAPMAN† in order to determine whether the nature of the substance subsequently bombarded by the electrons had any influence upon the

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* BARKLA, 'Proc. Camb. Phil. Soc.,' May, 1909.

† CHAPMAN and PIPER, 'Phil. Mag.,' June, 1910; CHAPMAN, 'Phil. Mag.,' April, 1911; 'Phil. Mag.,' March, 1913.

intensity or character of the fluorescent radiation emitted, show the same thing. When the greater portion of the energy of the expelled electrons, even in excess of that essential to the production of the fluorescent radiation, was absorbed in a second substance, the intensity of the fluorescent X-radiation was the same as when the electrons were completely stopped by the substance originally emitting them.

There appears to be no escape from the conclusion that the emission of fluorescent X-radiation is completely independent of the career of electrons subsequent to their expulsion from the atoms.

As ionization is produced by expelled electrons constituting the corpuscular radiation, it follows that the simple process of ionization is not accompanied by X-ray fluorescence.

Independence of Electron During or Preceding Expulsion.

It does not appear possible that the expelled electron is itself the source of this radiation during the final simple process of ejection, that is, during the final unidirectional flight which carries it beyond the bounds of the atom, for the homogeneous fluorescent X-radiation is both independent of the velocity of expulsion of these electrons, and thus of the period of actual escape, and according to our conception of homogeneous radiation implies a regular vibration.

Again, the vibration of the electron (which is finally expelled from an atom) or of other components of a normal atom when under the influence of a primary Röntgen radiation must of course depend in character upon the primary radiation and be ultimately of the same frequency. This forced vibration would produce a radiation with properties dependent upon and possibly ultimately identical with those of the primary radiation. Such a radiation, due to the forced vibration of electrons within the atom, is actually emitted; it however constitutes the scattered X-radiation.

On the other hand, the fluorescent X-radiation is characteristic not of the exciting primary radiation, but of the excited substance; it cannot be produced by such a controlled motion but only by a free vibration. The emission of a fluorescent radiation, too, is not general but conditional, that is to say, some special atomic condition appears to be essential to the production of the fluorescent radiation. We know that vibrations are produced within the atom both by Röntgen radiations of longer wavelength, and by the impact of electrons moving more slowly than the velocity critical to the production of a particular characteristic X-radiation; yet the characteristic radiation has never been observed in these cases.

We thus arrive at the conclusion that the fluorescent X-radiation is due to a free vibration occurring within the atom when in an abnormal state—probably after the ejection of a high speed electron.*

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* See BARKLA, "Der Stand der Forschung über die sekundare Röntgenstrahlung" ('Jahrb. d. Radioaktivität und Elektronik,' April, 1908).

Each Fluorescent X-*radiation Associated with Particular Group of Electrons.*

But of the electrons emitted with a velocity greater than the critical velocity, that is, with energy greater than that of a quantum of the fluorescent X-radiation, only a fraction are accompanied by the particular fluorescent radiation, say of series K.[*]

As pointed out, the total corpuscular radiation, though consisting of electrons ejected with one velocity, may be divided into several distinct portions, each portion being definitely associated with the emission of fluorescent radiation of a definite series. Thus the whole corpuscular radiation consists of K[†] electrons, associated with the emission of the characteristic X-radiation of series K, L electrons associated with the characteristic X-radiation of series L, and M, N, &c., electrons presumably associated with the emission of hypothetical lower frequency characteristic X-radiations of series M, N, &c. When few K electrons are emitted, the K fluorescent X-radiation is very weak; when K electrons increase in number the intensity of the fluorescent X-radiation (series K) increases, and indeed, as we shall see, there is certainly approximate if not perfectly accurate proportionality between the number of K electrons ejected and the intensity of the fluorescent X-radiation of series K. On the other hand, there is no simple relation between the intensity of fluorescent radiation of a particular series and the total number or energy of the electrons in the whole corpuscular radiation.

Connection with Absorption of Primary Radiation and with Corpuscular Radiation (Radiation in Quanta).

It has been seen that of the energy definitely absorbed in association with the emission of fluorescent X-radiation of series K—K absorption—the fraction re-emitted as fluorescent radiation (series K) is at its maximum value when the primary radiation is of just shorter wave-length than the fluorescent radiation itself, and that this fraction decreases with a decrease in wave-length of the primary radiation. Thus if F_K is the energy of the fluorescent radiation (series K) μ and μ_K are the wave-lengths of the primary and fluorescent radiations respectively, then as μ decreases from μ_K downward F_K/E_K decreases from about half, as shown in fig. 5.

On the other hand, as μ decreases from μ_K downward, of the energy E_K specially absorbed in connection with the emission of K radiation, an *increasing* fraction re-appears as energy of corpuscular radiation (C_K). In the case of the one substance examined in detail, and approximately in that of other substances, C_K/E_K increases from about $\frac{1}{2}$ towards 1. Thus when μ is just less than μ_K the energy of the primary radiation specially absorbed is approximately equally divided between the two types of secondary

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[*] See BARKLA, "Charakteristische Röntgenstrahlungen" ('Verh. d. Deut. Phys. Gesell.,' 1913).

[†] The case here considered is that in which the "J" radiation (which from most elements is of very high frequency) is not excited.

radiation; that is, for a given quantity of corpuscular radiation emitted, there is emitted sufficient K fluorescent radiation to produce an equal ionization. But as the K fluorescent radiation in this case differs little from the primary radiation, we see that for each K electron emitted there is also produced sufficient fluorescent radiation to set free another high speed electron with a velocity only just smaller than that of the electron ejected directly. As this electron possesses the energy of a quantum of the fluorescent radiation, we conclude that for each K electron emitted directly there is emitted also one quantum of the K fluorescent radiation. This experimental conclusion is so definite, so simple and significant, that we shall proceed to study the relations under other conditions. But before doing so we must again point out the extreme improbability of such an agreement by chance; *à priori* the energy of fluorescent radiation might be that of 100 quanta or $\frac{1}{100}$ part of a quantum for each electron emitted, yet it is one quantum within a small possible error.

As the wave-length μ of primary radiation decreases, the energy of a quantum of this primary radiation increases, but the quantum of the characteristic radiation remains constant. If, therefore, one quantum of this characteristic radiation is still emitted for each high-speed electron emitted, then

$$\frac{\text{Energy of K fluorescent X-radiation}}{\text{Energy of K corpuscular radiation}} = \frac{\text{quantum of K fluorescent radiation}}{\text{quantum of primary radiation}}$$

$$= \frac{\text{frequency of K fluorescent radiation}}{\text{frequency of primary radiation}} = \frac{n_K}{n} \text{ or } \frac{\mu}{\mu_K},$$

i.e., the energy of the fluorescent radiation becomes a smaller and smaller fraction of that of the corpuscular radiation. This is exactly what happens, and certainly approximately at the theoretical rate.

Possibly this argument is clearer as follows:—

$$\frac{\text{Total energy of K fluorescent radiation } (F_K)}{\text{Energy of a quantum of K fluorescent radiation } (hn_K)}$$

$$= \text{Number of quanta of fluorescent radiation } (N_F \text{ say}),$$

$$\frac{\text{Total energy of K corpuscular radiation } (C_K)}{\text{Energy of a quantum of primary X-radiation } (hn)}$$

$$= \text{Number of electrons in corpuscular radiation } (N_C \text{ say}).$$

Hence the number of quanta of fluorescent radiation emitted per electron of the corpuscular radiation $= \frac{N_F}{N_C} = \frac{F_K}{C_K}\frac{n}{n_K}$.

The experimentally determined number of quanta of fluorescent radiation emitted for each electron in the corpuscular radiation—*i.e.* $\left(\frac{F_K}{C_K}\frac{n}{n_K}\right)$—is given in the following table (V.) for primary radiations of various wave-lengths. These results show that one quantum of K radiation is emitted for each K electron expelled whatever be the velocity of its ejection.

TABLE V.

Approximate wave-length of primary X-radiation.	Number of quanta of K fluorescent radiation emitted per K electron ejected.
cm.	
$0 \cdot 87 \times 10^{-8}$	1·09
$0 \cdot 71 \times 10^{-8}$	0·95
$0 \cdot 56 \times 10^{-8}$	0·85
$0 \cdot 49 \times 10^{-8}$	0·81
$0 \cdot 35 \times 10^{-8}$	0·90

The variations from unity are irregular and obviously may be the result of observational or experimental errors. The maximum variation of 19 per cent. is small considering the number and nature of the experimental determinations involved. Apart from a quantum theory, the range of possible values is so enormous in comparison with the variation observed that the emission of one quantum of characteristic X-radiation for each electron in the associated corpuscular radiation must be regarded as an experimentally established fact. It is a fact of some significance.

Less accurate experiments on other substances lead to a similar conclusion approximately if not accurately. There is no reason to think the results would be less convincing. The fundamental physical truth one cannot for a moment question, though it is possible that certain conditions would produce greater irregularities than are exhibited above.

First Approximation to Energy Relations.

If the two K secondary radiations—the corpuscular and the characteristic X-radiation—together accounted for the whole of the K energy absorbed, we should have of the energy of the primary beam absorbed as K absorption, the fraction $\frac{n}{n+n_K}$ or $\left(\frac{\mu_K}{\mu+\mu_K}\right)$ re-emitted as K corpuscular radiation, and the fraction $\frac{n_K}{n+n_K}$ or $\left(\frac{\mu}{\mu+\mu_K}\right)$ as K fluorescent X-radiation.

It has been shown that when μ is somewhat less than μ_K, *i.e.*, when $\mu = 0 \cdot 84 \mu_K$, about 42 per cent. of the energy of the primary radiation specially absorbed in bromine appears to be re-emitted as fluorescent X-radiation of series K, while about 46 per cent. is re-emitted in the K corpuscular radiation. Thus the two together account for about 88 per cent. of the primary radiation. Also as μ diminishes, the two energies of fluorescent and corpuscular radiations remain approximately complementary, the energy of the former diminishing while that of the other increases. Table VI. gives the experimentally determined values of

$$\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}, \quad \frac{\text{K corpuscular radiation (energy)}}{\text{K primary absorption (energy)}},$$

$$\text{and } \frac{\text{Total K secondary radiation (energy)}}{\text{K absorption (energy)}}$$

in columns II., IV. and VI. along with the simple theoretical values for the first two $\frac{n_{\text{K}}}{n+n_{\text{K}}}$ and $\frac{n}{n+n_{\text{K}}}$ in columns III. and V. The agreement between the values in columns II., IV. and VI. with those in columns III., V., and with unity respectively, is certainly sufficiently close to permit us to say that these simple energy relations express the experimental facts exceedingly well for a first approximation. It should be observed that the recorded values are not simply relative values; each one is the result of an absolute determination in the sense that it is independent of the others, and might have had any value less than unity. There appears to be little loss of energy within the atom; but what there is appears most marked when μ is just less than μ_{K}. The values of $\frac{n_{\text{K}}}{n+n_{\text{K}}}$ and $\frac{n}{n+n_{\text{K}}}$ are plotted against wave-lengths of primary radiation in fig. 5 where they are indicated by the broken curves.

TABLE VI.

I.	II.	III.	IV.	V.	VI.
Approximate wave-length.	$\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}$.	$\frac{n_{\text{K}}}{n+n_{\text{K}}}$.	$\frac{\text{K corpuscular radiation (energy)}}{\text{K primary absorption (energy)}}$.	$\frac{n}{n+n_{\text{K}}}$.	$\frac{\text{K fluorescent + corpuscular radiation (energy)}}{\text{K primary absorption (energy)}}$.
cm.					
$0 \cdot 87 \times 10^{-8}$	0·42	0·46	0·46	0·54	0·88
$0 \cdot 71 \times 10^{-8}$	0·36	0·41	0·55	0·59	0·91
$0 \cdot 56 \times 10^{-8}$	0·31	0·35	0·66	0·65	0·97
$0 \cdot 49 \times 10^{-8}$	0·29	0·32	0·75	0·68	1·04
$0 \cdot 35 \times 10^{-8}$	0·23	0·26	0·76	0·74	0·99

It should, however, be pointed out that in elements of lower atomic weight a considerably smaller fraction of the energy of primary radiation appears to be transformed into fluorescent (characteristic) X-radiation. Measurements of the energy of corpuscular radiation, too, indicate a smaller fraction transformed into radiation of this type than is the case in bromine. Thus experiments point to a marked loss of energy in such substances.*

With elements of higher atomic weight, however, there appears to be a close approximation of the experimental values with those given by the above simple theory.

We shall, in what follows, deal principally with the results obtained with ethyl bromide, the behaviour of which is certainly typical of many substances. If in light elements, as seems probable, a considerable portion of the energy absorbed is unaccounted for, this is a matter for future investigation. It does not, however, affect the conclusions to be obtained with other substances, but indicates that the conditions are not the simplest possible.

Process of Radiation.

It is inconceivable that the processes resulting in the emission of fluorescent X-radiation and corpuscular radiation are either independent or even that they are alternative conclusions (dependent on some critical condition in the atom) to similar initial processes. The above experimental relations are inexplicable on any such assumption. The emission of each electron of the corpuscular radiation is associated with the emission of a quantum of the corresponding fluorescent X-radiation. But we have already shown that the electron after emission takes no part in the fluorescence, so are left with the conclusion that the atom which emits an electron emits also a fluorescent radiation characteristic of the atom itself. We shall now consider the process in greater detail.

The above approximate relations show that the energy of primary radiation *absorbed* per K electron expelled is greater than that per lower frequency electron expelled by a quantum of K radiation.† In the measurements upon which this conclusion is based we are unable to distinguish between L, M, and N electrons, but as L electrons constitute quite 80 per cent. of the whole, and for the others the energy

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* Further experimental work on the light elements is desirable, for it is remarkable that such a variation should occur with a comparatively small variation in the atomic weight of the radiating substance (fig. 4), for the line spectra of these elements are similar, and in addition the absorption curves (as in fig. 2) are exactly similar. Similar absorption curves indicate similar processes of absorption.

† If we ignore the first approximation altogether and examine the experimentally determined values of $\frac{\text{Energy absorption per K electron} - \text{energy absorption per L electron}}{\text{energy of quantum of K radiation}}$, we see that the possible error is necessarily very great. The experimental values 1·4, 1·15, 0·9, 0·7 and 0·9 are of the order of magnitude of unity.

absorption does not differ greatly from that for the L electrons, we may class them all as L electrons. As all electrons leave the atom with the same velocity, and as the emission of the fluorescent radiation is subsequent to the absorption of primary radiation, we may express the fact in the following way:—The energy of a quantum of K radiation is the energy required to move an electron from the position and state of a K electron to the position and state of a lower frequency electron, an L electron. (We are led to regard a K electron as being situated nearer to the centre of the atom than the lower frequency electrons, and, in general, the frequency of vibration of electrons to be in the order of their distance from the surface. Thus the J, K, L, M electrons are arranged in this order from the centre outwards.)

But when a K electron is hurled out of the atom, it is possible that, for stability, another electron will fall into the position and state of the K electron. If it falls from the position and state of an L electron, the energy of a quantum of K radiation must be re-emitted. The emission of a quantum of K radiation for each electron expelled we have found to be an experimental fact.

Reasoning by analogy, we conclude that to displace an L electron necessitates the absorption of the energy of one quantum of L radiation more than that required to eject a still lower frequency electron. This energy is re-emitted as a quantum of L radiation when an electron falls from the position and state of one of these lower frequency electrons to the position and state of the displaced L electron.

Thus, on this hypothesis, the energy of primary radiation absorbed per K electron emitted is $h(n+n_K+n_L+n_M+\ldots)$, *i.e.*, the sum of the kinetic energy of the ejected electron, which is hn, and the energy of one quantum of each of the characteristic X-radiations of series K, L, M, ... Similarly, the energy absorbed per L electron emitted is $h(n+n_L+n_M\ldots)$, and so on.

If, after a K electron is ejected, its place is taken by an L electron, and the place of that by an M electron, and so on, then for each K electron ejected there is emitted one quantum of each of the K, L, M, ... X-radiations.

In this case the fraction $\dfrac{\text{energy of K characteristic X-radiation}}{\text{energy of K corpuscular radiation}}$, *i.e.* $\dfrac{F_K}{C_K}$ is equal to $\dfrac{n_K}{n}\left(\text{or } \dfrac{\mu}{\mu_K}\right)$ as before. But what has previously been regarded as purely K corpuscular radiation is K corpuscular radiation together with a weak corpuscular radiation produced by the re-absorption of the L, M, ... characteristic X-radiations emitted in association with the K corpuscles. That is, if there be additional L characteristic radiation associated with the emission of K corpuscles, the ionization produced by its absorption must be added to that produced more directly by the K corpuscular radiation. Thus more accurately our comparison of the energies of fluorescent and corpuscular radiations has given

$$\frac{\text{K characteristic X-radiation (energy)}}{\text{K corpuscular radiation} + \text{L characteristic radiation accompanying K electrons (energy)}},$$

and this should be compared with the theoretical value $\frac{n_K}{n+n_L}$. The values in Table V. should in this case be multiplied by $\frac{n+n_L}{n}$ to give the number of quanta of K radiation emitted per K electron ejected. They then become 1·22, 1·04, 0·92, 0·86, and 0·94.

The fraction $\frac{\text{K characteristic X-radiation (energy)}}{\text{K primary absorption (energy)}}$ on this theory is equal to $\frac{n_K}{n+n_K+n_L+\ldots}$ (see Table VII., columns II. and III.); and

$$\frac{\text{K corpuscular radiation (energy)}}{\text{K primary absorption (energy)}} \text{ equals } \frac{n}{n+n_K+n_L+\ldots}.$$

TABLE VII.

I.	II.	III.	IV.	V.	VI.
Approximate wave-length (Kα_1 line).	$\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}$.	$\frac{n_K}{n+n_K+n_L\ldots}$.	$\frac{\text{K corpuscular radiation + L characteristic radiation with K electron (?)}}{\text{K primary absorption (energy)}}$.	$\frac{n+n_L}{n+n_K+n_L\ldots}$.	$\frac{\text{K secondary radiations (energy)}}{\text{K absorption (energy)}}$.
cm. $0·87 \times 10^{-8}$	0·42	0·43	0·46	0·57	0·88
$0·71 \times 10^{-8}$	0·36	0·38	0·55	0·62	0·91
$0·56 \times 10^{-8}$	0·31	0·33	0·66	0·67	0·97
$0·49 \times 10^{-8}$	0·29	0·31	0·75	0·69	1·04
$0·35 \times 10^{-8}$	0·23	0·25	0·76	0·75	0·99

But again, what we have observed is in this case

$$\frac{\text{K corpuscular radiation} + \text{L characteristic radiation accompanying K electrons (energy)}}{\text{K primary absorption (energy)}},$$

which should accordingly be compared with $\frac{n+n_{\mathrm{L}}}{n+n_{\mathrm{K}}+n_{\mathrm{L}}+\ldots}$, as in columns IV. and V. In column VI. the total energy of secondary radiations associated with the emission of K electrons is expressed as a fraction of the K absorption, as in Table VI., column VI.

The agreement between theory and experiment, as shown in Table VII., is, on the whole, very close.

The experimentally observed energy relations, however, are not sufficiently accurate to enable us to determine with certainty the exact process by which the original configuration of the atom is regained.

In fundamentals, however, the theory can scarcely be questioned. It explains so many facts and is so simple in itself that there seems no alternative but to accept it in outline at least.

[The principal facts which may be regarded as giving support to the theory may be summarised as follows:—

(1) When μ is just less than μ_{K} for any one of the heavier elements, the fraction of the primary energy absorbed (K absorption) transformed into K characteristic radiation $\left(\frac{\mathrm{F_K}}{\mathrm{E_K}}\right)$ is slightly less than 0·5.

(2) There is evidently a limiting value of about 0·5 for the fraction.

(3) As μ diminishes this fraction invariably diminishes.

(4) In the one substance carefully investigated—a substance giving the maximum value just below 0·5—the rate of diminution of this fraction with diminution in μ is almost perfectly that given by theory.

(5) When μ is just less than μ_{K} for the one substance thoroughly investigated, the fraction of primary energy absorbed (K absorption) transformed into K corpuscular radiation $\left(\frac{\mathrm{C_K}}{\mathrm{E_K}}\right)$ is also slightly less than 0·5. This is approximately true for many substances, though a value appreciably but not considerably less than 0·5 has been obtained.

(6) The value exceeding 0·5 has never been observed.

(7) As μ diminishes, the fraction invariably increases.

(8) In the one substance investigated, the rate of increase of the fraction is approximately the theoretical rate when μ is not near to μ_{K}. (But when μ is near to μ_{K} there is probably a real deficiency of corpuscular radiation.)

(9) There is no evidence against the theory in its essentials.

(10) The theory is a very simple one.]

Experiments were commenced with Mr. Shearer with the object of determining whether the emission of K electrons was accompanied by a weak L radiation additional to that associated with L electrons, but the investigation was interfered with by war work, and did not get beyond the preliminary stage. The intensity was, however, seen to be very small. Theory as indicated above would lead us to expect that such an L radiation would *at most* account for only 7 per cent. of the K absorption, for n_L is only about $\frac{1}{7}n_K$. If no such additional L radiation is discovered, the natural conclusion is that the displaced K electrons are replaced by electrons of still lower frequency or possibly, though highly improbably, from outside the atom.

It is possible that there are not electrons of every series in every atom of the same substance, or, if there are, they may not be in the best position to enable them to replace an electron of an adjacent higher series. If, for instance, a K electron were ejected from an atom which did not contain an L electron, or in which the L electron was situated on the other side of the centre, its place might be taken by an M electron, with the result that the energy emitted as characteristic radiation would be equal to that of one quantum of K radiation + one quantum of L radiation. This would be equal to one quantum of radiation of slightly greater frequency than what we have previously regarded as the K radiation, and might account for a neighbouring spectral line in the K radiation.

The origin of various spectral lines in a particular series (say the K series) was first explained by KOSSEL as the result of electrons falling from the various outer rings into the K ring, and was not given in the early communications of the writer.* According to KOSSEL, the K_α radiation is that emitted when an electron falls from the L ring into the K ring; K_β that resulting from the fall from the M ring into the K ring, and so on. In support of this he shows that the necessary energy relations hold. Thus the energy emitted when an electron falls from the M ring into the K ring is the sum of the energies of fall from the M ring into the L ring, and from the L ring into the K ring; what KOSSEL shows is that $hn_{K_\beta} = hn_{L_\alpha}+hn_{K_\alpha}$, that is, one quantum of K_β radiation possesses the sum of the energies of one quantum of L_α radiation and one quantum of K_α radiation. This indicates that, while the fall of electrons takes place between consecutive rings, it sometimes takes place across an intermediate ring position.

These observed relations thus confirm the conclusion to which the writer was led in a most direct manner from measurements of the energies of corpuscular and fluorescent (characteristic) radiations and their relation with the associated absorption of primary radiation.

The experiments described above lead to the conclusion that a characteristic radiation (of series K, say) is probably emitted when an outer electron falls into the position of a displaced K electron, the energy previously absorbed in displacing the K electron in excess of that carried away as kinetic energy being now re-emitted as a quantum of K radiation, or, what seems more probable, as a quantum of K radiation accompanied by quanta of lower frequency radiations.

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* Sir ERNEST RUTHERFORD kindly sent a copy of KOSSEL'S paper to the writer a few weeks after the publication of the preliminary notes in 'Nature,' drawing attention to some similarity of conclusion. This paper was evidently published some time previous to the writer's notes.

Quantum Theory.

In the above investigation of the energy transformations accompanying the phenomenon of X-ray fluorescence the results of greatest significance in their bearing on the quantum theory are probably the following:—

(1) The energy absorbed per K electron expelled is greater than that per L electron expelled by the energy of one quantum of K radiation approximately. This leads to the statement that the energy of a quantum of K radiation is that which must be absorbed to displace a K electron from its normal position and state to the position and state of an L electron.

(2) A quantum of K radiation is emitted for each K electron ejected.

(3) The number of electrons in the secondary corpuscular radiation plus the number of quanta of fluorescent X-radiation, that is, the total number of electrons emitted by the direct action of the primary X-radiation together with those emitted indirectly through the agency of the associated fluorescent X-radiation is not equal to the number of quanta of primary radiation absorbed, but varies from equality with to double that number. Thus if, for the sake of clearness, we regard the first approximation as being accurately true, N quanta of primary radiation cause the emission of

$\frac{1}{2}$N electrons (directly) + $\frac{1}{2}$N (indirectly through the fluorescent radiation) when μ is just less than μ_K,

$\frac{2}{3}$N (directly) + $\frac{2}{3}$N (indirectly) when μ is $\frac{1}{2}\mu_K$,

N (directly) + N (indirectly) when μ is very small,

or, in general,

$$\mathrm{N}\frac{\mu_K}{\mu+\mu_K}\text{ (directly)} + \frac{\mu_K}{\mu+\mu_K}\mathrm{N}\text{ (indirectly) for any value of } \mu.^*$$

Thus, contrary to what has sometimes been supposed, the energy of a quantum does not persist through these energy transformations as an indivisible entity.

(4) If we consider the energy *absorbed* by each atom from which a K electron is expelled, we see that when μ is just less than μ_K, approximately two quanta of primary radiation are absorbed per atom,

when $\mu = \frac{1}{2}\mu_K$, $1\frac{1}{2}$ quanta of primary radiation are absorbed per atom,

,, $\mu = \frac{1}{4}\mu_K$, $1\frac{1}{4}$,, ,, ,, ,, ,,

or, in general,

when $\mu = f\mu_K$, $(1+f)$,, ,, ,, ,, ,,

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* If there are L, M, ... characteristic X-radiations associated with the emission of K electrons—indicated above as a possibility—the number of electrons emitted will be greater than is given by this expression; in this case it will depend on the number of series (K, L, M, ...) of characteristic radiations.

Consequently the number of quanta of radiation absorbed per atom (*i.e.*, per absorbing atom) varies from about two to just more than one as the wave-length of primary radiation diminishes from just less than μ_K to a very small quantity. A quantum is a quantity of radiation evidence of the absorption of which has not been obtained. Frequently however—when μ is a small fraction of μ_K—the absorption per atom approximates to the energy of a quantum.

It should be pointed out that the last two conclusions concerning the quantum theory, although expressed in precise terms, are in no way dependent on a close agreement between the experimental results and those given as a first approximation.

A NEW SERIES OF CHARACTERISTIC RADIATIONS. (J SERIES.)

A marked deviation of the experimental results from what was expected on the above theory has led to the discovery of a new series of characteristic X-radiations.* From light elements these newly-found radiations are of only moderate penetrating power, but are much "harder" (of shorter wave-length) than the K radiations emitted by these same elements; they are of the same order of wave-length as the K radiations from the heavier elements—silver, tin, &c. The irregularity was found in the relation between the energy of K corpuscular radiation and the K absorption of the primary beam (p. 331). Thus it appeared that the fraction $\frac{\text{K corpuscular radiation (energy)}}{\text{K primary absorption (energy)}}$ increased with the diminution of wave-length of the primary radiation only up to a certain wave-length; beyond this there was a sudden diminution in its value. This result, however, was based on the assumption that the ionization in air was produced by electrons of a definite number of groups, K, L, M, &c., throughout the whole range of wave-lengths employed: in other words, it was assumed that within this range of wave-lengths there was no radiation characteristic of the elements nitrogen and oxygen, consequently that no fresh group of electrons was emitted as corpuscular radiation as the wave-length of the primary radiation was reduced.

Thus it will be observed that the values given in column IX. of Table III. depend upon the ratio $\frac{\text{ionization coefficient in air}}{\text{absorption coefficient in air}}$. But the value of the absorption coefficient in air for the radiations of shorter wave-length were obtained by simple proportion from those in aluminium after the subtraction of the scattering coefficient,

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* There has been some evidence of this for many years. The writer in 1903 found that unless the primary radiation was kept "soft" an additional radiation of some kind was emitted by substances of low atomic weight. It was also observed that to obtain evidence of the most perfect scattering from light elements as shown by polarization experiments "soft" radiation had to be used. Again, experiments on the distribution of scattered radiation showed that this approximated to that for the fluorescent radiation when the primary radiation was not very "soft." These and other experiments suggested the possible emission of a characteristic radiation of another series.

that is, they were based on the absorption laws on the assumption that air had no spectral line within this range of wave-lengths. An unobserved spectral line would involve greater absorption on the shorter wave-length side, and would be accompanied by increased ionization. The ionization was, of course, experimentally observed; but this was originally thought to be that accompanying what might be termed normal absorption in air. A greater absorption would necessitate a correction of the values obtained and would account for the apparent discrepancy.

The existence of a characteristic X-radiation may, however, be shown by various methods—by experiments on (*a*) X-ray fluorescence (excitation by a primary X-radiation); (*b*) corpuscular radiation; (*c*) ionization; (*d*) absorption. All these methods have been applied and the results have demonstrated the existence of a series of X-radiations previously unknown; the absorbabilities (consequently the wave-lengths) of these radiations from several elements have been determined.

[The experiments, the results of which are given under the headings (*b*), (*c*), and (*d*) of this section, were undertaken in collaboration with Miss M. P. WHITE, whom I also wish to thank for help in the preparation of diagrams and tables for the lecture. The results briefly referred to in section (*a*) were obtained during an investigation with Miss J. DUNLOP of the scattered radiation. A more detailed account of these investigations will be published later.]

Ionization Method.

Experiments showed that with a primary radiation of decreasing wave-length the value of $\frac{\text{ionization coefficient in } C_2H_5Br}{\text{ionization coefficient in air}}$ failed to increase at the expected rate beyond a wave-length of about $0{\cdot}56 \times 10^{-8}$ cm. It was evident, however, that the emission of a characteristic radiation from air would be accompanied by a rise of the air ionization and consequent fall of the ratio. Experiments were therefore made upon the ionization in sulphur dioxide and methyl iodide relative to air, in order to determine whether the sudden change occurred in the ethyl bromide ionization or in the air ionization.

The ionization coefficient in sulphur dioxide had been shown to bear an approximately constant ratio to that in air through a long range of wave-lengths.* The range of wave-lengths employed had, however, not included that at which the observed change occurred. On extending the series of experiments it was found that the ratio $\frac{\text{ionization coefficient in } SO_2}{\text{ionization coefficient in air}}$ underwent a diminution at the same wave-length as had given a low value for $\frac{\text{ionization coefficient in } C_2H_5Br}{\text{ionization coefficient in air}}$. A similar effect was observed in comparing the methyl iodide and air ionization coefficients.

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* BARKLA, 'Proc. Camb. Phil. Soc.,' May, 1909; 'Phil. Mag.,' August, 1910; BARKLA and PHILPOT, 'Phil. Mag.,' June, 1913.

It was evident then that the sudden change was due to an increase in the ionization in *air*, and was such as would be given if nitrogen gave an X-ray spectral line of absorbability in aluminium $(\lambda/\rho)_{Al}$ equal to about 2·5, or wave-length about $0{\cdot}56 \times 10^{-8}$ cm.

On continuing the SO_2 ionization experiments with X-rays of shorter wave-length still, the ratio of ionizations rose again. This effect indicated that sulphur emits a characteristic X-radiation of shorter wave-length than that from nitrogen and oxygen (as might be expected from analogy with the K and L series of radiations), and as the primary radiation became of shorter wave-length than the radiation characteristic of sulphur, this characteristic radiation was excited, and was accompanied by the corresponding corpuscular radiation from that substance producing an increased ionization in sulphur dioxide. The rise and fall of the ratio $\frac{\text{ionization in air}}{\text{ionization in } SO_2}$, with decreasing wave-length or increasing penetrating power is shown in fig. 6, curve 3.

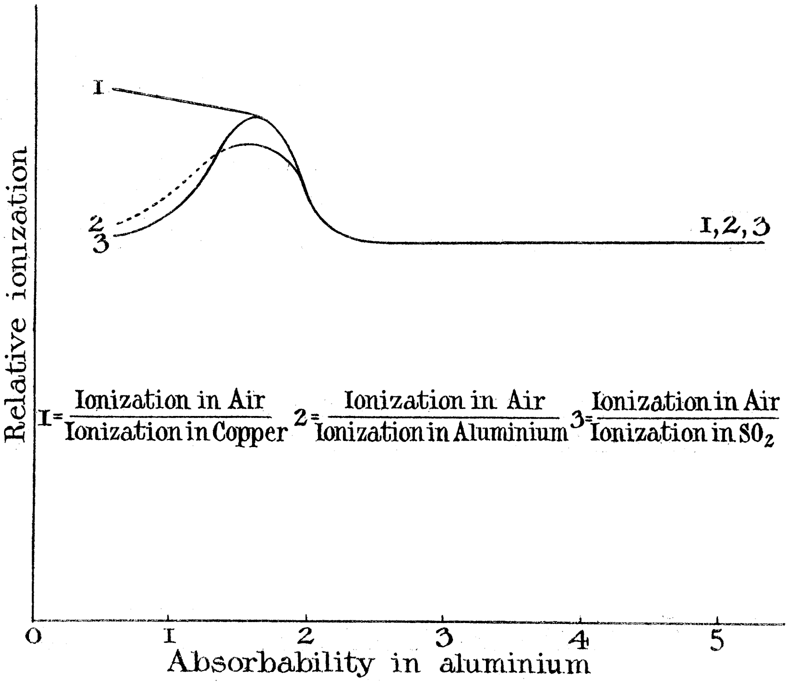

Fig. 6.

Corpuscular Radiation Method.

To obtain further confirmation of this, it was decided to compare the ionization in aluminium with that in air. As the ionization can only be directly measured when the substance is in the gaseous state, the method adopted was of necessity an indirect one. Ionization is usually produced by the high speed electrons from a gas passing through the same gas. Instead of this the electrons from aluminium were allowed to pass through hydrogen (the direct ionization in which is negligible), and this indirect ionization was measured. Though the ionization produced in hydrogen by the secondary corpuscular radiation is not necessarily quite the same as that produced in aluminium by the absorption of its own corpuscles, the factor giving aluminium ionization from that in hydrogen is constant or nearly so. Consequently changes in the *relative* values of the ionization in aluminium and air may be observed equally well by this indirect method.

The ionization in a chamber with its back face of aluminium and filled with hydrogen was compared with that produced by the same beam of X-rays in air. In the first case the ionization was ionization by the electrons ejected from hydrogen plus that by the net gain of electrons from aluminium at the end. In the second case the ionization was produced by electrons from the air itself plus that produced by electrons from aluminium ends. Approximately these are (*a*) ionization in hydrogen by electrons from the aluminium plates, and (*b*) ionization in air by its own electrons plus a comparatively small ionization in air by a net gain of electrons from the aluminium plates at the end of the chamber. (The latter of these might have been approximately eliminated from the results of experiments on the corpuscular radiation from aluminium. This was unnecessary, however; an approximate correction was obtained by extrapolation.)

Homogeneous beams of various wave-lengths were employed, and the relative ionizations in air and in aluminium were obtained. A correction had, however, to be made to the relative ionizations obtained in this way, for the air ionization was due to the electrons ejected from a given mass of air, whereas the aluminium ionization was produced by the electrons from a mass which increased with the frequency of the primary radiation. This is due to the fact that the shorter the wave-length of the primary radiation, the greater is the velocity of electrons which this radiation ejects, consequently the greater is the depth of material from which they emerge. An approximate correction for this may, however, be found by extrapolation. This is explained below in its application to the determination of the relative ionizations in air and in copper. The final results of the experiments on air and aluminium are shown graphically in fig. 6, curve 2. The rise in the air ionization at a wave-length about $0 \cdot 56 \times 10^{-8}$ cm. (λ/ρ in Al $= 2 \cdot 5$) is well marked, and the subsequent rise in aluminium ionization is shown in the change in relative ionization in the opposite direction at a wave-length of about $0 \cdot 52 \times 10^{-8}$ cm. (λ/ρ in Al $= 1 \cdot 9$). It will be seen that the curve so obtained is very like the relative ionization curves for SO_2 and air obtained directly. This, of course, is as it should be, the atomic weights of aluminium and sulphur being close together, and their characteristic radiations consequently being of neighbouring wave-length. The difference between the two indicates that the radiation characteristic of sulphur is more penetrating than that of aluminium, for the relative ionization begins to approach the normal value with more penetrating primary radiation (of shorter wave-length) in the case of sulphur than that of aluminium. This means that the special additional corpuscular radiation is excited in sulphur only by primary radiation slightly more penetrating than that necessary to excite the corresponding corpuscular radiation in aluminium.

In order to obtain the ionization in a substance of atomic weight differing considerably from that of nitrogen and oxygen, and thus to get rid of the effect of the neighbouring spectral line in one of the ionized substances, the ionization in copper was compared with that in air by the same method as in the case of aluminium and air.

The uncorrected results for the ratio $\frac{\text{ionization in air}}{\text{ionization in copper}}$ are shown graphically in fig. 7. The effect of the varying thickness of metal from which the corpuscles emerge is seen in the downward slope of the curve with decreasing wave-length of the primary radiation; but for this effect the line should be approximately horizontal.

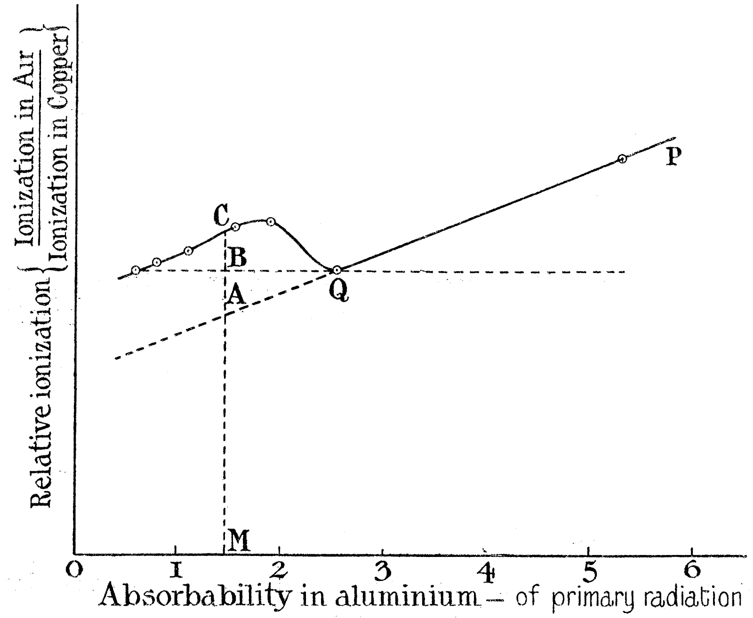

Fig. 7.

Producing the relative ionization line PQ towards the left we get the relative ionization if there had been no additional corpuscular radiation associated with the spectral lines of nitrogen and oxygen. Thus the ordinate at C should be multiplied by the ratio $\frac{\text{MB}}{\text{MA}}$ to bring it to the true relative value of the ionization for a primary radiation of absorbability OM.

Treating the values in this way we get the curve 1, fig. 6, giving the relative ionizations in air and copper for various radiations.

The shape of the curve shows that the explanation given in the above cases is the correct one; for beyond the wave-length $0{\cdot}56 \times 10^{-8}$ (λ/ρ in Al $= 2{\cdot}5$) the value of

$\frac{\text{ionization in air}}{\text{ionization in copper}}$ rises with diminution of wave-length, and with further diminution there is no return of the relative ionizations to the original value.* Thus the ionization in air increases beyond the spectral lines of air; but there is no rise of the ionization in copper, as there is no spectral line characteristic of copper within the range of wave-lengths used. The ionizations in aluminium and sulphur dioxide relative to that in copper may be obtained by division from the values more directly determined and plotted in fig. 6; the results are given in fig. 8, from which we see

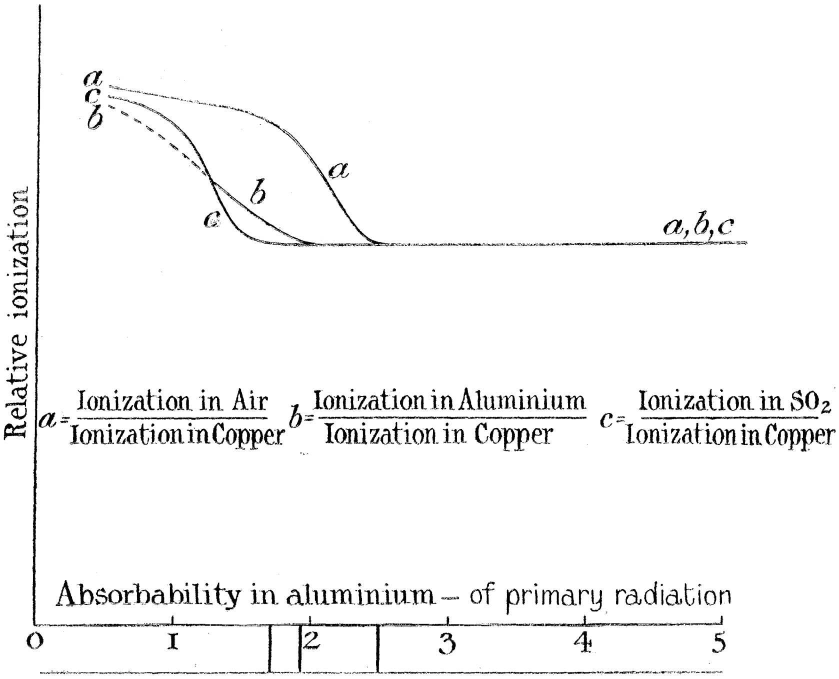

Fig. 8. Showing approximate positions of the J spectral lines of N, Al, and S obtained from relative ionization curves.

more clearly that these radiations characteristic of air, aluminium and sulphur, are progressively more penetrating. The J spectral lines for nitrogen, aluminium and sulphur obtained from these curves are shown at the foot of the figure. A similar increase of penetrating power with atomic weight of radiating substance had been found to hold among the radiations of series K and L.

A point worthy of notice is that with primary radiation of much shorter wave-length than those of the characteristic radiations (J series) of the substances compared, the relative ionization is approximately the same as that obtained when

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* The last two values in Table III., column IV., giving $\frac{\text{ionization coefficient in } C_2H_5Br}{\text{ionization coefficient in air (K, L, ...)}}$ were corrected by the factors 1·32 and 1·39 respectively, because the observed ionization in air was partially due to J electrons. To obtain the ionization in air due to K, L, ... electrons alone, the observed total ionization had to be multiplied by $\frac{AM}{CM}$ (fig. 7), or the above fractions had to be multiplied by $\frac{CM}{AM}$, which had values 1·32 and 1·39 in the two cases.

the primary radiations were of longer wave-length than these characteristic radiations. This denotes that the number of J electrons emitted from air bears the same ratio to the total number of electrons (K, L, M, &c.) emitted by air as is the case from aluminium or sulphur.

Fluorescence Method.

The more direct method of demonstrating the existence of a characteristic radiation is to excite it by a primary radiation of shorter wave-length and observe it in the secondary radiation emitted. The secondary radiation emitted by the substance and detected by an electroscope in many cases is very approximately a homogeneous radiation; in others a second (softer) characteristic radiation must be filtered out by absorbing sheets before the homogeneity of the radiation can be demonstrated; in other cases again, the scattered radiation produces considerable effects and cannot be filtered out, but in this the effect of the scattered radiation can be calculated and eliminated. The last method was used by BARKLA and NICOL,* and was afterwards applied by CHAPMAN† to substances of highest atomic weight. In this case the whole of the secondary radiation emitted by a substance was compared with that emitted by another substance whose secondary radiation under the condition of the experiment was almost purely a scattered radiation.

In experimenting upon light elements this scattered radiation becomes a very important factor, and the elimination of the effect of this from the whole secondary radiation becomes very difficult. For our present purpose it is sufficient to show that in addition to scattered radiation a characteristic X-radiation is emitted by the light elements. As scattering substances, paper, paraffin wax, and aluminium were used. It had previously been shown that X-radiations differing considerably in wave-length are scattered to an equal extent by these light elements, and that scattering takes place without appreciable change of type. The introduction of a fluorescent characteristic radiation into the secondary radiation from one of these light elements would be shown by an increase in the total intensity of secondary radiation, and by a change in its penetrating power.

A primary radiation of varying wave-length was directed on to a sheet of paper, paraffin wax, or aluminium, and the ratio between the intensities of the primary and secondary radiations was observed by means of two electroscopes, while the absorbabilities of both primary and secondary radiations were tested by screens of aluminium. It was found (1) that the intensity of the secondary radiation rose and fell as the wave-length of the primary radiation was diminished in the same way as did that of a characteristic radiation; (2) the penetrating power of the secondary radiation varied as it would by the superposition on the scattered radiation of a homogeneous characteristic radiation of intensity varying as above; (3) in aluminium the

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* 'Proc. Phys. Soc. Lond.,' September, 1911.

† 'Roy. Soc. Proc.,' February, 1912.

corresponding features all occurred with radiation of shorter wave-length than in paper and paraffin wax which consisted of lighter elements.

In these experiments comparatively heterogeneous primary beams were used, so that the particular absorbability or wave-length at which the characteristic radiations appeared could not be determined with any accuracy. The absorbability in aluminium, however, was of the order of magnitude of that obtained more exactly by other methods.

Absorption Method.

It has been shown that over the range of wave-lengths between those of the spectral lines of two consecutive series and not near to the longer wave-length series, the absorptions in any pair of substances are in an approximately constant ratio for any wave-length. Any marked deviation from proportionality in the absorptions in two substances as the wave-length of the radiation changes, shows the existence of a characteristic radiation. Thus as the wave-length of a radiation diminishes, the fraction $\frac{\text{absorption in substance A}}{\text{absorption in substance B}}$ remains approximately constant until the radiation becomes of shorter wave-length than that of a radiation characteristic of A or B. In this case the corresponding absorption increases rapidly and the ratio of absorptions is changed. The absorptions of homogeneous radiations were therefore determined in iron and aluminium, so as to provide a further test of the existence of a radiation characteristic of aluminium.

Passing from long waves to shorter, the ratio $\frac{\text{absorption in Fe}}{\text{absorption in Al}}$ suddenly rises at wave-length approximately $1{\cdot}9 \times 10^{-8}$ cm., which agrees with the determined wave-length of the K radiation of iron (fig. 9). There is, further, a sudden drop in the ratio,

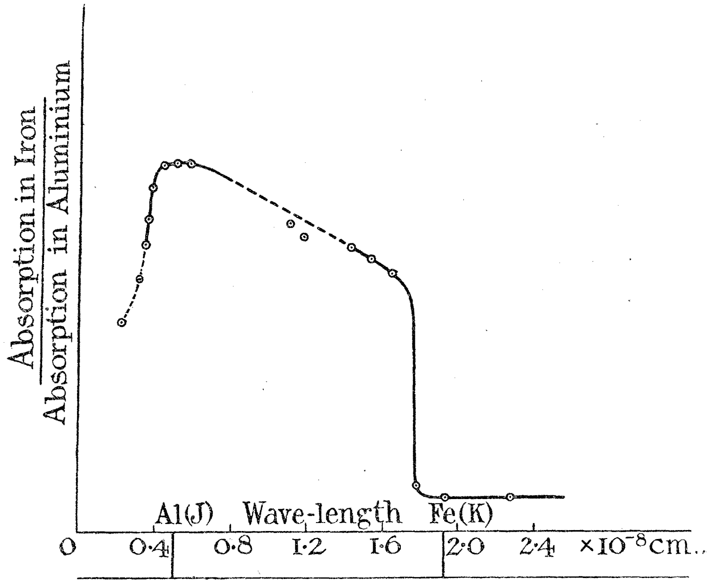

Fig. 9. Showing approximate wave-lengths of the K radiation from Fe and the J radiation from Al from relative absorption curve.

or rise in the absorption in Al for a wave-length of $0 \cdot 5 \times 10^{-8}$ cm. approximately, which again shows that Al has a characteristic radiation of about the same penetrating power as that of the K radiation from tin.

Thus all the methods, direct and indirect, show that under the usual conditions the light elements emit characteristic radiations of moderate penetrating power, and that the higher the atomic weight of an element, the more penetrating is its radiation. As these radiations are very much harder (of shorter wave-length) than those of the K series in the lighter elements, it is evident that they constitute a new series of characteristic radiations; and as there is no evidence of an intermediate series, this series should be called the J series. The mass absorption coefficients in Al $(\lambda/\rho)_{Al}$ for the radiations from N to S vary from about 2·5 to 1·75, or the wave-lengths from $0 \cdot 56$ to $0 \cdot 5 \times 10^{-8}$ cm. approximately.*

PRIMARY X-RADIATION.

The theory of emission of characteristic X-rays outlined above should also be extended to the process of production of X-rays by the incidence of cathode rays on any material, as in the ordinary X-ray tube. For it has been shown by BEATTY† that the generation of a radiation of given penetrating power or frequency necessitates the incidence of electrons with energy greater than that of a quantum of that radiation. This applies not only to the production of radiation which is evidently characteristic of the particular anti-cathode employed, but to that heterogeneous radiation which becomes more and more penetrating as the speed of the exciting cathode rays increases. Such a law indicates a similarity in the process of production of all the X-rays generated in the anti-cathode. If mere collision between an electron of the cathode stream and an atom or a component of an atom in the anti-cathode resulted in the generation of X-rays, the resultant radiation consisting of all kinds of pulses produced by random collisions would possess the properties of a mixture of homogeneous radiations but without such a definite superior limit to the frequency of its components as has been actually observed. The definite law indicates a definite process, a process similar in essentials to that described in connection with the production of the characteristic X-radiations.

There is no reason to deny that what has usually been regarded as the method of production of X-rays is inoperative; the probability is rather that the electromagnetic radiation generated in an anti-cathode by the random collision of the exciting cathode particles is of small intensity; it does not constitute the bulk of the radiation recognised as X-radiation. (Yet a complete theory must take account of the experimental fact of a decided polarization in the primary beam—indicating an

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* [These values are probably rather high, as they were obtained by comparison of the wave-length of the α line with the absorbability of the whole K-radiation.—*August*, 1917.]

† 'Roy. Soc. Proc.,' 1912.

amount of polarized radiation which ought very easily to have been observed in Beatty's experiments if it differed in method of production from that of the bulk of the heterogeneous primary radiation.)

If in the phenomenon of X-ray fluorescence we find it is essential that an electron be displaced from its normal position, and are led to conclude that X-rays are produced when the displaced or some other electron falls back into this position, we ought to look for a similar process in explanation of the more direct generation of X-rays. This naturally leads to the following considerations:—

The cathode particles in the cathode stream by collision expel electrons from their normal positions in the atoms in the anti-cathode; these displaced electrons thus receive an amount of energy—measured from the normal position and state—which must be less than the original kinetic energy of the impinging electron and may be much less. When they fall back to their normal positions they re-emit as radiation the potential energy which they lose in the fall. Further, if an electron in falling from one definite position to another emits radiation whose frequency n is given by the relation $hn =$ energy lost in falling from position to position—a law for which we have given direct experimental evidence and which was assumed by Bohr—we need only assume an extension of the law to apply to *any* fall within the atom. We must assume that when an electron falls from any position within an atom to some normally stable position it emits radiation, a quantum of which is equal to the potential energy lost in the fall.

Thus when an electron falls back from its position of greatest displacement, the frequency of the resultant radiation is given by $hn =$ potential energy of electron in its position of greatest displacement measured from its normal position and state—which may have any value less than the original kinetic energy of the cathode particle. When it happens that the place of the displaced electron is taken by an electron from one of the outer rings in the atom, a characteristic radiation is emitted.

Such a mixture of heterogeneous and characteristic radiations is actually emitted from the anti-cathode. This theory suggest a definite upper limit to the penetrating power or frequency of the radiation possibly emitted by an anti-cathode, for the highest frequency would be that generated when an electron falls freely from the surface of the atom to the innermost stable position of an electron, on the assumption that such a limit exists. A limit to the frequency of the X-radiation generated in a particular anti-cathode has not yet been proved, nor is there any certain experimental evidence in support of the hypothesis, though from considerations indicated above it seems probable theoretically.

[Though results have been obtained by certain experimenters which from a superficial examination appear to indicate such a limit, these results might have been foretold not only qualitatively, but with fair accuracy quantitatively, from the observed laws of scattering and absorption.

An approximate limit to the penetrating power of a radiation does not indicate a limit to the frequency or wave-length, for the absorption of penetrating radiations is principally due to the process called scattering, the laws governing which are entirely different from the laws of absorption connected with the emission of electrons. The process of scattering imposes the limit on penetrating power, and where scattering varies little with wave-length, gives the appearance of an approximate limit to that wave-length. Such a small variation of absorbability with a variation of wave-length (as measured by absorption in heavy substances) has been observed in the region for which results have been given.

Again, an empirical formula which connects wave-length and penetrating power, when absorption is due to one process, can scarcely be expected to hold when absorption is due to an entirely different process and is governed by entirely different laws.

In addition, since the discovery of the J series of radiations of higher frequency than those of the K series (see p. 349), it seems highly probable that radiations of higher frequency than that of the radiation supposed to have been observed can be generated, for this has been indicated as belonging to the K series.

For these reasons we think that further evidence will be needed in support of such conclusions, though results of the same kind may perhaps be expected elsewhere.]

GENERAL CONCLUSIONS UPON X-RADIATION AND THE QUANTUM THEORY.

Thus all the available evidence shows that X-radiation may be and is emitted by electrons—probably in certain cases by groups of electrons, or even atoms—as a continuous process and in any quantity whatever. It is frequently emitted in quantities almost infinitesimal in comparison with a quantum. It is, however, emitted in quanta from atoms when certain critical conditions resulting in the ejection of certain electrons are reached, the process of radiation then taking place in a perfectly definite manner involving the radiation of a definite amount of energy which is proportional to the frequency of vibration.

Absorption, too, normally takes place in very minute quantities—very small in comparison with a quantum. But in certain processes, which usually account for nearly the whole absorption, the radiation is absorbed in quantities greater than a quantum of the primary radiation, quantities varying with the conditions from one to two quanta approximately. There is no evidence of absorption of X-radiation in whole quanta, though the conditions are frequently such as to give an approximation to this.

All this evidence seems to indicate that a quantum of radiation in the sense in which it has frequently been used, *i.e.*, as an indivisible bundle of radiant energy, does not exist. The process of radiation may be, and is, continuous—at any rate, within limits extending to far smaller quantities than the quantum. The quantum is a unit of atomic energy which must be absorbed to change the configuration of the atom, and is radiated when that configuration returns to its original state. It thus of necessity appears in certain processes of absorption and radiation.*

The results obtained by certain experimenters on the ordinary production of primary X-radiation suggest, too, that mere collision of electrons with an anti-cathode is not sufficiently sudden, or of sufficiently violent a nature, to result in the production of the X-rays as ordinarily detected. The probability is rather that the function of the cathode particle is to displace electrons from their normal positions in atoms of the anti-cathode, and thus to produce in these atoms vibrations—some characteristic, others not—which result in the emission of the primary radiation.

* There is no need to indicate the problems of absorption and radiation still awaiting solution. Though there is no evidence as to the nature of the mechanism involved in these processes beyond what is indicated by a change from certain initial to certain final conditions these investigations seem to establish many important facts, and to show the narrow limits within which the quantum theory is in any sense applicable.