Some Contemporary Advances in Physics—III

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ELECTROMAGNETIC waves of every frequency from 10^4 to 10^{20} exist; they can be generated and perceived; their frequencies in nearly every instance can be measured; their actions and reactions with matter can be studied. This brief statement is the synthesis of a great multitude of inventions, experiments and observations upon phenomena of extraordinary diversity and variety. When Herschel in 1800 carried a thermometer across the fan-shaped beam of colored light into which a sunbeam was resolved by a prism, and observed that the effect of the sunbeam on the mercury column did not cease when it passed beyond the red edge of the fan, he proved that the boundary of the spectrum beyond the red is imposed by the limitations of the eye and not by a deficiency of rays. Almost at the same time Ritter found that the power of the violet rays to affect salts of silver was shared by invisible rays beyond the violet edge of the beam. Maxwell developed the notion of electromagnetic waves from his theory of electricity and magnetism, and described some of the properties they should have; and the light-waves and the infra-red and ultra-violet rays were found to have some of these properties, while the outstanding discordances were explained away by Maxwell's successors. Hertz and many others built apparatus for producing Maxwell's waves with frequencies far below those of light, and apparatus for detecting them, with consequences known to everyone. Years after X-rays and gamma-rays were discovered emanating from discharge-tubes and disintegrating atoms, Laue proved that these too are waves, lying beyond the visible spectrum in the range of high frequencies. Radiations emerging from collapsing atoms and radiations diverging from wireless towers; waves conveying the solar heat and waves carrying the voice; rays which disrupt atoms by extracting their electrons, rays which alter atoms by rearranging their electrons, rays which almost ignore atoms altogether, were successively discovered or created; and all these radiations were brought into one class, and identified with light.

This enormously extended electromagnetic spectrum was interrupted until lately by two regions unexplored. They were known as the gap between the X-rays and the ultra-violet, and the gap between the infra-red and the Hertzian waves, according to the names by which the various explored regions of the spectrum commonly go; but to understand why they remained unclosed for so long, and what kinds of rays are being found within them, it is necessary to consider how certain properties of the waves vary along the spectrum. Enough is known about the origin of electromagnetic waves to justify using it as a basis of classification. Classifying the rays, therefore, by *mode of production*, we can distinguish at least four sharply-contrasted types: first, rays emitted from atomic nuclei in process of disintegration; second, rays emitted from atomic electron-systems in process of rearrangement; third, rays due to atoms vibrating to and fro about their positions of equilibrium as constituents of molecular groups or of space-lattices; and finally, waves generated by oscillating electrical circuits.[1] For each of these classes there is a region of the spectrum which is particularly, although not exclusively, its own.

The rays emitted from disintegrating nuclei lie at the topmost end of the frequency-scale; they overlap the rays of the second class, but do not approach either of the gaps. The rays resulting from rearrangements of the electron-systems surrounding atom-nuclei extend over an enormous range. The minimum wave-length of this range is .1075A, the K-frequency of the uranium atom; it is and will almost certainly remain the definitive limit, unless someone should succeed in discovering a substance further up the periodic table than uranium, or in removing some of the deepest electrons from the electron-system of some heavy[2] atom. As maximum wave-length we might take that of a line 40500A lately recognized by Brackett as belonging to atomic hydrogen; but this is certainly not the definitive limit. Emission-bands due to atoms vibrating within molecular groups are found in and beyond the "near infra-red" (and indeed in the ultra-violet around 3000A, if we include bands of "compound" origin, resulting from processes occurring together which if happening separately would produce rays of the second and third types, respectively); while the "residual rays," which are ascribed to atoms vibrating within the gigantic molecular group which is a crystal lattice, extend as far as 0.152 mm. (residual rays of thallium iodide). Between 0.1 mm. and 0.4 mm. rays have been discovered emanating from the mercury

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[1] This classification is obviously not an exhaustive one. Continuous spectra have been omitted—thermal emission spectra of solids, and continuous X-ray spectra, which may be ascribed to random accelerations of free electrons. The continuous bands in gas spectra, of which one has just been explained by Gerlach (*ZS. f. Phys.*, 18, pp. 239–248; 1923) and others by Bohr (*Phil. Mag.* 26, p. 17; 1913), can be included in the second class by a slight generalization; and so, probably, can some fluorescence and phosphorescence spectra, at least if we extend "atomic electron-systems" to include "electron-systems of grouped atoms." There is also the possibility of rays due to changes in rate of rotation of molecules, not compounded with changes in oscillation or electron-arrangement.

[2] Meaning an atom with a large nuclear charge, which would have heaviness, or more properly massiveness, as a secondary characteristic. A short and simple adjective to describe where an atom stands in the scale of nuclear charge, i.e. in the periodic table, would be very welcome.

arc, which probably belong to the second or third class, but it is not certain which. If we gather all these classes together into a single great class of *natural* rays, extending from .02A or 2.10^{-10} cm. to 4,000,000A or 0.04 cm., they may be contrasted with the *artificial* rays generated by man-made electrical circuits, lying entirely beyond the long-wave limit of their range.[3]

One of the two lacunae in the spectrum, extending from 0.4 mm. to 7 mm., separated the range of natural rays from the range of artificial rays. To close this gap it was necessary literally to invent new rays, by designing oscillating electrical circuits which would generate frequencies which perhaps had never existed before in nature. The other lacuna, extending from 13A to 1200A, lay by contrast in the very centre of the range of natural rays, and precisely where we expect to find the frequencies resulting from certain peculiarly interesting and important processes in the electron-systems of atoms. These processes, it appears, are not in all cases easy to incite by the usual methods of stimulating atoms to radiate; but this difficulty is only one, and probably the least serious one, of the three hindrances which combined to delay the exploration of this region. A second impediment comes from the limitations of our devices for measuring wave-length, every one of which is unavailable over a certain sector of the region, extending roughly from 13A to 150A (limits which may later be forced somewhat closer together); but the most conspicuous obstacle is the extraordinary obstructiveness and opacity of every kind of matter to these rays.

The ability of electromagnetic waves to penetrate matter varies enormously from one part of the spectrum to another. At the uppermost end of the frequency-scale, the rays penetrate every sort of matter with astonishing ease. A layer of lead 8 mm. thick is required to remove half of the energy of a ray of wavelength .025A; and even this, it is probable, is not absorbed in the strict sense of being converted from radiant energy into another form, being merely deflected or *scattered* out of its original direction of motion.[4] With rays of greater wave-length, a true absorption is superposed upon the scattering, and increases very rapidly, about as the third power of the wave-length. The absorbed energy is used in extracting electrons from

[3] The distinction between natural and artificial rays is striking, but I fear not quite exact, since lightning-discharges and the causes of "static" offer instances of natural sources of radio frequencies. Also the selective absorptions of certain substances in the Hertzian range strongly suggest natural emission-frequencies. Still the distinction is not yet unsound enough to be dangerous.

[4] If A. H. Compton's theory of X-ray scattering is eventually triumphant, it will be necessary to admit that some radiant energy is transformed into kinetic energy of moving masses when scattering occurs.

the deeper levels of atomic electron-systems, as I described in the second of these articles. The absorption in any particular substance does not increase with an uninterrupted upward sweep; there are occasional setbacks, each of which occurs at a critical frequency where the radiation ceases to be able to extract electrons from a particular level. But though the lower-frequency rays cannot extract the deeper electrons of the atoms, they more than make up for it by expelling the outer electrons in greater and greater abundance; and when wave-length 13A is reached, they can remove only the outermost electrons or shift them from one orbit to another,[5] but they perform these actions so often that the beam is rapidly absorbed (even at 0.5A, 0.01 mm. of lead is sufficient to abstract half its energy).

Beyond 13A there is a region of well-nigh total eclipse. All we know about it is derived from a few measurements by Holweck. According to him, rays of wave-length 40A lose half their energy in traversing half a millimetre of air at atmospheric density; at 100A, the same proportion is consumed in a twentieth of a millimetre of air, or in a quarter of a millimetre of hydrogen, the most tenuous of all substances; and even these are not the most absorbable rays. A sheet of celluloid, .0001 mm. thick, which absorbs only 8% of the energy of a beam of wave-length 40A and 36% at 100A, abstracts 94% of the energy at 250A. It actually absorbs 97.3% of a ray of wave-length 308A; but this may be the least penetrating radiation of the entire scale, for the transmission apparently is a little greater at 400A (although Holweck seems to distrust the reliability of the last result). It must be admitted that the various beams of radiation on which these measurements were made are not monochromatic, but comprise each a continuous range of wave-lengths extending down to the quoted value, which is the minimum. Since the beam is in every case filtered through as many absorbing layers as possible before the final measurement of transmission through the celluloid sheet is made, and those remove preferentially the longer waves, it is probable that each datum refers to a finite, yet comparatively narrow, band of wave-lengths with its lower end at the specified value.[6]

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[5] Some of the absorbed energy may be utilized in other ways, but there is no known alternative mechanism.

[6] The curve of Fig. 1, taken from Holweck's article, shows his data for the absorbing power of celluloid plotted (logarithmically) against wave-length. All the points refer to wave-lengths between 40A and 400A except the one marked "a," which refers to the rays emitted by gaseous hydrogen bombarded by electrons of energy between 13 and 38 volts (the transmission is the same for every bombarding-voltage within this range). It is probably a sort of "weighted-mean" value for the various radiations of the Lyman series and possibly the secondary spectrum of hydrogen, and the value 1140A which Holweck assigns as its effective wave-length is probably as good as any. The straight line on the left relates to nitrogen.

Whether or not Holweck's measurements are accurate enough to fix the point of greatest opacity, it is certain that somewhere between 300A and 1200A the eclipse begins to pass off. Fluorite commences to transmit at about 1200A, quartz and gelatine at about 1800A (each of these was, for reasons of experimental technique, long the limit of the explored region). Air begins to let through the light at about 1800A; the atmosphere indeed arrests the rays of the sun and stars as far along as 2900, but this is ascribed to ozone in the upper strata. Henceforward the absorption of radiant energy in gases consists mainly in shifting the valence-electrons of the atoms from one level to another, or in altering the amplitude of vibration of atoms built into molecular groups. The characteristics of individual atoms become steadily less influential; the groupings of the atoms into molecules, crystals, liquid or solid continua determine the amount of absorption. The question whether a particular solid is a conductor or an insulator, entirely irrelevant at high frequencies, eventually becomes the only

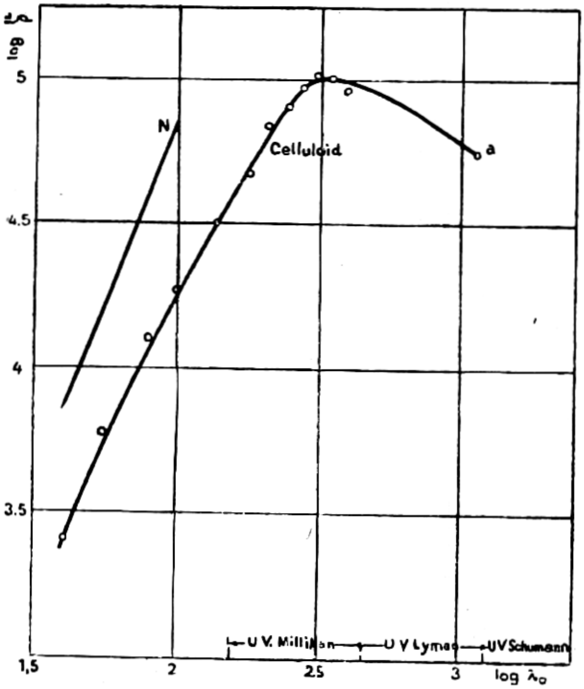

Fig. 1—Absorbing power of celluloid and of nitrogen plotted versus wave-length in the region of greatest opacity. (*Annales de Physique.*)

question that matters; and radio-frequencies penetrate great thicknesses of rock or brick more readily than the thinnest sheet of metal foil.

To explore the region of the spectrum in which the absorbing-power of matter is at its greatest, it is necessary to make a high vacuum over the entire path of the rays from their source to the receiver (photographic plate, ionization-chamber, or electrode for photoelectric emission). This necessity can be escaped only if the obligation of measuring wave-lengths is evaded, for then the path may be very short; the receiver may be brought quite close to the piece of solid substance or the stratum of gas in which the rays are excited. If the wave-lengths are measured, it must be done with a ruled or crystalline diffraction-grating, which enforces a lengthy path (often as much as two metres). No solid windows can be interposed in it to confine a diffusing gas to the region where the rays are excited (the only exceptions yet developed are Holweck's .0001-mm. celluloid windows, which when stretched over and sustained by a fine-meshed gauze are said to be able to support a 5-cm. pressure-difference between their two faces). The excitation must therefore take place, whenever possible, in vacuo. This is simple enough when dealing with the rays excited from solids by electron-bombardment, and originating from displacements of electrons deeper down in the atomic system than the valence-electron; for the bombardment can be carried on in vacuo. But the arcs and sparks which are commonly used to displace the valence-electrons of free atoms or molecules, and so produce the frequencies for which these are responsible, are usually operated in an atmosphere composed of a comparatively few of the atoms being studied, mingled with a large amount of air or some other permanent gas. Yet it has been found possible to operate both arc and spark discharges "in vacuo," that is, without the atmosphere of permanent gas; though they differ in various ways from the like-named and familiar discharges in air, and do not display quite the same spectra.

Vacuum arcs, when once ignited, can be maintained with a moderate voltage between electrodes of various metals; the mercury vapor lamp is the familiar example, but arcs of such metals as magnesium, aluminium, and lead were developed as early as 1905. The name "vacuum arc" is, of course, a misnomer; the discharge occurs in an atmosphere of the vapor of the metal, but this congeals as soon as it starts to diffuse away from the discharge, and does not impair the vacuum in the light-path. The condition for an easily-maintained vacuum arc is that the vapor-pressure of the metal involved be comparatively high. Yet arcs between carbon electrodes in vacuo seem to be easy to maintain, though the vapor pressure of carbon is immeasurably small; one is led to suspect the gases inevitably occluded in this element.[7] Saunders produced waves as short as 978A with an arc in calcium vapor, and Simeon waves down to 375A with a "carbon vacuum arc."

These vacuum arcs are started either by heating the electrodes to produce a momentary high vapor-density, and applying a transient high voltage between them; or by touching them together and drawing them apart while the moderate voltage is applied. If the latter method is tried when the voltage is too low to maintain an arc, there is a transitory flash, the *breakspark*; its spectrum in the visible region has been noticed by von Welsbach, who finds the relative intensities of certain lines strangely altered from what they are in the ordinary spark; but according to McLennan and Lang, it yields no rays of wave-length inferior to 2000A.

The *vacuum spark* or *hot spark* employed by Millikan and his associates is an altogether different affair; it is a brilliant spark which occurs between electrodes a millimetre or so apart (the limits 0.1 mm. and 2 mm. have been assigned) in an extremely high vacuum, when a transient potential-difference of the order of several hundreds of thousands of volts is laid across them. This is a mysterious phenomenon, which has been studied by several scientists, without satisfactory conclusions. Whatever the vacuum spark really is, there is no doubt that it exists, and that wave-lengths are found in its spectrum which are shorter than any hitherto observed in any spectrum of arc or spark; and it is likely that these high-frequency rays are not excited at all in the ordinary electrical discharges of relatively low voltage, so that the high vacuum provides the conditions for stimulating as well as for transmitting them. The least wave-length yet measured with an optical method (ruled grating), which is 136A, occurs in the spectra of some of these sparks.

Most difficult of all is obviously the problem of detecting the rays emitted by the atoms or molecules of a permanent gas, which must of necessity occupy the entire path of the light from the place where it is excited to the place where it is received, unless intercepted by a solid partition which would intercept the desired waves also. If the discharge-tube containing the luminous gas communicates only by a narrow slit with the chamber containing the diffracting and receiving apparatus, it is practicable to connect a powerful pump to

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[7] The minimum maintaining voltage for arcs in vacuo is given by Simeon as follows, for electrodes of the following materials: *C* 30 to 40 volts, *Na* 30 to 40, *Al* 80 to 100, *Si* 95 to 105. The distance between the electrodes is described as "slight," the degree of vacuum before arcing is not stated.

a branch-tube opening near the slit into the latter chamber, and so maintain in it a considerably lower density of gas than is required in the discharge. Hopfield has succeeded in maintaining an atmosphere of one kind of gas in the discharge-tube, and an atmosphere of another and a more transparent kind of gas in the chamber; the two gases are prevented from mingling by the same pumping-arrangement.

As for the measurement of wave-lengths from 1200A down to about 100A, it must be made with a concave diffraction-grating, which separates rays of different wave-lengths and itself focusses them at different places; for the rays cannot penetrate the prism of a prism spectograph, or the lens which is commonly used[8] to focus the beams diffracted by a plane grating. Rowland of Johns Hopkins, the first great master of the art of making diffraction-gratings, ruled them both upon plane and upon concave surfaces. The plane grating was so much the more easily ruled, that the concave grating fell into desuetude; but it became invaluable as soon as Lyman began to work in the region where the lenses extinguish the light. One might have anticipated that it would refuse to diffract rays the wave-lengths of which are only one-twentieth, one-fiftieth, even one one-hundredth of the spacing between its lines; but as Lyman and Millikan advanced farther and farther beyond the earlier limit of the ultra-violet, the concave grating proved itself competent to an extent which would probably have astonished its inventor. In one of Millikan's articles we may read an account of the ruling of new gratings by Pearson of Chicago; the spacing of the lines was by no means unusually small (about 500 per mm.) but they were ruled "with a very light touch so as to leave a portion of the original surface functioning in the production of spectra"—partly so that successive rulings might be nearly alike, but chiefly because if just half the original surface could be left intact, a large proportion of the total radiant energy would be diffracted into the first-order spectrum (this is the only usable one, because the higher-order images formed by the small wave-length rays encroach on the first-order images of the rays of greater wave-lengths). The arrangement of apparatus in experiments with the concave grating has varied little from the form which Lyman originally gave it. In Fig. 2 (from an article by McLennan) one sees the cross-section of a large tubular air-tight chamber, containing the grating at L (it is mounted on a carriage Q sliding on rails O, P), the slit at S and the photographic

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[8] There is no apparent reason against using concave mirrors instead of lenses, unless the multiple reflections consume too much of the light. Luckiesh mentions an instrument designed with focussing mirrors of nickel (Houston, Proc. Roy. Soc. Edinb., 1912), which, however, were found inferior to quartz lenses in the range in which it was tested.

plate at C. The rays are excited at the centre of a tube V communicating by the slit with the grating-chamber. In this instance the source of light was a vacuum-spark between the electrodes sketched; had it been a vacuum arc or a glow-discharge in a permanent gas, the tube might have been different in appearance, but would have been sealed onto the chamber at the slit in the same manner. The distance SL and LC are each one metre, and the sum of them constitutes the major part of the light-path (Lyman has reduced the sum to 40 cm. by using a more curved grating).

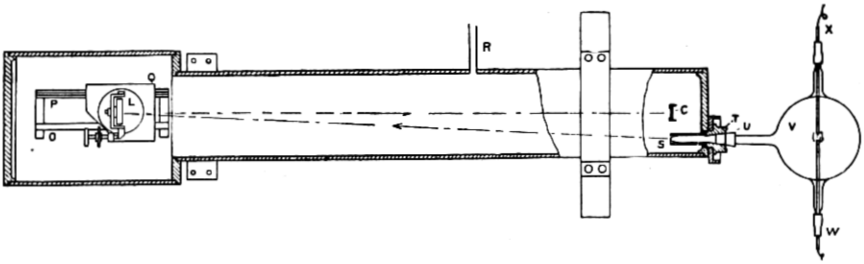

Fig. 2—Vacuum spectrograph with concave grating. (*Proceedings of the Royal Society.*)

The extension of the explored or explorable region of the spectrum from 1200A onward to 136A does not entirely close the lacuna; but it brings into the accessible range every one of a certain very important class of rays—the rays emitted by a free atom when its valence-electron has been displaced and is returning towards or to its normal position. The reason for distinguishing one electron of the atomic electron-system above the others as the *valence electron* (the name is chosen rather for its meaninglessness than for its meaning) lies in the existence of line-series in the spectra. Magnificently regular series of rays are observed in the spectra of the atoms of hydrogen and of ionized helium, each of which has an electron-system consisting of a single electron in the inverse-square field surrounding the atom-nucleus.[9] Series which resemble these, though they are not arranged according to so elegantly simple a numerical law, are found in the spectra of the elements of the first column of the periodic table (Fig. 3) and suggest forcibly that one of the electrons of the atom of lithium, or sodium, or potassium lies so much farther out than all the others that it moves by itself in a field which is almost identical with the inverse-square field of a nucleus of charge e (the resultant of the fields of the nucleus and the inner electrons approaches such a

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[9] This inverse-square field seems to be assured by the experiments on deflections of alpha and beta particles by atom-nuclei, quite apart from the successes of Bohr's special assumptions about atomic structure and radiation.

field as the distance from them increases). The same argument applies to elements of the second, third, and fourth columns, though with diminishing force, for the series become more difficult to trace and depart greatly from the archetype. In the crowded and complicated spectra of elements such as neon, argon, and iron, it is very difficult, though apparently not impossible, to arrange frequencies into series, and this is in accord with the belief (founded on evidence of other kinds) that in these atoms there is no single outer electron far beyond all the others, but rather an outer shell of several similarly-placed electrons. Any one of these might imitate the behavior of a valence-electron, however, when removed to an unusually large distance from the nucleus and from the rest. It is to be observed also that when atoms are brought close together in the liquid or solid state, the line series can no longer be excited.

	I	II	III	IV	V	VI	VII	VIII	O
1	1 H 13.54								2 He 24.6$^{\times}$
2	3 Li 5.36	4 Be	5 B	6 C	7 N 11$^{\times}$?	8 O 13.56	9 F		10 Ne 21.5$^{\times}$
3	11 Na 5.12	12 Mg 7.61	13 Al 5.9	14 Si 7.2 ?	15 P 13.3$^{\times}$?	16 S 10.31	17 Cl 8.2		18 A 15.3$^{\times}$
4	19 K 4.32	20 Ca 6.09	21 Sc 5.7	22 Ti 6.0	23 V	24 Cr 6.8	25 Mn 7.38	26 Fe 27 Co 28 Ni	
	29 Cu 7.69	30 Zn 9.35	31 Ga 6.0	32 Ge	33 As 11.5$^{\times}$	34 Se	35 Br 10.0		36 Kr 12.7$^{\times}$
5	37 Rb 4.16	38 Sr 5.67	39 Yt	40 Zr	41 Nb	42 Mo 7.0	43—	44 Ru 45 Rh 46 Pd	
	47 Ag 7.54	48 Cd 8.95	49 In 5.6	50 Sn	51 Sb 8$^{\times}$	52 Te	53 I 9		54 Xe 10.9$^{\times}$
6	55 Cs 3.88	56 Ba 5.19	RARE EARTHS	72 Hf	73 Ta	74 W	75—	76 Os 77 Ir 78 Pt	
	79 Au 8.7	80 Hg 10.39	81 Tl 6.1	82 Pb 7.38	83 Bi 8	84 Po	85—		86 Nt
7	87—	88 Ra 5.3	89 Ac	90 Th	91 Pa	92 U			

Fig. 3—Periodic table of the elements showing their atomic numbers and ionizing-potentials. (Cf. footnote 15.)

Wherever, therefore, there are discernible line-series, one infers an electron far enough beyond all the others to have a behavior and deserve a title of its own. Generalizing Bohr's wonderfully successful model of the atoms of hydrogen and ionized helium, we imagine that this electron enjoys a particular set of orbits, in the narrowest and deepest-lying of which it normally abides, while in any one of the others it can make only a transient halt.[10]

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[10] It may not be superfluous to complete the description of Bohr's model by saying that when the electron goes from one orbit to another, the difference ΔU between the values of the energy of the atom in the two states is radiated in a ray of frequency $\Delta U/h$.

Now all the line-series observed in the spectra of excited atoms and all which there is any reason to imagine as existent but undiscovered, lie entirely at wave-lengths greater than 136A; indeed most of them lie in the already-accessible region beyond 1200A, but a few of the most important are in the newly-opened range. Hydrogen is entitled to first mention, being the leader of the procession of elements as well as the most completely understood of them. The visible spectrum of (atomic) hydrogen consists of the archetype of all line-series, the Balmer series, extending from 6563A to 3650A, the frequencies of its lines being equal to the numbers of the series

$$\text{(A)} \qquad R\left(\frac{1}{2^2}-\frac{1}{3^2}\right),\ R\left(\frac{1}{2^2}-\frac{1}{4^2}\right),\ R\left(\frac{1}{2^2}-\frac{1}{5^2}\right),$$

and so forth, in which R is a certain constant ($R=3.29 \cdot 10^{15}$). According to Bohr's theory, this means that the energy-values[11] of the consecutive orbits of the valence-electron (in this case the only electron) are given by the numbers of the succession

$$\text{(B)} \qquad -Rh\left(\frac{1}{2^2}\right),\ -Rh\left(\frac{1}{3^2}\right),\ -Rh\left(\frac{1}{4^2}\right),\ -Rh\left(\frac{1}{5^2}\right),$$

and so forth, and the consecutive rays of the series are emitted when the electron drops into the first of these orbits from the second, third, fourth and consecutive orbits. Most people, on looking at the succession of numbers (B), would instinctively complete it by adding a term $-Rh$ at the beginning; and if there is truly an orbit of which the energy-value is $-Rh$ there must be an additional line-series,[12] the frequencies of its lines being equal to the numbers of the series

$$\text{(C)} \qquad R\left(1-\frac{1}{2^2}\right),\ R\left(1-\frac{1}{3^2}\right),\ R\left(1-\frac{1}{4^2}\right), \text{ and so forth.}$$

The first three lines of this series should lie at 1216A, 1026A and 972A. They were discovered by Lyman in 1913, and the series bears his name.

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[11] The energy-value of an orbit is the energy of the atom when the valence-electron is in this orbit; the energy of the atom being set equal to zero, when the valence-electron is removed to infinity. It follows from this last convention that the energy-value of an orbit, with sign reversed, is equal to the energy which must be imparted to the atom to remove the valence-electron completely from the atom when it is initially in the orbit in question. Thus the energy-value of the orbit which the valence-electron normally inhabits is equal to the ionizing-potential of the atom, when it is expressed in appropriate units and its sign reversed. The practical advantages of this convention are so great that we endure its annoying and confusing consequence of making all the energy-values of non-ionized atoms negative.

[12] The existence of this series was anticipated long before Bohr's interpretation of the Balmer series, being suggested by the form of the series itself.

Helium follows hydrogen in the procession of elements. Its spectrum includes several line-series. The frequencies of the first four members of one of these series, the principal series of the singlet or parhelium spectrum, are as follows (all the numbers in the successions *D*, *E*, *F*, *G*, and *H* should be multiplied by 10^{14}):

(D) 1.457, 5.981, 7.567, 8.300

Subtracting each from the frequency of the series-limit, which is 9.609, we obtain the succession of numbers

(E) $(9.609-8.152)$, $(9.609-3.628)$, $(9.609-2.042)$, $(9.609-1.309)$

which suggests a succession of orbits, having the following consecutive energy values[13]:

(F) $-9.609h$, $-8.152h$, $-3.628h$, $-2.042h$, $-1.309h$.

The consecutive frequencies of this series are emitted when the valence-electron falls from the second, third and consecutive orbits of this succession into the first one. One would suppose that the valence-electron normally abides in this first orbit. But if this were so the energy required to ionize the atom would be $9.609h \cdot 10^{14}$, equivalent to 3.96 volts; and waves of the frequencies given by (D) could displace the electron and be absorbed thereby. But the ionizing-potential of the atom is about 25 volts and the frequencies (E) do not appear as dark lines in the absorption-spectrum of helium. Therefore there must be still another orbit much deeper down, with a much higher (negative) energy-value, than any listed under (F). In 1921–22 Lyman discovered (with his highly-curved grating and shortened light-path, and pumping arrangement for keeping the pressure low) a new series of lines of wave-lengths 584.4A, 537.1A, 522.3A and 515.7A. Their frequencies are

(G) 51.34, 55.85, 57.44, 58.18

which may be written as the succession of numbers

(H) $(59.49-8.15)$, $(59.49-3.64)$, $(59.49-2.05)$, $(59.49-1.31)$.

Comparing these with the succession (E) we recognize the same set of subtrahends,[14] and accordingly identify the common quantity $59.49 \cdot 10^{14}$

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[13] It is customary to designate the orbits by their energy-values divided by hc, or $19.68 \cdot 10^{-17}$.

[14] It would not be necessary to call attention to this if we could calculate the frequency of the series-limit, which would give the energy-value of the new orbit immediately; but the four discovered lines are hardly sufficient for such an extrapolation (there are fourteen of the other series to use for calculating its limit).

as $-1/h$ times the energy-value of an additional orbit. If this orbit is the permanent home of the valence-electron, the energy required to ionize the atom must be $+59.49h \cdot 10^{14}$, equivalent to 24.5 volts. When the new lines were discovered, the accepted value was 25.3 volts, largely because of a certain measurement by Franck. After the publication of Lyman's discovery, Franck re-examined his method and data and found them compatible with the value 24.5 volts; and very recently C. A. Mackay has ascertained that the ionizing-potential of helium is 14.1 volts greater than that of mercury, which is quite definitely known to be 10.4. One could hardly desire a better illustration of the confluence of measured values of the energies of atoms and measured values of their radiation-frequencies, when both are interpreted according to the contemporary theory of radiation.

These newly-discovered waves must be the shortest in the spectrum of helium; the atom cannot emit a ray of wave-length less than the series-limit 504A, calculated by the equation

$$h\nu = hc/\lambda = \text{energy-value of the deep-lying orbit} = 59.49 \cdot 10^{14} h.$$

They are much shorter than the waves of the Lyman series of hydrogen, which Bohr's theory, together with the observed value of ionizing-potential of atomic hydrogen, justify us in declaring to be the shortest waves emitted by that atom. Furthermore, it is almost certain that they are shorter than any waves for which the valence-electron of any atom is responsible; for the ionizing-potential of helium is greater than any other measured ionizing-potential, and there is no reason to believe that any of the yet unmeasured ones exceed it. Its nearest rivals are the ionizing-potentials of the inert gases which share the last column of the periodic table. The experimentalists have not agreed very well in their estimates of these, although all agree that the values are comparatively high. Hertz, the latest to make measurements upon neon and argon, gives 21.5 volts for the first and 15.3 volts for the second. Both, therefore, should emit some rays lying below 1200A, but above 575A and 800A, respectively, and resulting from transitions of the valence-electron. Dejardin gives 12.7 volts for the ionizing-potential of krypton and very lately 10.9 volts for that of xenon. In the other columns of the periodic table, the values of ionizing-potential are prevailingly lower than in the column of inert gases. The value 10.4 volts (for mercury) is the highest among the metals; several of the non-metallic elements appear to have ionizing-potentials between 12 and 17 volts, but for some of these it is difficult to tell whether the observed value pertains to the atom or to a molecule. The experimental material is abundant[15] enough to give practical certainty that "valence-electron rays" below 1000A occur in the spectra of only a few elements, and below 500A in none.

Nevertheless, Millikan and Bowen, photographing the spectra of all of the first twenty elements (neon and argon excluded, and chromium and copper added) down to the extremity of the region accessible with the concave grating, discovered great numbers of lines, of which they attribute dozens or scores to particular elements (for example, some forty lines ascribed to potassium, though its ionizing-potential of four volts corresponds to a minimum wave-length exceeding 2500A). Some of these may be lines of compound origin, resulting from two simultaneous changes in the electron-system of the atom, one being a transition of the valence-electron and the other a rearrangement of the other electrons. (Saunders mentions such lines in the spectra of elements of the second column of the table.) Others are due to rearrangements of internal electrons following upon a displacement of one of these. Many others are attributed to displacements of the valence-electrons of ionized atoms. Of this new field of research, the spectroscopy of ionized atoms, I wrote briefly in the first article of this series. In the more easily accessible regions of the spectrum, Paschen had discovered rays of doubly-ionized aluminium and Fowler rays of trebly-ionized silicon.[16] Millikan and Bowen go a step further by identifying certain rays of quadruply-ionized phosphorus; indeed they believe that, under the violent excitation provided by their vacuum-spark, the waves emitted by atoms which have lost all but one of the electrons from their outermost electron-shells (the three just specified are in this state) are especially abundant and intense.

[15] In the periodic table of Fig. 3 the ionizing-potentials of the elements are given along with their atomic numbers. Overlined figures are values calculated from series-limits and confirmed by direct experiment; starred values are data of experiment, for elements of which the series have not been worked out; the remaining values are calculated from series-limits and have not been verified. The data are from the cited sources, from Foote and Mohler, and from Saunders' graphic tabulation (*Science*, volume *59*, pp. 50–51, January 18, 1924;). Interesting variations with atomic number are observed which yield bases for estimating the values for still other elements by interpolations.

[16] "It might be mentioned that the spectrum of silicon was first selected for investigation on account of its astrophysical interest. The lines representing successive stages of ionization of this element appear in stars which there is every reason to believe are at successively higher temperatures. The complete series-data for the four spectra [trebly,- doubly-, once- and non-ionized atoms] and the ionization-potentials deduced from them, may be expected to find an important application in fixing the scale of stellar temperatures . . . All the series predicted in [these four] spectra of silicon; in the spectra of doubly-, once-, and non-ionized aluminum, of once-ionized and neutral magnesium, and of neutral sodium, have been actually produced and have been found to have the character and constants expected."—A. FOWLER.

The "valence-electron" rays emitted by ionized atoms should lie at lesser wave-lengths (roughly ¼ as great) than the valence-electron rays of neutral atoms, and therefore should be particularly at home in the region newly opened to exploration. The highest frequencies emitted by the ionized-helium atom are perfectly calculable from Bohr's theory; they are the frequencies of the Lyman series, quadrupled, and the wave-lengths therefore lie between 304A and 230A. They have not been reported, but Lyman in 1919 observed two lines in the spectrum of violently-excited helium, near the positions 1214.9 and 1640.1A calculated for the first and third lines of the next helium series (having the frequencies of the Balmer series, quadrupled). The place of the second member of the series was obscured by an alien line.

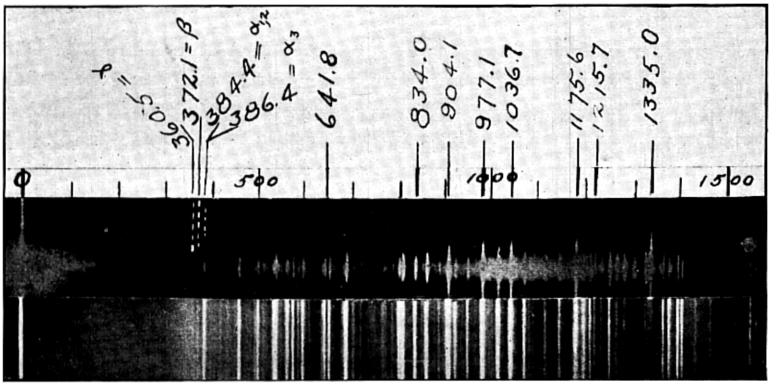


Fig. 4—Spectrum of a vacuum spark between carbon electrodes. (*Astrophysical Journal.*)

The once-ionized lithium atom, judging from the example of neutral helium, should display higher frequencies than any other once-ionized atom, and they should be arranged in recognizable series, somewhere near the extreme limit of the explorable range as it stands at this moment. They have not, however, been reported; Millikan says that his plates show no lithium lines of any sort from 1700A down at least to 370A, if not farther.

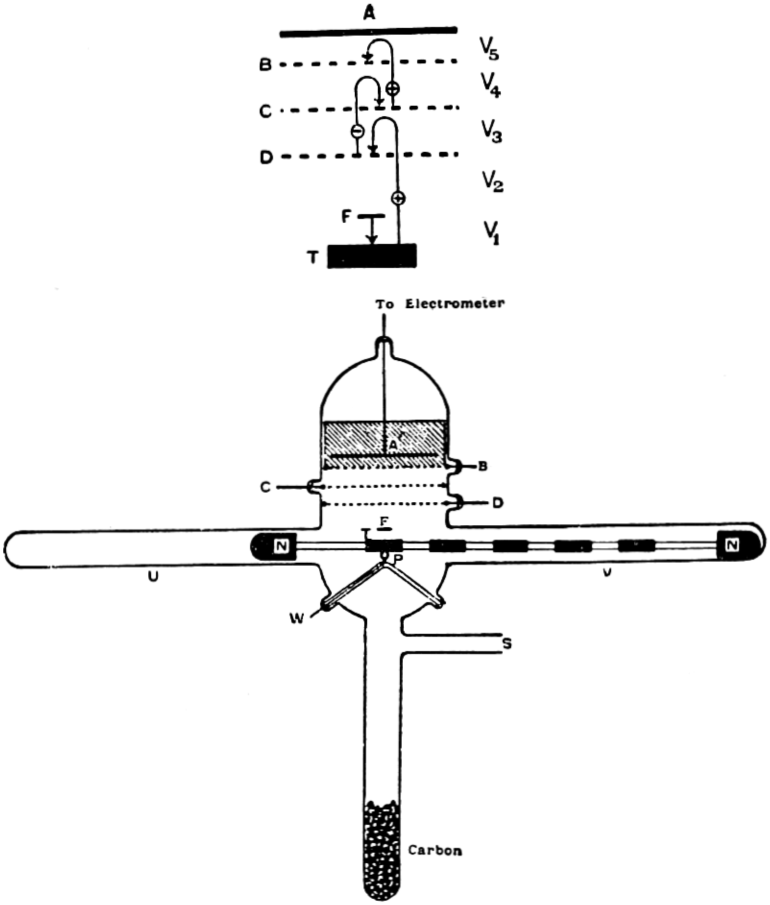
As an example of a spectrum extending far into the newly-conquered field, a plate representing the spectrum of a vacuum spark between carbon electrodes is reproduced from one of Millikan's articles as Fig. 4. The actual spectrum is in the middle; it is drawn out for better intelligibility, at the side. Most of the marked lines, including the extreme line at 360.5A and the strongest line at 1335A, are attributed to carbon; some to other elements, particularly the one at 1215.7 which is the first line of the Lyman series of hydrogen. The interpretation of spectra like this is not a simple matter of putting electrodes of the desired substance into the tube and ascribing to it all the lines which come out on the plate. It appears that impurities, even when present in what might be considered small proportions, contribute their own rays to the spectrum in great abundance and intensity. Millikan found that all the lines present in the spectrum of the vacuum spark between magnesium electrodes were also present when aluminium electrodes were used, and vice versa, and finally assigned them all to oxygen. Lyman found it extremely difficult to decide which lines belong to hydrogen and which to helium, since the spectra of glow-discharges in these gases have so many lines in common. Helium has a pronounced habit of encouraging excitation of the rays of whatever other gases are mixed with it, since the helium atoms require so much energy to displace their valence-electrons that free electrons shot into helium gas are liable to bounce harmlessly from one helium atom to another until they strike and excite an atom of another variety. Even if one can be sure that all the rays in a spectrum belong to a single element there remains the problem of assigning them to neutral or variously-ionized atoms. It is clear that the completion of the spectroscopist's task is deferred by this extension of it to what the Germans call the unforeseeable time.

We return to the consideration of the lacuna in the spectrum, which extends from 13A up to a boundary which by the use of high vacua, concave gratings, and violent excitations, has been forced from 1200A down to 136A. This wave-length 136A stands for the moment as the lowest which has ever been actually measured with the ruled grating; and in spite of the unexpected and fortunate adequacy of the instrument down even to this point, little more can be demanded from it. The reason is, that the substance on which the rulings are made must eventually cease to reflect the rays on account of its own looseness of texture. Being a congeries of atoms themselves separated by finite distances, the metal will not behave as a continuum towards waves of a length not very large compared to its own atomic spacing. Below 13A waves are not reflected. Little is known of the rate at which the reflecting-power dwindles away to zero between 136A and 13A and this little we owe again to Holweck. He directed a beam of radiation (it was a mixed beam, as was previously made clear, and the wave-length-value is merely the minimum wave-length in it) against a polished bronze mirror at the very oblique incidence of 73.°8; the reflected beam had one-third the intensity of the incident beam at wave-length 123A (practically the extreme wave-length of Millikan's experiments), but only 10% at 60A and only 3% at 40A. The performance was much better at a still more oblique incidence; on the other hand Holweck thinks that it gets rapidly worse as the incidence is made more nearly normal, and if this is true the outlook for the concave grating, with its condition of almost normally-incident light, is most unpromising.

Below the boundary 13A, the atomic constitution of solid substances turns from a hindrance into an advantage, and crystals serve as natural diffraction-gratings of incomparable fineness—too fine, indeed, for our convenience in this part of the spectrum, since the boundary is fixed by the smallness of the distance d between successive layers of atoms in the diffraction-grating. Rocksalt, one of the standard crystals, for which $d=2.814$A, has been used successfully up at least to 4A (by Fricke) and the rest of the way to 13A has been explored with crystals of gypsum ($d=7.58$A) or sugar ($d=10.56$A); in this region it was necessary to evacuate the light-path, precisely as in the region beyond 136A. The only possibility of a new advance depends on the utilization of crystals of still greater inter-atomic spacings. Holweck mentions a crystal with a formidable name, for which $d=19$A, and de Broglie and Friedel found that the oleates of sodium, potassium and ammonium presented spacings of the order of 40A between consecutive molecule-layers. If these substances can be adapted for use in crystal spectographs, the boundary of the explored region may be pushed far beyond its present place. It may be found, however, that the crystal absorbs the rays before they go deeply enough to be diffracted.

As for the region between 13A and 136A, no one has ever measured the wave-length of a radiation lying within it; but there is a method which indicates the existence and something about the wave-lengths of rays which almost certainly belong in it. In applying this method the photographic plate is replaced by a metal electrode (usually of platinum) which, when irradiated by rays of any wave-length (less than a certain critical one which always lies far above this range) emits electrons. For this reason it is often known as the *photoelectric method*, although the substitution of one kind of receiver for another is not its most distinctive characteristic. A target made of the substance to be studied is sealed into a tube, opposite a source of electrons (generally a filament for thermionic emission); the photosensitive electrode is placed somewhere in the tube where whatever rays are excited at the surface of the target will fall directly upon it. It is all-important to protect this electrode from electrons and ions, negative or positive, proceeding from target, filament, or anywhere else.

Usually the electrode is screened by a family of gauzes, with their potentials adjusted as is indicated in Fig. 5 (with the paths of intruding ions of both signs, including those excited from the outer gauzes themselves, mapped out to show how they are rebuffed). Naturally the arrangement of potentials in front of the electrode must be such that the emitted electrons are all drawn away from it, not driven back onto it. The rate of emission of electrons, the *photoelectric current*, may be measured with an electrometer connected either to the sensitive electrode or to a gauze so placed as to gather in all the electrons emitted from it. Figs. 5 and 6, the latter of which shows a



Figs. 5 and 6—Horton's apparatus for determining excitation-potentials by the "photoelectric method." (*Philosophical Magazine.*)

completely equipped tube with filament at F, a row of targets which can be moved consecutively into place at T, and the photosensitive electrode at A with its gauze shields in front of it, come from the work of Horton, Andrewes and Davies. A tube designed and used by E. H. Kurth is shown in Fig. 7; the filament is seen in perspective at C, the target at T, and the sensitive disc at D; the family of diverging straight lines represents a set of metal laminae, which being charged alternately to potentials 0 and +135 volts gather in any ions which start up towards the disc. The method can also be adapted to gases, and this application has an interesting and important history; but as nearly all the data respecting gases refer to wave-lengths superior to 1200A, they fall out of the province of this discourse. Foote and Mohler, however, penetrated to 26A with the apparatus of Fig. 8, filled with oxygen. The filament is at A; the electron-accelerating voltage V is applied between A and the gauze B, so that the target is essentially a thin layer of gas enveloping B; the photosensitive electrode is the gauze C, the photoelectric current from which is gathered in by the plate D (screened against positive ions by its high potential).

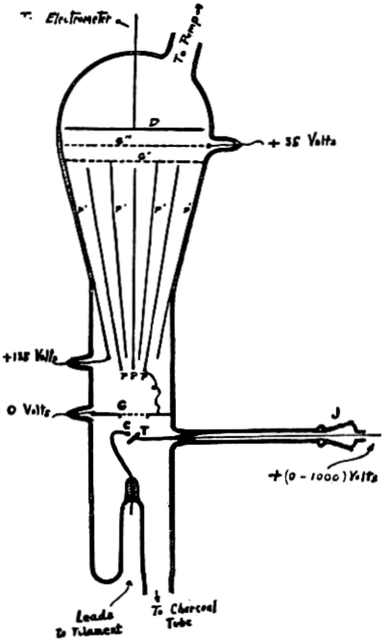


Fig. 7—Kurth's apparatus for determining excitation-potentials. (*Physical Review.*)

The art of detecting radiations by this method consists in giving various values to the "bombarding voltage" V between target and filament, which is the measure of the energy of the electrons impinging on the target; measuring the photoelectric current i, which is the measure of the intensity of the rays; plotting i (or better the ratio of i to the current of bombarding electrons) versus V; and examining the curve to see whether it displays sudden changes of slope. If it does, one infers that at the corresponding voltages new radiations suddenly burst forth. The method therefore consists in finding critical bombarding-voltages, that is, critical electron energies which just suffice to excite particular sorts of radiation; it is a method for discovering *excitation-potentials*. Three excellent instances of such abrupt changes in slope, or *breaks* as they are frequently called, appear in the (i, V) curve determined with an aluminium target by Horton and his associates (Fig. 9). Very many such curves appear in the literature, with more or less conspicuous breaks; some are as striking as these in the figures, some require a good deal of care and experience to locate them properly, and some, one is driven to conclude, are visible only to the eye of faith. But it is hardly possible to doubt that such a

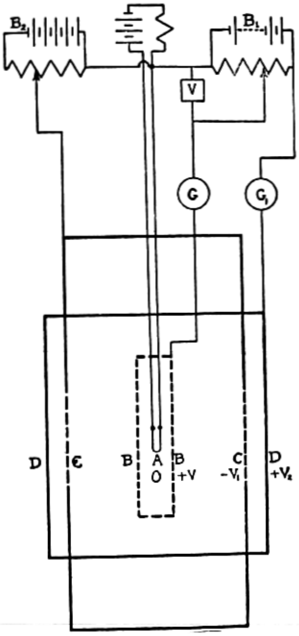


Fig. 8—Mohler and Foote's apparatus for determining excitation-potentials of gases and vapours. (*Bulletin of the Bureau of Standards.*)

corner as the three here reproduced marks the *entrée en scène* of a new ray or set of rays.[17]

But a determination of an excitation-potential is not a measurement

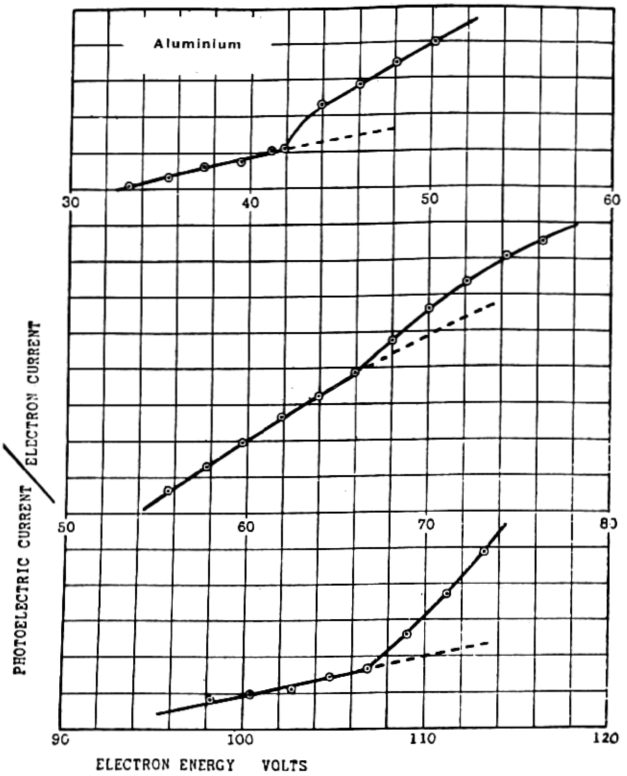


Fig. 9—Breaks in a photoelectric-current curve indicating excitation-potentials. (*Philosophical Magazine.*)

of the wave-lengths of the excited rays; and while it is supposed that excitation-potentials between 1000 volts and 100 volts are associated with rays of wave-lengths between 12A and 123A, this is merely a supposition.[18] We require a theoretical relation between excitation-

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[17] It is clear from this account that the photosensitive disc might be replaced by a photographic plate, on which the opacity due to the rays produced by consecutive values of V could be measured; or by an ionization-chamber, in which the ionization-currents could be measured. It is equally clear that neither method would be so suitable for detecting slight discontinuities in rate of increase of radiant energy with increase of V. However, both methods are used at higher frequencies, where by dispersion of the waves a discontinuity in the intensity at a single wave-length is made more conspicuous.

[18] This is the best place to remark that electrons of voltage V bombarding a solid, in addition to exciting (if V is high enough) rays characteristic of the bombarded atoms, excite also a continuous spectrum of rays of all frequencies up to a maximum

potentials and excited frequencies. The question is of high importance, not simply because we are interested to know whether some of the excited rays really lie in the hitherto unpenetrated range, but primarily because excitation and emission are among the fundamental qualities of atoms. Excitation-potentials exceeding 1000 volts generally produce rays of which the wave-lengths are less than 12A and can be measured with the crystal spectrograph, so that a rule or law can be deduced from the two sets of measurements. Excitation-potentials inferior to 25 volts generally produce rays of which the wave-lengths are greater than 500A and can be measured with optical apparatus, and again a law can be deduced from the two sets of data. But the law is not the same in the two cases; this is because excitation, in the former case, consists in displacing a deep-lying electron, while in the latter case it consists in a displacement of the valence-electron. We are forced to the disconcerting conclusions that excitation-potentials between 1000 volts and 25 volts involve electrons of an intermediate type, and that the still-unverifiable law connecting them with the frequencies of their excited rays is not identical with either of the laws in the accessible regions of the spectrum.

The law for excitation-potentials involving displacements of the valence-electron is twofold. Each atom has at least two such excitation-potentials. One of them is its ionizing-potential. When the accelerating-voltage of an electron-stream playing against a multitude of free atoms forming a gas is raised just past the value V_i at which an individual electron has just enough energy to remove the valence-electron of an atom, there is an outburst of radiation. This comprises rays of many frequencies—probably all those which we have called valence-electron rays—and they are emitted as the valence-electrons descend step-by-step along their ladders of orbits. All these frequencies conform to the relation

$$h\nu < eV_i. \qquad (1)$$

The other excitation-potential is the *resonance* potential of the atom (there may be more than one of these [19]). When the accelerating-

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equal to eV/h. The heterogeneous beams used by Holweck in the experiments previously cited consisted chiefly, if not entirely, of this continuous spectrum. All the excitation-potentials mentioned in these pages, however, relate to individual rays or groups of individual rays characteristic of atoms.

[19] This question is still incompletely solved, in spite of much labor. At one time it was supposed that the valence-electron could be raised either altogether out of the atom, or else to the deepest-lying of the transient-sojourn orbits (or to either of the two deepest-lying orbits, if there are two complete families of orbits such as the mercury atom possesses); but not to any of the other transient-sojourn or "virtual" orbits. This restriction would apply only to displacements caused by impinging electrons; quanta of appropriate frequencies can lift the valence-electron to any of

voltage of the electron-stream is raised just past the value V_r at which the individual electron has just enough energy to raise the valence-electron from its normal to one of its transient-sojourn orbits, there is an outburst of radiation. This comprises rays of a single frequency, emitted when the valence-electrons return in single leaps from the orbits to which they were momentarily raised to the orbits of their normal habitation. This frequency conforms to the relation:

$$h\nu = eV_r. \tag{2}$$

The law for excitation-potentials involving displacements of deep-lying electrons bears a certain resemblance to the first of the foregoing laws. When the accelerating-voltage of an electron-stream playing against a multitude of atoms assembled in a solid or liquid is raised just past the value V_e at which an individual electron has just enough energy to extract a certain deep-lying electron, say a K-electron, there is an outburst of radiation comprising many frequencies, all conforming to a relation resembling (1), to wit:

$$h\nu < eV_e. \tag{3}$$

But it would be misleading to assume that the processes resulting in (1) and in (3) are identical. In the first place, it is not certain that the deep-lying electron need be completely extracted. Suppose it possessed a set of transient-sojourn orbits in the outskirts of the atom, their energy-values differing from one another and from that of the "orbit at infinity" (the state in which the electron is quite detached) by amounts less than the 25 volts which is the maximum difference between the energy-values of any valence-electron. Then there might be several excitation-potentials, differing from one another by 25 volts at most; but this difference would be so inconsiderable a fraction of the value of the extraction-potential V_e, which ranges from more than 100,000 volts for the K-electrons of uranium to about 1100 volts for those of neon, that they would be difficult to distinguish. Indications of multiple excitation-potentials have, how-

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an immense number of orbits of a certain set, but not to transient-sojourn orbits of certain other sets. Lately it has been affirmed that impinging electrons of the right energy can lift the valence-electron to any one at all of its transient-sojourn orbits, even those to which it cannot be lifted by quanta; but this rule, if it is the true one, has not yet been illustrated by any extensive set of experimental data, though Hertz has lately intimated in a brief note that he has assembled such a set by experiments on helium. Franck and Knipping detected excitation-potentials corresponding to the lifting of the valence-electron of helium from its normal orbit to several distinct P-orbits; but I gather from a later paper by Franck that nobody has been able to reproduce the result. Olmstead and Compton discerned excitation-potentials corresponding to the lifting of the electron of hydrogen from its normal orbit to each of the next six transient-sojourn orbits.

ever, been discerned in the "fine structure" of the *K* absorption-edges of the lighter elements (notably the elements from sodium to potassium). In the second place, the process of emission is different in the two cases described by equations (1) and (3). In the former case, the rays were emitted as the valence-electron (or another replacing it, which comes to the same thing) redescended its ladder of orbits; but when a deep-lying electron is extracted, the resulting rays are emitted because of rearrangements of the other internal electrons of the atomic electron-system, which occur irrespective of whether the departed electron quickly returns to the atom, or remains a long time away.

I will now risk the making of a distinction which may eventually turn out not to be the most natural or practical, by reserving the name *deep-lying electrons* for those electrons which lie entirely within at least one completed electron-shell of an atom, and designating the others (exclusive of the valence-electron, which has already been set apart from the rest) as the *shallow-lying electrons*. It follows from this definition that the first nine atoms of the periodic table, up to fluorine (inclusive) possess only shallow-lying electrons; the next eight (*Ne* to *Cl*) have one set of deep-lying electrons, the *K* set; the next eighteen (*A* to *Br*) have at least four sets of deep-lying electrons, the *K* set and three *L*-sets (the last three can be grouped as one). It follows also that every instance in which an excitation-potential has been measured, and the wave-lengths of the excited rays have also separately been measured, is an instance in which a deep-lying electron is involved. For example, the excitation-potentials involving extraction of the *K*-electrons have been measured from the top of the periodic table down to the twelfth element (*Mg*), over which range they decline from 115,000 volts to 1100 volts; the excited waves have been measured over the same range and down to the eleventh element (*Na*), over which range they rise (for the principal ray) from .10A to 11.88A. At this point, and just before the *K*-electrons pass over into the category of shallow-lying electrons at the ninth element, the wave-lengths enter into the inaccessible range. The wave-lengths of the rays excited when one of the *L* electrons is displaced have been measured from the top of the table down to the twenty-ninth element (*Cu*) where, arriving at 13.3A, they too pass into the immeasurable class.

The general consequence of all this is, that the excitation-potentials involving shallow-lying electrons must be below 1000 volts; that, conversely, the excitation-potentials observed between 25 volts and 1000 volts are chiefly those of excitations which consist in displacements of shallow-lying electrons; and finally, that the wave-lengths of the excited rays lie below 13A, many of them in the inaccessible range, some in the range newly opened to exploration. This is a most unfortunate coincidence, for instead of being able to apply laws which prevail in other ranges to compensate for our inability to measure wave-lengths in this range, we have to expect distinct laws within it. Must shallow lying electrons be extracted altogether from the atom if they are to be displaced at all or have they certain transient sojourn orbits to some or all of which they may be raised by electron-impacts? Do the emitted rays result from a step-by-step return of the displaced electron? or from a return in a single leap? or from a rearrangement of the remaining electrons? or from a compounding of changes of the two latter types? So long as the emitted wave-lengths are not measured, these questions cannot be answered with confidence.

Some little can be inferred from numerical relations among excitation-potentials. McLennan and Clark, for example, observed three excitation-potentials of lithium, at 37.0, 31.8 and 12.0 volts. The first two of these voltages stand nearly in the ratio of the first two frequencies of the Lyman series in the hydrogen spectrum, which suggested to the discoverers that the processes involved in the excitations were the raising of a K-electron to the first and second of a pair of transient-sojourn orbits, standing in the same relation to the normal orbit of the K-electron as the orbits of energy-values $-Rh/4$ and $-Rh/9$ stand to the normal orbit of energy-value $-Rh$ in the hydrogen atom. That is to say, they conceive these excitation-potentials to be comparable to resonance-potentials, and the K-electron of lithium to behave like a valence-electron. They also found excitation-potentials of beryllium at 20.3 and 16.0, and of boron at 27.92 and 23.45. The ratio of each pair of numbers is about equal to the ratio of the first two frequencies of the Balmer-series, suggesting that these are resonance-potentials of an L-electron; the details of the analogy may be left to the reader to work out. Each of the latter elements displayed additional higher potentials, to be associated with the K-electrons. Rollefson lately discovered seven excitation-potentials of iron in the range between 160 and 264 volts, expressible by a formula $(a-b/n^2)$ if the integer values 5, 6, 7, 8, 9, 10 and 12 are successively given to n. If these seven potentials correspond to elevations of a certain shallow-lying electron to seven transient-sojourn orbits, the extraction-potential for this electron can be calculated by an extrapolation (so also in the cases cited from McLennan and Clark). Rollefson interprets certain other excitation-potentials as corresponding to elevations of certain deep-lying electrons to transient-sojourn orbits.

Some assistance in identifying the excitation-potentials of the light atoms can be obtained by plotting the recognized excitation-potentials of the heavier atoms, and also the frequencies of the rays excited; plotting curves representing them as functions of atomic number; and extrapolating the curves into the range of low atomic numbers. The best procedure is to plot the square roots of the excitation-potentials and the emission-frequencies, as then the curves are nearly straight lines (Moseley's law). Some of these lines are shown in Fig. 10 (from Kurth). Since the atomic numbers are laid off (contrary to usage) along the axis of ordinates, the lowest-lying line represents the highest recognized emission-frequencies (the $K\beta$ and $K\gamma$ frequencies, which actually are slightly different, but are not indicated separately upon the graph). The next line, marked $K\alpha$, represents another particular emission-frequency. Excitation is the same for every ray of this group, and consists in extracting one of the deepest-lying or K electrons of the atom; and the excitation-potential for the

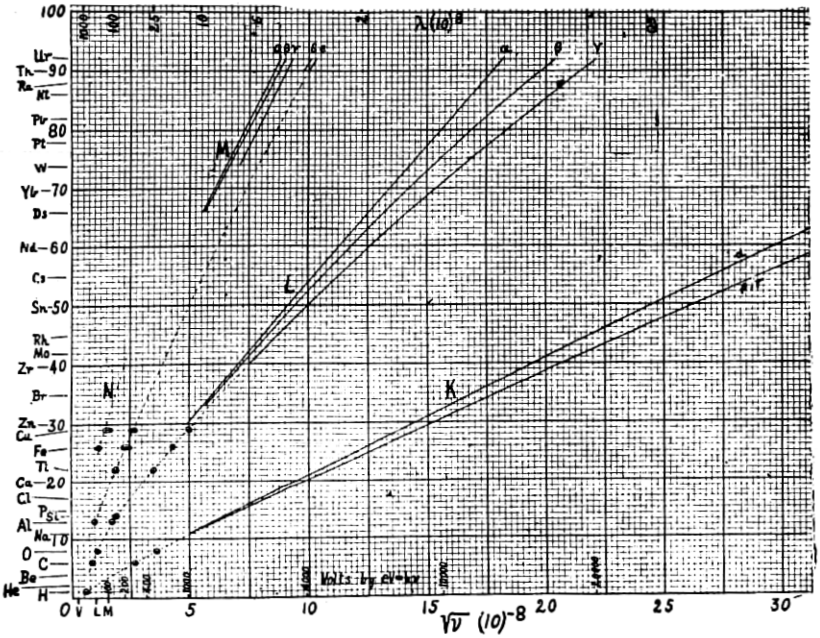

Fig. 10—Curves representing square roots of emission-frequencies of heavier atoms as functions of atomic number. (*Physical Review.*)

entire group, the K excitation-potential, is also represented by a straight line, the K line, which may be taken as coincident with the lowest-lying line in the graph, provided that we translate frequencies into potentials by the relation $V=h\nu/e$ (both frequencies and potentials are laid off along the axis of abscissae). This K line, it must be realized, extends the whole way from atomic number 92 to atomic number 12.

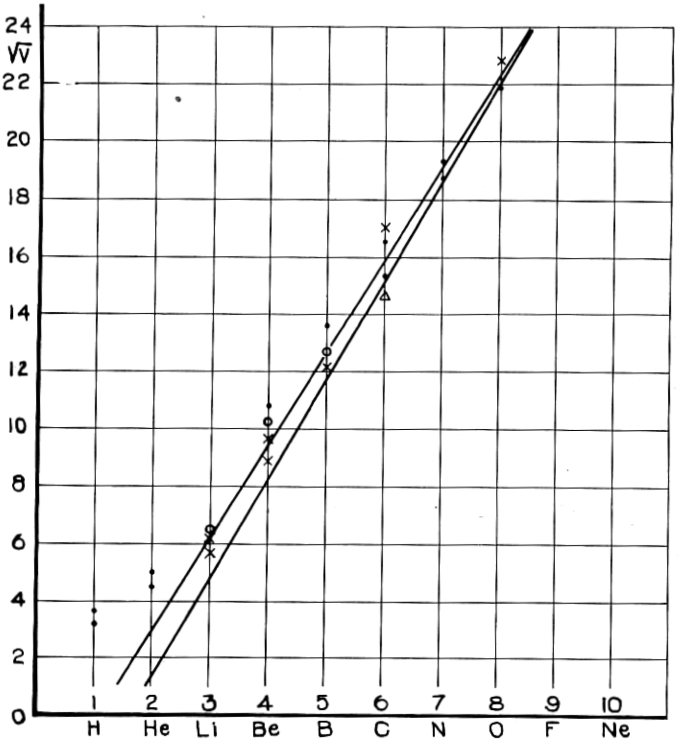

Fig. 11—Excitation-potentials of light elements, correlated with displacements of K electrons. (Cf. footnote 20.)

The circles upon the graph represent excitation-potentials inferior to 1000 volts, observed by Kurth. Three of these lie very close to the downward prolongation of the K line; the almost inevitable inference is, that in these three cases the excitation consists in the extraction of one of the electrons nearest the nucleus. The others lie so much above the extended K-line that they must belong to a distinct class. Many additional measurements have been made since this graph was published, and in Fig. 11 I have set down all the experimental values known to me which have been given for excitation-potentials of the first eight elements, omitting those which are so small that they obviously do not belong to the *K* class.[20] The

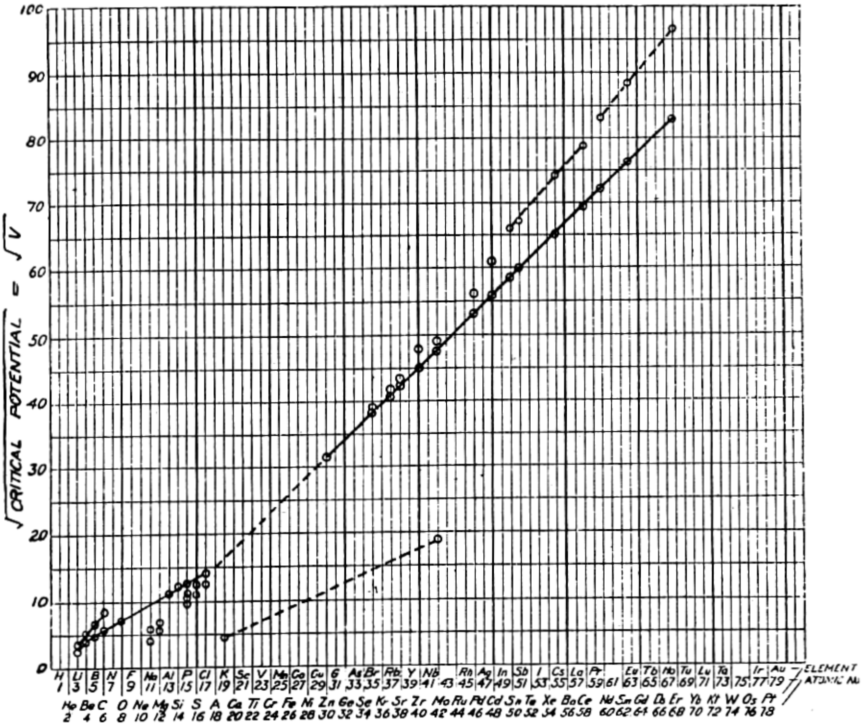

Fig. 12—Emission-frequencies of heavier and excitation-potentials of lighter elements, correlated with *L* electrons. (*Proceedings of the Royal Society.*)

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[20] The data are from various sources, as follows. The dots for hydrogen and helium represent the observed ionization and resonance potentials of these atoms. The dots for *Be*, *B*, *C*, *N* and *O* are at values of excitation-potentials given by Mohler and Foote from experiments on gaseous compounds of these atoms. All the other data except Holweck's are values of excitation-potentials for solids. The crosses for *Li* and *Be* stand for the excitation-potentials observed by McLennan, the circles for the extraction-potentials of the *K* electrons which they infer from these data. The cross for *B* represents three values lying so close together as to be indistinguishable (from McLennan, Hughes, and Holtsmark) and the cross for *C* also three coincident values (Kurth, Richardson and Bazzoni, Holweck). The circle for *B* is at the potential corresponding to a discontinuity in absorption, observed by Holweck. The triangle for *C* is a value observed by Hughes, and the cross for *O* a value from Kurth (obtained with oxidized copper). No data for *F* or *Ne* are available. At *Na* measurements on the wave-length of $K\alpha$ and at *Mg* measurements on the *K* absorption-edge commence.

lower of the continuous straight lines coming downward from the right is the prolongation of the K line from the heavier elements downward; the upper is the prolongation of the $K\alpha$ line. The fact that these intersect proves that linear extrapolation from the range of heavier atoms is unjustifiable.

Reverting to the graph in Fig. 10, the problem of properly extrapolating the L and M curves is clearly not so simple as it was for the K curve; since they extend over shorter segments and do not come so far down into the range of light elements. In Fig. 12 (from McLennan and Clark) the circles for the elements from number 3 to number 17 represent observed excitation-potentials which they attribute to displacements of L electrons; those for the elements from number 30 to number 69 represent the highest and the lowest recorded emission-

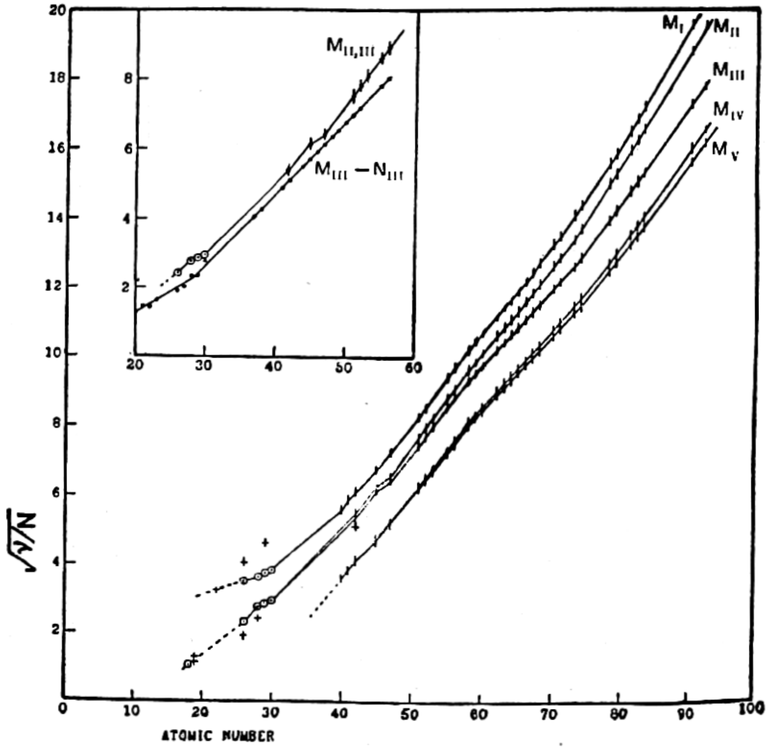

Fig. 13—Excitation-potentials correlated with M electrons. (*Philosophical Magazine.*)

frequencies of the L-series for these elements, frequency being translated into equivalent voltage by the same relation as above. As for the excitation-potentials of the heavier elements, few measurements on potentials of the L class have been made, and very few indeed upon potentials of the M class—not nearly enough for an extrapolation. The deficiency is partially compensated by calculating the L and M excitation-potentials from the K, L and M emission-frequencies—an elaborate process, requiring a good deal of care in measuring and properly interpreting the various emitted rays. In this manner the potentials for the group of five M levels have been estimated for the various elements from the ninety-second down to the fortieth, and Horton has attempted to link onto them certain excitation-potentials which he and others observed when bombarding elements between number 20 and number 30 with electrons (Fig. 13). The curves must be supposed to bend, somewhere between the thirtieth and the fortieth elements; it is in this region that the M electrons pass from the status of deep-lying to the status of shallow-lying electrons. The excitations and emissions involving the shallow-lying electrons of the heavy atoms form a complicated system, of which the study has scarcely been begun, and will certainly prove perplexing. When research in this field is completed, each of the excitation-potentials and each of the emission-frequencies of every kind of atom will be entered upon curves, each of the curves corresponding to a definite and definitely-pictured process of rearrangement in the atomic electron-system, and extending over all the atoms of the periodic table which can be theatres of that process. This achievement may be reserved for a later generation.

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