

THE SOFT X-RAY ABSORPTION LIMITS OF CERTAIN ELEMENTS.

Thesis presented for the degree of Ph.D.

by

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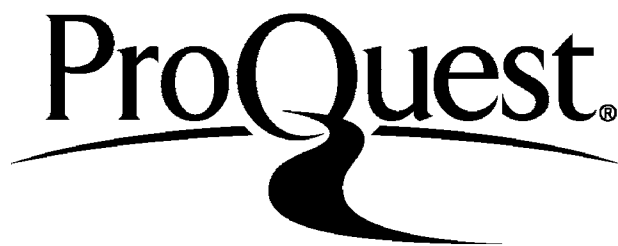
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The Soft X-ray Absorption Limits of certain Elements.

According to Bohr's theory of atomic structure, in the normal configuration of the electrons round the nucleus in any atom, each electron is bound so that its final orbit is that which is in most stable equilibrium with the nucleus and with the other electrons already bound. The building up of a heavy atom is marked by periods at the end of which an energy level is completed.

The orbits of the electrons in the different groups in the atom are characterised by different total quantum numbers n , this number being equal to 1 for the innermost K group, 2 for the L group, 3 for the M group and so on. Within each group, the electrons are again divided into sub-groups corresponding to different types of orbits and characterised by different values of the azimuthal quantum number k .

The X-ray spectra arise from the displacement of an electron from one of the inner groups in the atom and the subsequent readjustment of the remaining electrons. The K series of characteristic emission lines, for instance, arises from the displacement of an electron from the innermost group, which is complete at helium, and remains unchanged throughout the periodic table. The binding of the two electrons in this

group in any atom depends on the nuclear charge, but is practically independent of the presence of electrons in outer groups.

The L group is complete at a later stage in the periodic table, at neon ($z = 10$), and the M group later still, but each group when finally complete, then remains unchanged for elements of higher atomic number.

In his well-known researches on X-ray spectra published in 1913, Moseley investigated the K series of emission lines for a number of elements lying between aluminium and silver and the L series for elements between zirconium and gold. He concluded that for any one line, the square root of the frequency is proportional to the atomic number. In all the elements which he investigated the K and L groups are both complete, and the relationship which he found is to be attributed to the persistence of these inner groups unchanged throughout these elements. A similar relationship might be expected to hold for absorption limits as for emission lines.

The Moseley relation can only be expected to hold where the electron groups concerned in the emission of the line are complete, and in passing down the periodic table it is to be expected that the relation will break down for the elements in which these groups are in process of formation.

On Bohr's theory, the M group of electrons changes

between the elements calcium ($Z=20$) and copper ($Z=29$) from two sub-groups containing four electrons each to three sub-groups containing six electrons each.

From a consideration of the optical spectra of the elements in this region, Bohr finds that, in passing from potassium ($Z=19$) through calcium ($Z=20$) to scandium ($Z=21$), the orbit of the type belonging to the third M sub-group ($3, \text{ }_3$) corresponds to a firmer and firmer binding relatively to that of an orbit of the first N sub-group type ($4, \text{ }_1$) and that for scandium an electron is bound in the third M sub-group rather than in an N sub-group. The third M sub-group is thus begun at scandium, and, from a consideration of the copper spectrum, Bohr concludes that all three sub-groups are complete at copper. In contrast to the complicated spectre of the preceding elements, the spectrum of copper possesses a simple structure very like that of sodium and this is to be ascribed to the simple symmetrical structure of the inner system of electrons in this element.

It might be expected that evidence as to the constitution of the M group of electrons for the elements between scandium ($Z=21$) and copper ($Z=29$) could be obtained from the Moseley lines, but no M emission lines have been measured in this region owing to the fact that the wavelength is too long to be measured by the crystal method and too short

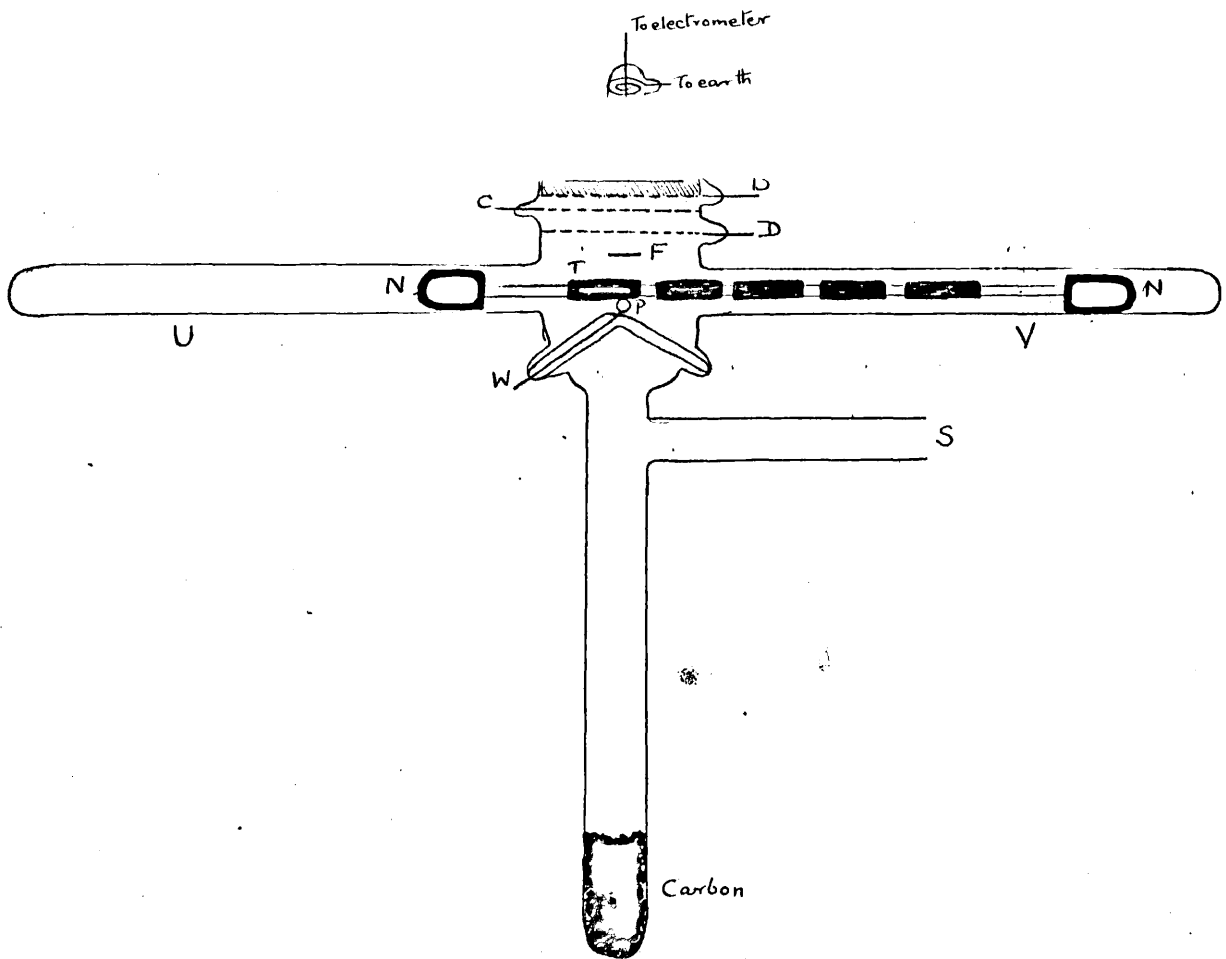
to be measured readily by a spectroscopic method. The excitation potential method can however be employed to investigate the M absorption limits in this region. This method consists in measuring the photo-electric current from a suitably situated metallic disc, caused by the X radiation emitted by a given element under electronic bombardment with gradually increasing energy of the electron stream. The critical points at which new radiations are produced are determined from the positions of discontinuities in the current — potential difference curves.

Experiments¹ were therefore made by this method with the elements iron, nickel, copper and zinc, and reasons were deduced for associating certain of the critical potentials observed with the removal of an electron from the first M sub-group and others with the removal of an electron from the second M sub-group. The results of these experiments supported the view that a change in the constitution of the M group is in progress in this region of the periodic table, but it was thought that more details of the stages in the development of the group might be obtained by making a fuller investigation of the critical potentials for the elements already used and by extending the research to other elements in this region.

Further experiments have therefore been made and a

1. F. Horton, O. Andrewes and A. C. Davies. Phil. Mag. XLVI. Nov. 1923.

FIGURE I



series of seven elements occurring consecutively in the periodic table have now been examined.

They are chromium ($z=24$), manganese ($z=25$), iron ($z=26$), cobalt ($z=27$), nickel ($z=28$), copper ($z=29$) and zinc ($z=30$).

Apparatus and method.

It is essential for the success of the experiments that the electronic bombardment of the element under test should be carried out in a vacuum as nearly perfect as it is possible to obtain. The glass vessel in which the electrodes were contained was therefore constructed without any waxed or cemented joins. It was designed by Professor Horton and is shown in figure I.

The tube containing the carbon was 2 cm. wide and was cooled in liquid air during the observations. The apparatus was connected by a side-tube S through a wide bore stop-cock and a U tube immersed in liquid air, with a diffusion pump which was maintained in operation throughout the measurements. Before beginning the observations the apparatus was pumped out and the residual gas removed as completely as possible from the filaments, electrodes and glass walls by long-continued heating in an air oven and simultaneous pumping by the diffusion pump. The pressure was read before and after a series of observations was made and in no case was

more than .00001 mm and generally less, being frequently not measurable on the gauge.

The targets, each 2 cms. long by 1 cm. broad by .5 cm. wide, in the first experiments were arranged in a row on two quartz rods which passed through holes drilled in them. It was found impossible to drill holes in the chromium and manganese targets and all the targets were therefore grooved down their long sides and fitted between the quartz rods which were bound with wire to the iron end pieces N N. The targets were kept apart by pieces of quartz tubing 1.5 cm. long which fitted over the rods between them. By means of an electro-magnet, acting on the soft iron end pieces, each target in turn could be placed underneath the tungsten filaments F which supplied the bombarding electron stream. An electrical connection to the particular element under investigation was made by means of the platinum wire W, at the upper end of which was a small platinum ball P which pressed against the lower face of the target. This arrangement has the great advantage that the element under investigation can be quickly changed so that each element can be examined in turn, and it can be rapidly ascertained whether an indication of a critical point in a current-voltage curve is a genuine effect due to the element, or whether it arises from some other cause, in which case it would be common to the whole series of curves.

The row of targets could be turned over in the apparatus by means of the electromagnet so that if one face was ~~not~~ contaminated by sputtering from the filaments, the other could then be used, and the whole row of targets could be moved into one of the side tubes U or V during the preliminary heating out of the apparatus, so that the surfaces were not contaminated during this process by sputtering from the filaments.

The apparatus contained two V-shaped tungsten filaments, each about 1.5 cm. long in the glowing portion. They were introduced from opposite sides of the main glass tube, and were close together in the same horizontal plane in the position indicated by F in the figure. The two filaments were used in series in nearly all the experiments.

The radiations stimulated by the electron bombardment of the targets were detected by means of their photoelectric effects on a platinum disc A connected to a delicate electrometer. The platinum wire leading to A was protected by earthed guard rings from collecting charges by leakage along the inner or outer surfaces of the glass tube through which it was sealed. A hangs inside a short hollow platinum cylinder, the base of which is of fine platinum gauze B. C and D are two circular pieces of fine platinum gauze which fill the horizontal section of the central tube of the apparatus.

as indicated in the diagram. B, C and D are about 8 mm. apart, while D is about 13 mm. above the filaments.

The arrangement of the plate A and of the three platinum grids is similar to that which has been employed by Horton and Davies in their measurements of the critical potentials for the production of radiation from gases. By suitably selecting the values of the electric fields between these grids it is possible to arrange that the electrometer is only influenced by radiation illuminating the plate A or the surrounding platinum cylinder. An arrangement of electric fields

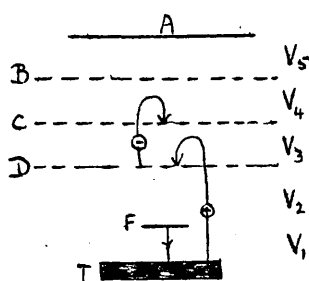


FIGURE II

which secures this result is indicated diagrammatically in figure II.

Electrons from the filament F bombard the target T with energy due to a fall through a potential difference V_1 .

The lower gauze D was maintained at V_2 volts negative to the filament; C was V_3 volts positive to D, V_3 being always greater than $V_1 + V_2$, so that none of the positive ions which are liberated by the electron bombardment of the target and which pass through the gauze D can travel to the level of C. The experiments of Horton and Davies have shown, however, that such positive ions will liberate electrons from the platinum gauze D when their velocity of impact exceeds a certain small

amount (that due to a fall through about 20 volts in the case of the positive ions from platinum). Any electrons so liberated are accelerated by the field V_3 towards the collecting electrode, but are prevented from reaching that electrode by the field V_4 between the gauzes C and B. Any positive ions liberated from C under the bombardment of these electrons could be turned back by the field V_5 between the plate A and the gauze B, but experiment showed that the number of these positive ions was too small to give a detectable effect. The field V_5 was therefore usually kept at a small constant value during the observations, so as to give greater steadiness to the electrometer readings than is obtained if this field is large. By reversing the direction of V_5 the direction of the photoelectric current between A and B is reversed, thus making it possible to verify that the current measured by the electrometer is due to photoelectric action and not to some spurious ionization effect.

In several cases, runs were made, in which the observations were taken with the field V_5 first in one direction and then in the other for every value of the field V_3 . Thus two curves were obtained simultaneously and a genuine discontinuity appeared in both of them. Some of the double curves are shown in the following figures.

The actual values of the most suitable potentials on the gauzes can only be determined by experiment and it

was found that if the positive potential on the gauze C was too large, it acted through the gauze D and electrons were able to get through to the disc even when there was a field, between the filament and first gauze D, of 6 or 7 volts against them.

The field V_1 could be varied from 0 to 230 volts in steps of 1/10th volt if necessary, but it was usually found that nothing was to be gained by using steps smaller than two volts apart. The field V_2 was usually about 10 volts. V_3 was about 20 volts greater than the maximum value of $V_1 + V_2$ used in the run, and V_4 about 10 volts greater than V_3 . The field V_5 , which was constant in any one experiment, varied from about 10 to 20 volts in different experiments.

During the measurements of the photoelectric current with the electrometer, the total electron current between the filament and the target was also measured on a galvanometer. In this way a series of values of the photoelectric current per arbitrary unit bombarding current was obtained, and these values were plotted against the corresponding values of the energy of the bombarding electrons. These values were obtained by adding to the applied potential differences V , a small correction due to the initial velocity of emission of the electrons. This was determined by reducing the accelerating voltage V , to zero and, if necessary, increasing it in the opposite direction, until no thermionic

current could be measured, with the galvanometer shunted as in the original experiment. The field is thus found which is just necessary to prevent the electrons from reaching the target, and which therefore gives a measure of their initial energy.

The correction was in most cases less and never more than a volt and in stating the results and plotting the curves which follow the corrected values of the voltages are used throughout.

Experimental results.

The range of voltages used was up to 230 volts. Observations were first taken over ranges of from 40 to 60 volts at a time. The regions at which indications of bends in the curves were found were then investigated and some of the curves obtained are given below.

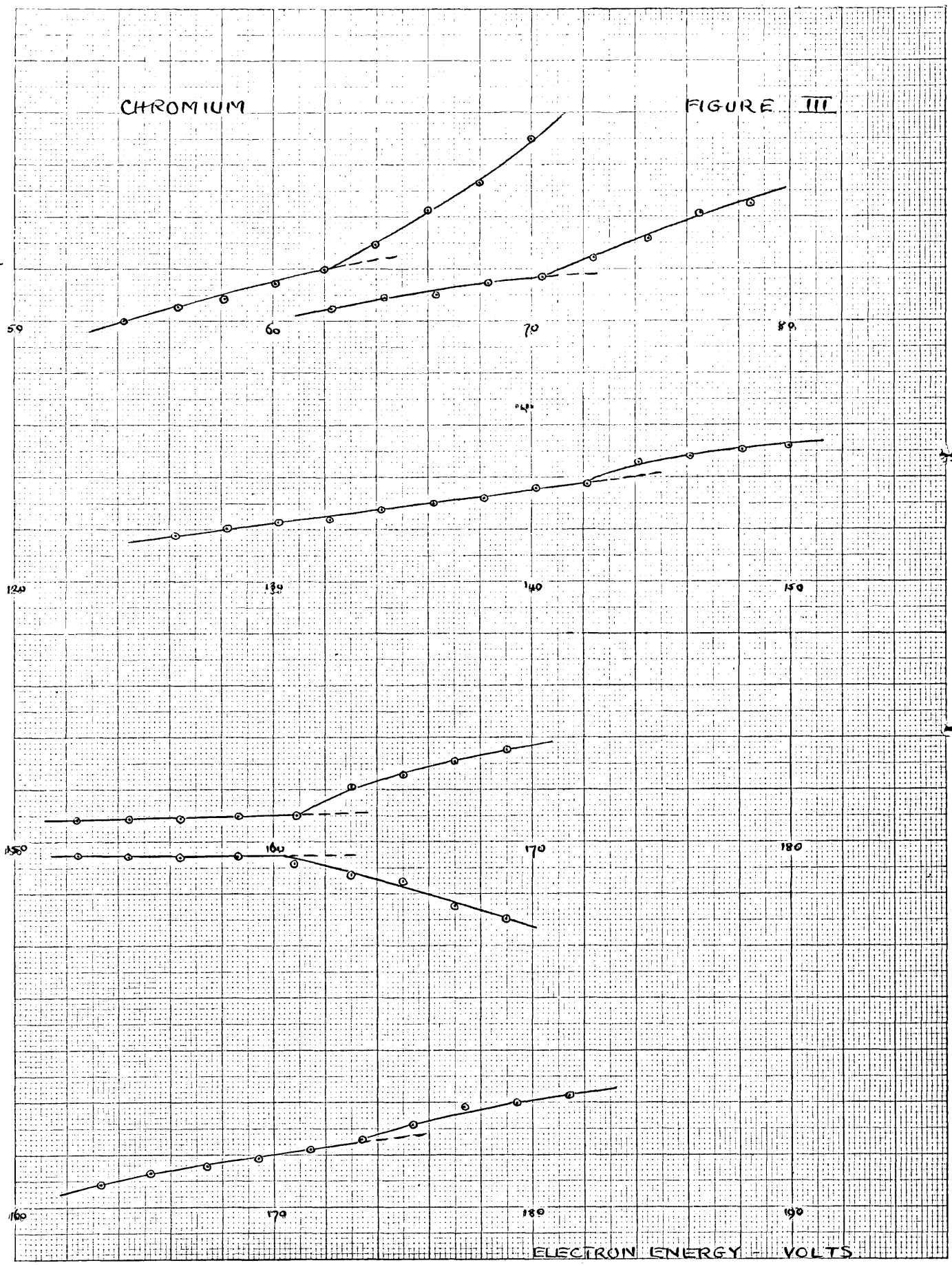
Indications of bends in the curves were obtained at points corresponding to electron energies of less than 30 volts, but it is difficult to say whether these bends correspond to the stage at which the first effect of the general radiation becomes measurable with this apparatus, or whether they are really characteristic of the targets. Further experiments are necessary to settle this question, with more sensitive apparatus, capable of detecting the small photoelectric currents at these low voltages.

The maximum variation in the position of a point observed for any one critical potential from the mean value given was ± 2 volts and in most cases the agreement between the curves was better than this. In each case the value of the critical potential given is the mean value deduced from several curves, one of which is given in the figures.

PHOTO ELECTRIC CURRENT / ELECTRON CURRENT

CHROMIUM

FIGURE III



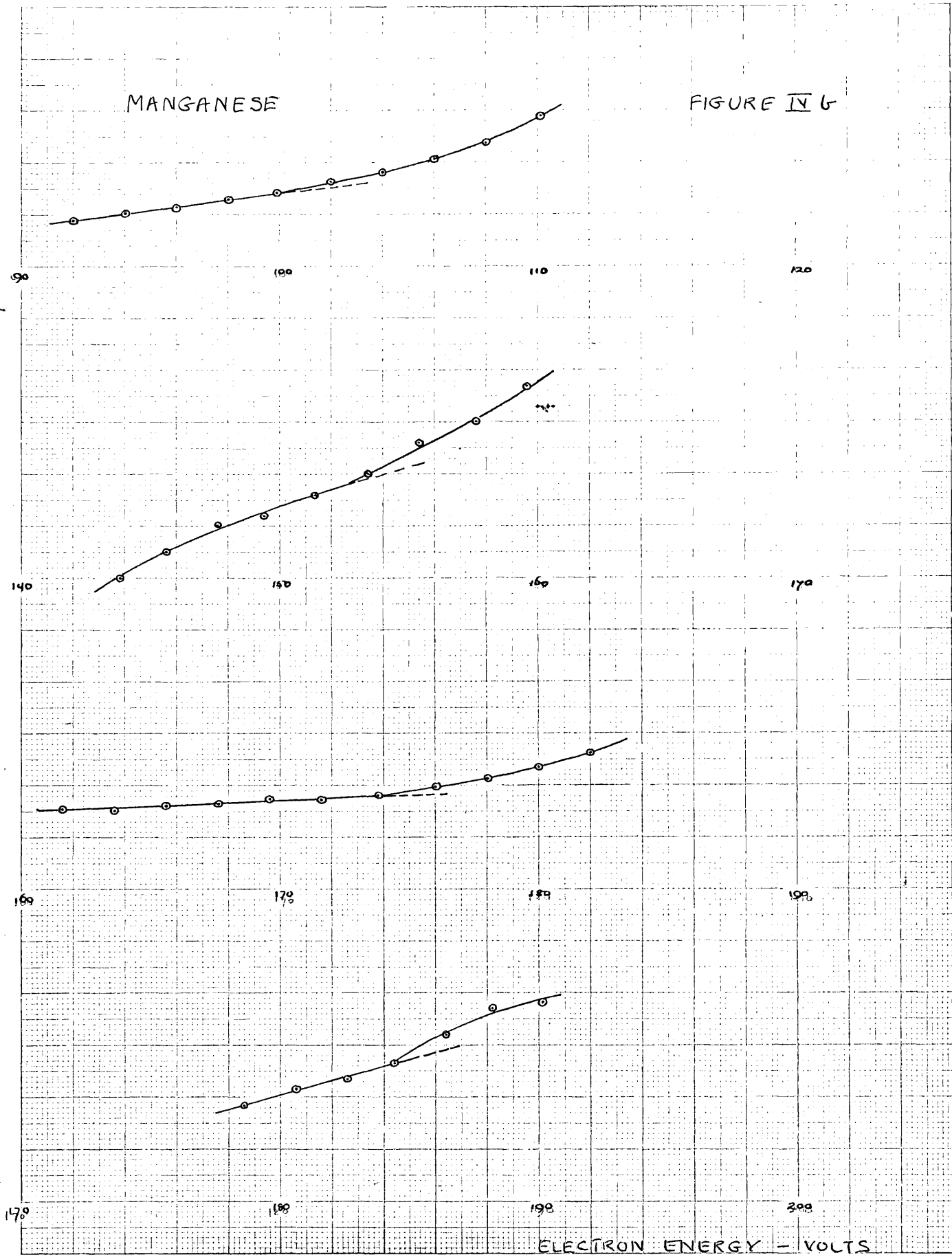
Chromium. Atomic number 24.

Five critical potentials were found for this element at 60, 70, 143, 160 and 173 volts respectively. Examples of the curves obtained are given in figure III. The curves shown for the point at 160 volts are an example of the double curves mentioned above.

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MANGANESE

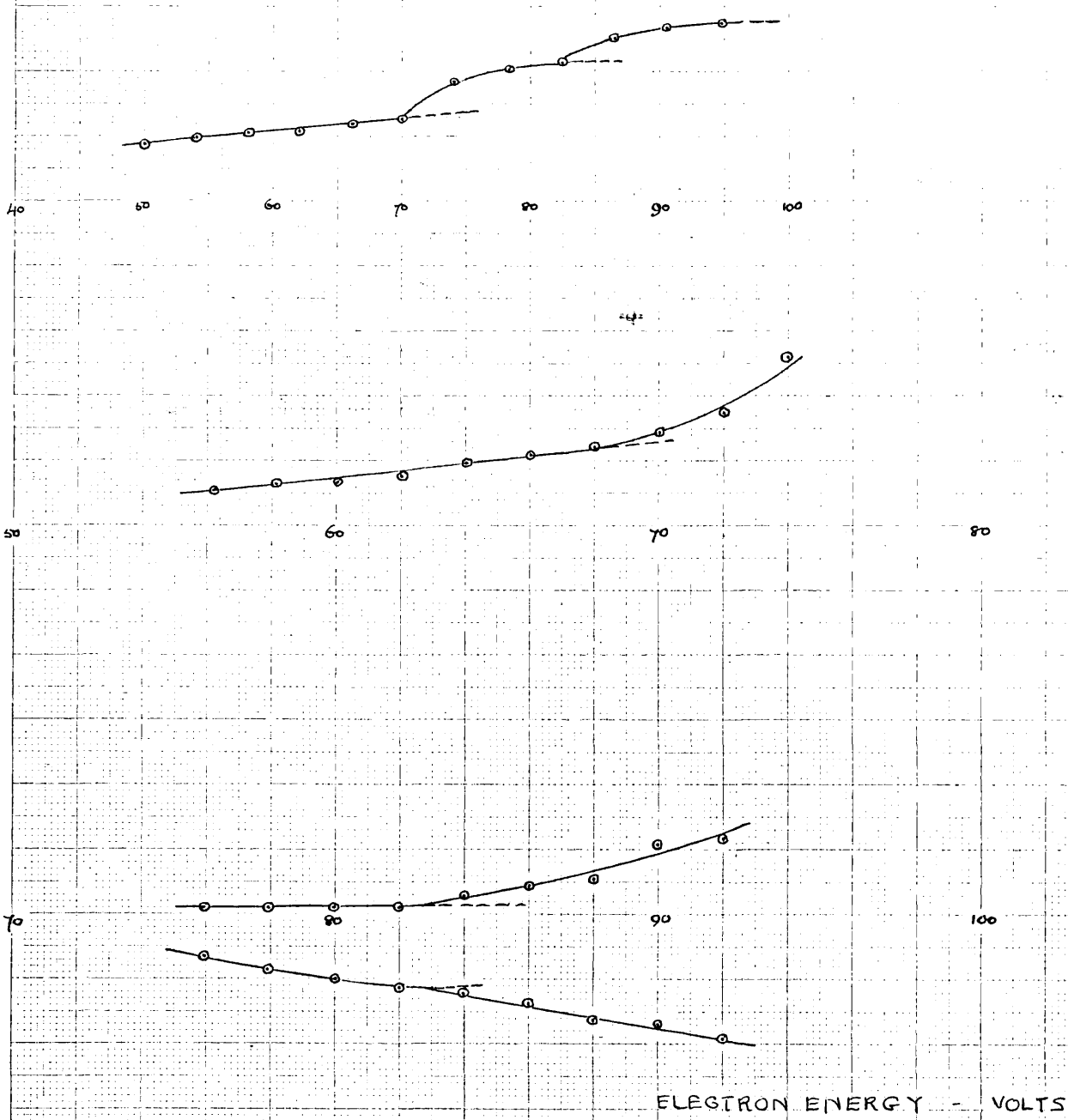
FIGURE IV 6



PHOTOELECTRIC CURRENT / ELECTRON CURRENT

MANGANESE

FIGURE IVa



ELECTRON ENERGY - VOLTS

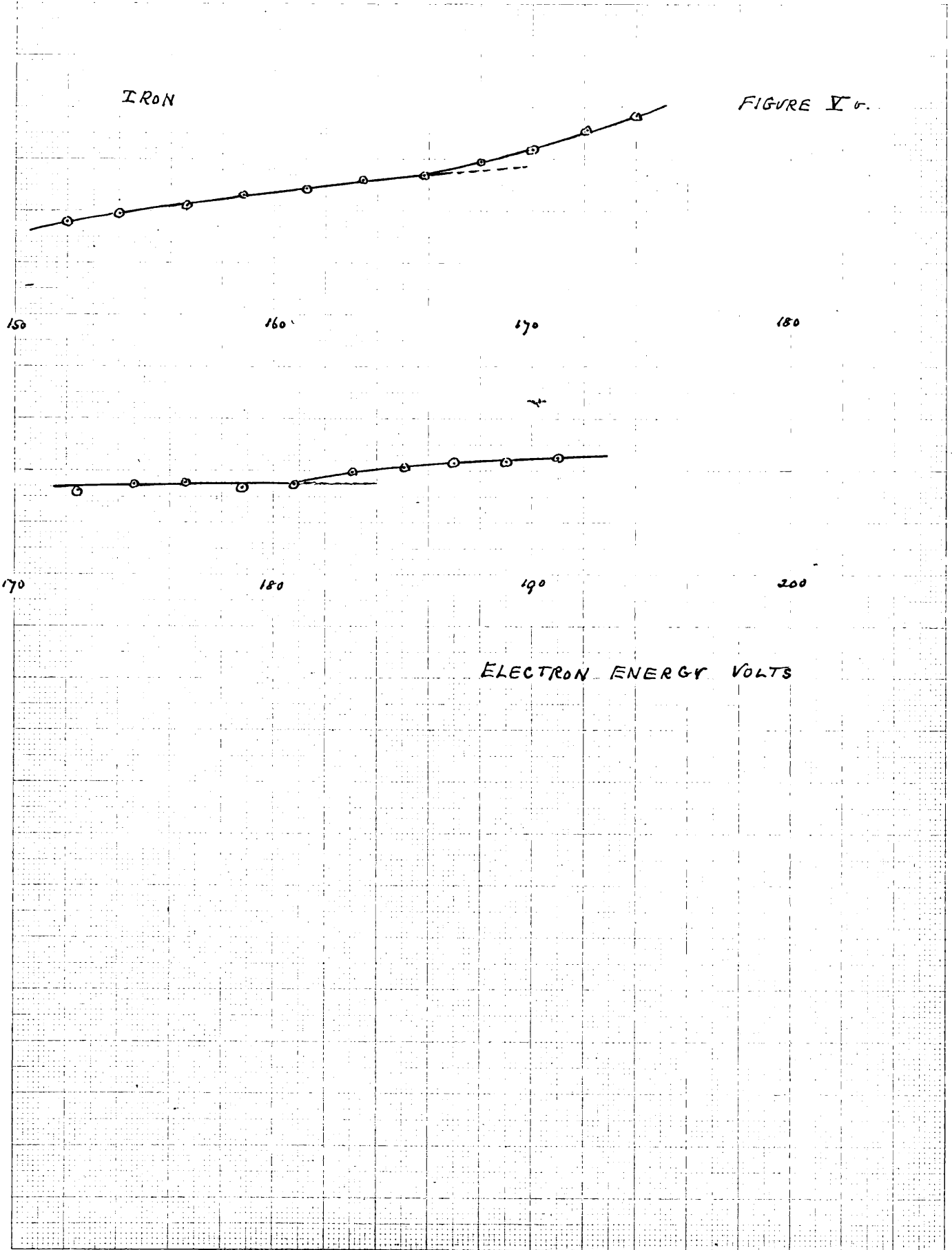
Manganese. Atomic number 25.

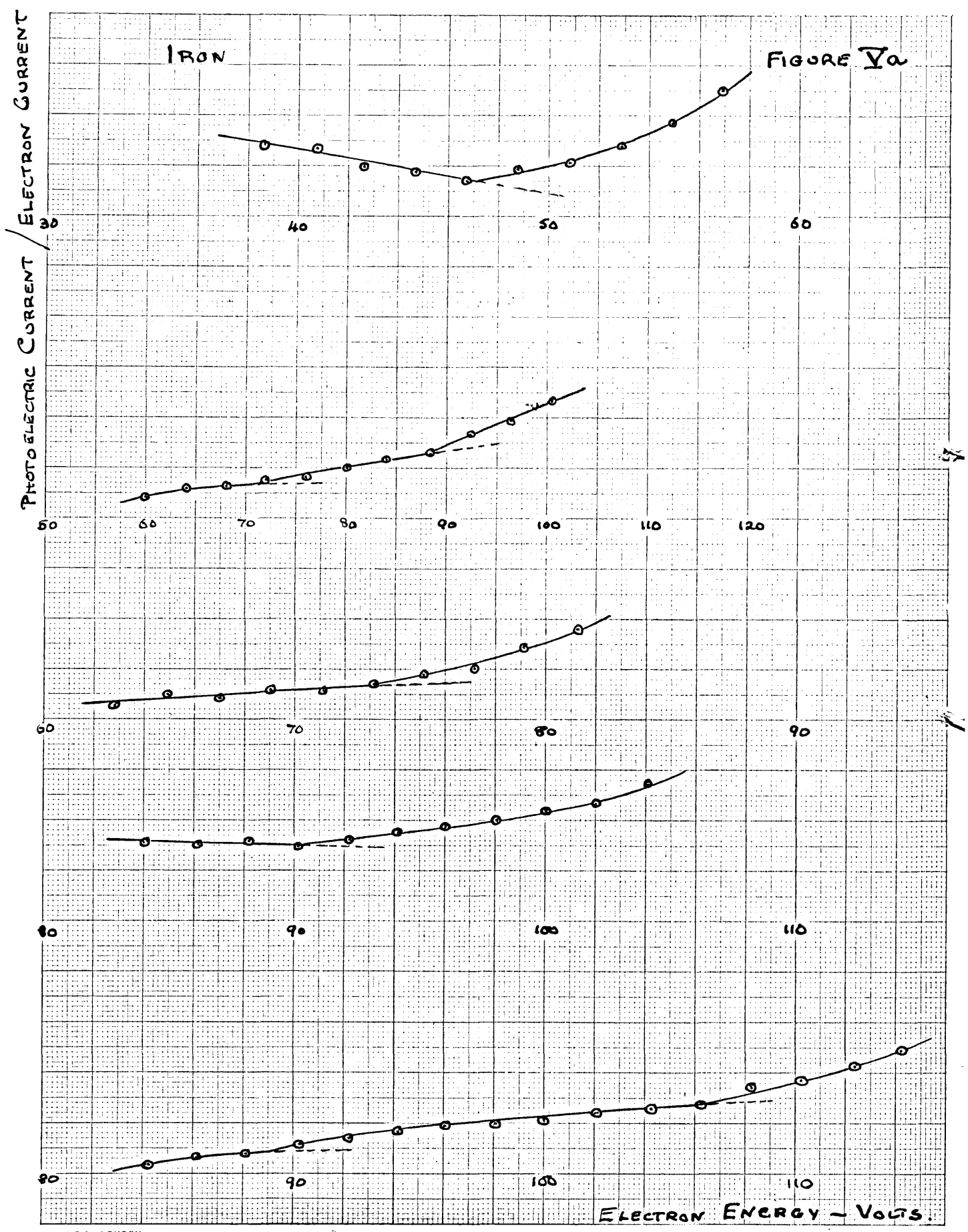
Six critical potentials obtained for this element are shown in figures IVa and IVb. Again, in one case, a double curve is shown. The mean values of the discontinuities are at 68, 83, 100, 152, 174 and 184 volts.

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IRON

FIGURE Vc.





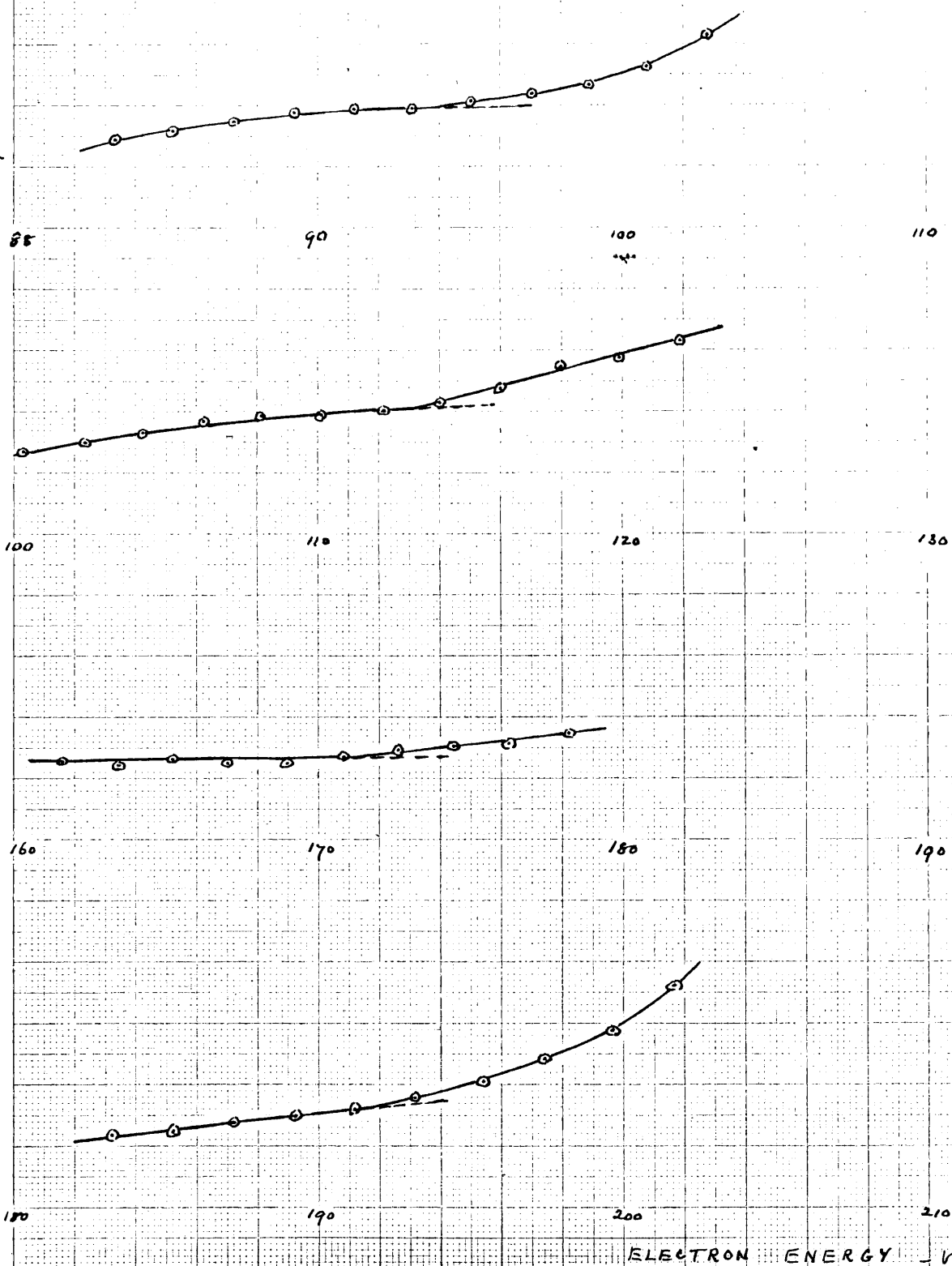
Iron. Atomic number 26.

In the case of iron, six critical points again were found, the mean values being 47, 73, 90, 106, 166 and 181 volts. Curves are given in figures Va and Vb.

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COBALT

FIGURE VI



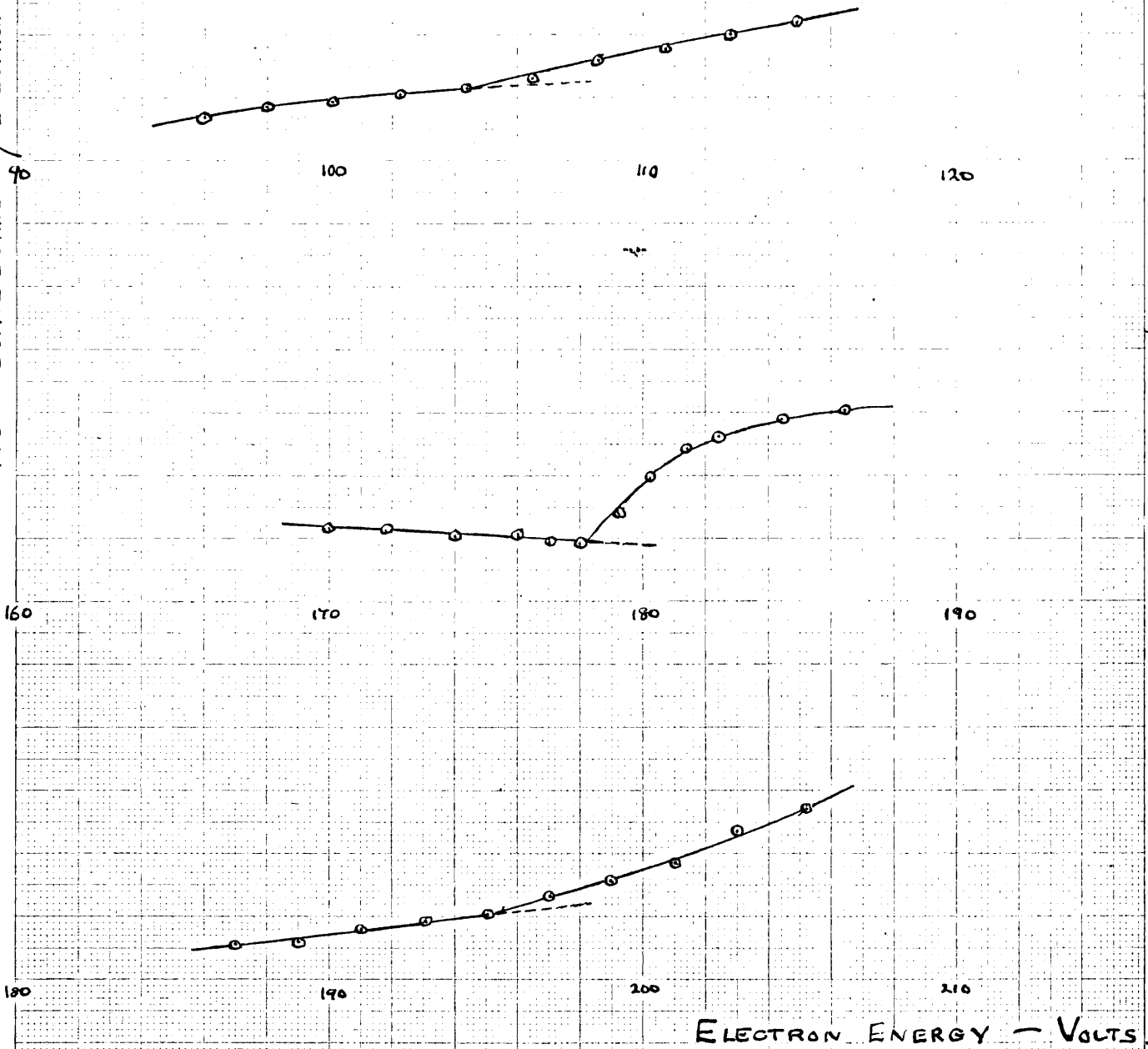
Cobalt. Atomic number 27.

Figure VI shows the four breaks located for this element. The mean values are 94, 113, 171 and 191 volts. .

PHOTOELECTRIC CURRENT / ELECTRON CURRENT

NICKEL

FIGURE VII



Nickel. Atomic number 28.

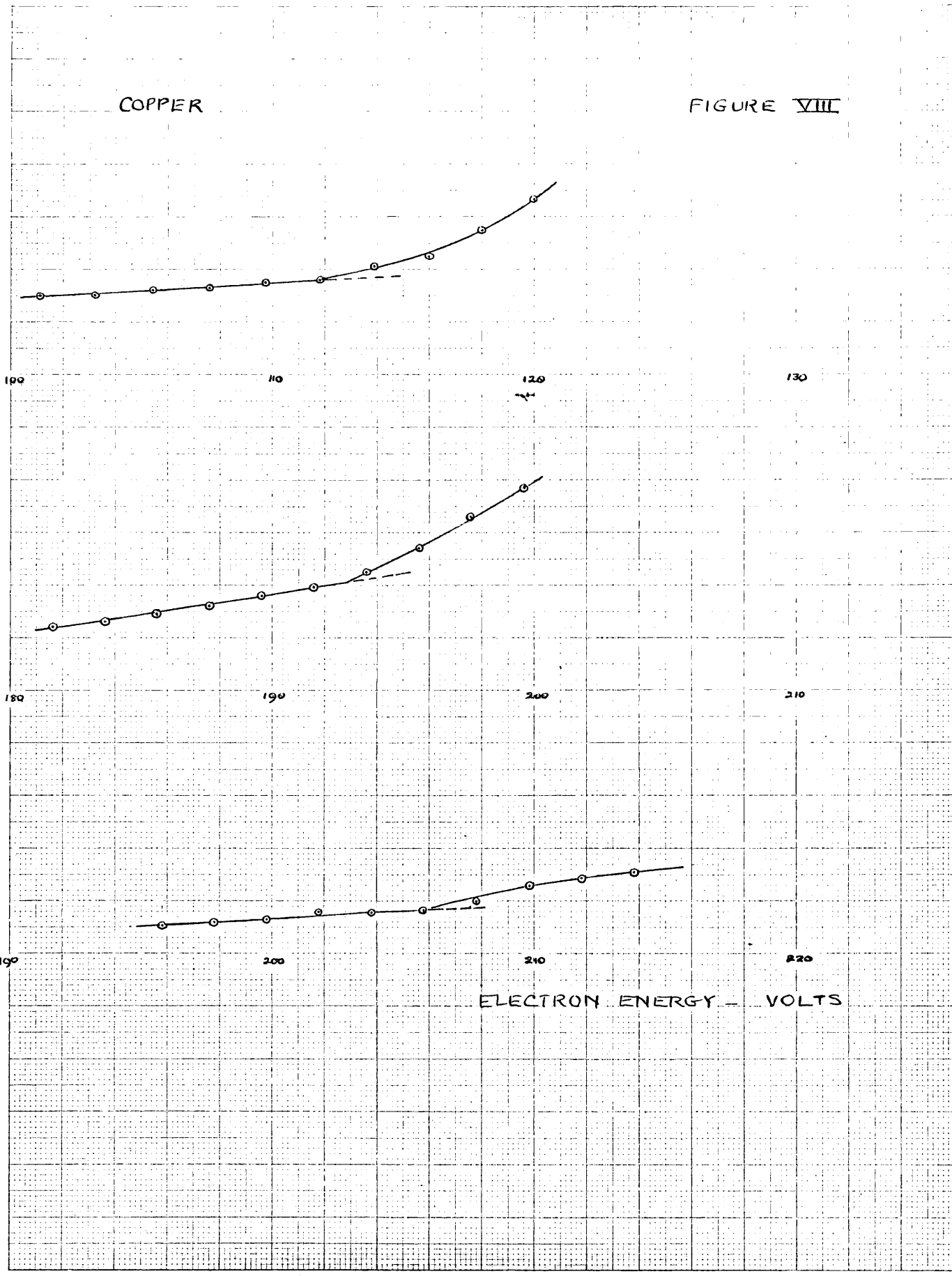
Three critical potentials have been found for this element as shown in figure VII, at 104, 178 and 195 volts.

Copper

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COPPER

FIGURE VIII



Copper. Atomic number 29.

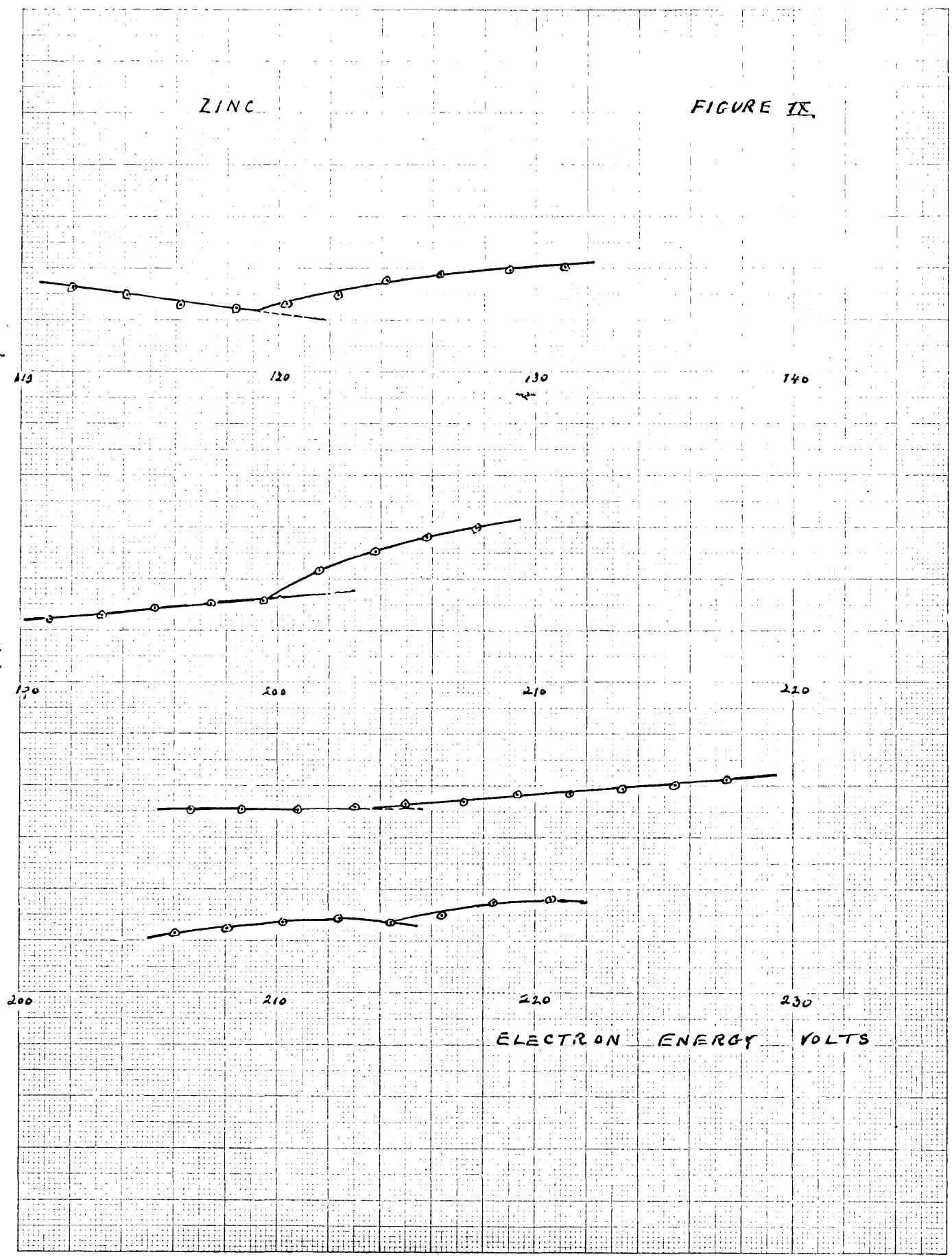
Again three critical potentials have been located at 112, 193 and 206 volts. Indications of perhaps two lower critical points were found in the region between 50 and 90 volts but the values obtained varied over too wide a range to be fixed down with any certainty and are not therefore given.

The curves are shown in figure VIII for the three points mentioned above.

PHOTOELECTRIC CURRENT / ELECTRON CURRENT

ZINC

FIGURE IX



Zinc. Atomic number 30.

In this element too there were indications of a critical point below 119 volts but the curves are very uncertain. The three critical points definitely found are at 119, 200 and 214 volts and examples of curves are shown in figure IX.

It is seen that in some cases, the portion of a curve before the critical point is reached, has a downward slope. This does not mean that the photoelectric current itself was decreasing with increasing electron energy.

It was, at these stages, constant or perhaps slightly increasing and the downward slope is due to the fact that the curves are ratio curves and in these cases, the electron current was increasing more rapidly than the photoelectric current. This was noticed more particularly at the lower voltages, as was to be expected, since, for these low voltages, the electron current has not nearly reached the saturation value.

The results are collected in table I
 given below.

Table I

| Element | Volts | $\frac{V}{R}$ | $\sqrt{\frac{D}{R}}$ | Element | Volts | $\frac{V}{R}$ | $\sqrt{\frac{D}{R}}$ |
|---------|-------|---------------|----------------------|---------|--------|---------------|----------------------|
| Cr. 24 | 60 | 4.43 | 2.10 | Co. 27 | 94 | 6.94 | 2.63 |
| | 70 | 5.17 | 2.27 | | 113 | 8.34 | 2.89 |
| | 143 | 10.55 | 3.25 | | 171 | 12.60 | 3.55 |
| | 160 | 11.92 | 3.45 | | 191 | 14.10 | 3.76 |
| | 173 | 12.77 | 3.57 | | Ni. 28 | 104 | 7.68 |
| Mn 25 | 68 | 5.02 | 2.24 | 178 | 13.14 | 3.63 | |
| | 83 | 6.13 | 2.48 | 196 | 14.46 | 3.80 | |
| | 100 | 7.33 | 2.72 | Cu 29 | 112 | 8.27 | 2.88 |
| | 152 | 11.09 | 3.33 | 193 | 14.24 | 3.77 | |
| | 174 | 12.85 | 3.59 | 206 | 15.21 | 3.90 | |
| Fe 26 | 184 | 13.58 | 3.69 | Zn. 30 | 119 | 8.78 | 2.96 |
| | 47 | 3.47 | 1.86 | 200 | 14.77 | 3.84 | |
| | 73 | 5.4 | 2.32 | 214 | 15.80 | 3.98 | |
| | 90 | 6.64 | 2.58 | | | | |
| | 106 | 7.82 | 2.80 | | | | |
| | 166 | 12.26 | 3.50 | | | | |
| | 181 | 13.36 | 3.66 | | | | |

As is seen the values of the critical points are given in volts and in multiples of ν/R where ν is the wave number and R the Rydberg constant. The wave number ν is calculated from the Planck-Einstein relation,

$$ch\nu = eV$$

where h is Planck's constant, e the electronic charge and c the velocity of light.

Discussion and interpretation of results.

Coster has shown¹ that nearly all the lines of the X-ray spectra of the heavier elements can be arranged in a simple scheme involving the existence of one K level, three L levels, five M levels and 7 N levels. (There are indications of O and P levels also but the numbers of these cannot definitely be stated). Five M absorption edges have been measured spectroscopically for uranium and thorium and three for bismuth. The levels are denoted by the symbols M_I^* , M_{II} , M_{III} , M_{IV} , and M_V , M_I having the highest frequency. For elements of lower atomic number the levels M_{II} and M_{III} and the levels M_{IV} and M_V merge together and in the region of the periodic table under consideration the three M levels are denoted by the symbols M_I , M_{IIIII} and M_{IVV} .

¹D. Coster. Zeit. f. Phys. v and vi. (1921).

* Another notation is used by some writers; — M_5, M_4, M_3, M_2, M_1 , M_5 having the highest frequency.

It is hoped to show that the critical potentials which have been observed correspond to the energies required to remove an electron from two of these sub-groups M_I and M_{II} to different orbits normally unoccupied.

In photographic measurements of X-ray absorption spectra, an absorbing screen of the substance of suitable thickness, is placed between the source of X-rays and the photographic plate. In earlier experiments, the resulting photograph showed a darker portion, due to almost unabsorbed incident continuous radiation, separated by a sharply defined edge from a lighter portion due to the absorption of the radiation by the substance.

More recent experiments¹, however, have shown that the structure of the absorption spectra is not so simple as this but that it possesses a kind of "fine structure." In the later photographs there are distinct white lines, sometimes three in number, separated from each other by darker bands, the most intense of the lines lying on the long wave-length side and coinciding in position with the absorption edge mentioned above.

¹H. Fricke. Phys. Rev. *xvi*. 1920.
Stenström, Dissertation Lund. 1919.
Hertz. Zeit. f. Phys. *iii*. 1920.
Coster, Nishina and Werner. Zeit. f. Phys. *xviii* 1923.
Nishina. Phil. Mag. March 1925.

Nishina, for instance, in a recent paper¹ has measured two absorption lines for several elements and three for holmium ($z=67$) in the case of the L_{III} level. He compares his measurements of the principal line, i.e. the one on the long wave-length side, with the values of the L_{III} absorption limit given by Bohr and Coster² which have been interpolated or measured photographically before, and finds very good agreement. He states that "the discrepancies with the measured values lie within the limit of experimental error in most elements."

To explain this "fine structure," Kossel³ has suggested that the principal (most intense) line corresponds to the removal of the electron from the level concerned to the "periphery" of the atom, and the lines following it of shorter wave-length, to its removal from the same level to certain virtual orbits beyond the "periphery."

The "periphery" used in this sense must be taken to mean the region, in the atom, of the most loosely bound electrons, and it is in this sense that the word will be used.

It was shown before⁴ that the observed critical potentials are to be associated with the removal of an

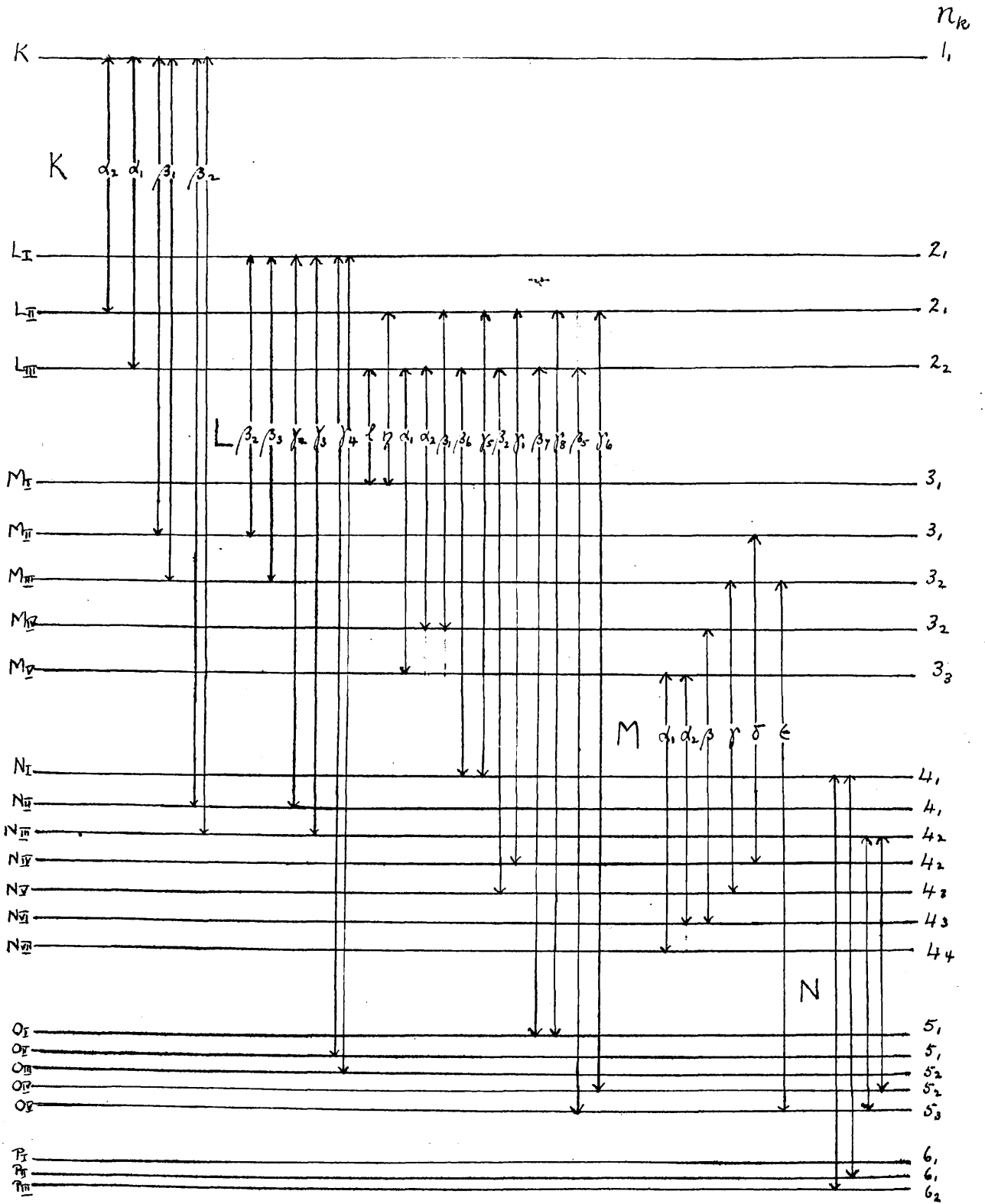
¹Nishina. loc. cit.

²Bohr and Coster. Zeit. f. Phys. *xii*. 1923.

³Kossel. Verhandlungen d. D. Phys. Ges. *xviii*. 1916.

⁴Horton, Andrewes and Davies. loc. cit.

FIGURE X



electron from the M_I and M_{IIIII} levels and it is now suggested that the number of critical potentials found in this research for any one element is to be connected with the "fine structure" of these limits.

Seeing that good agreement has been found, in the case of several levels, between the frequencies of the principal line of the fine structure and the absorption edges, measured or computed previously, it seems reasonable to suggest that all the absorption limits denoted by K , L_I , L_{II} , L_{III} etc. correspond to these lines of smallest frequency which, if Kossel's explanation is correct, represent the removal of an electron from the levels concerned to the periphery of the atom.

Some evidence in support of this suggestion may be obtained from a comparison of measured X-ray emission lines and the levels associated with them.

Figures X and XI are given for reference.

FIGURE XVI

| | K | L | M | N | O | P | |
|---------------------|---|-------------------|----------------------------------|-------------------------------------------------|----------------------------------------------------------------|-------------------------------------------------------------------------------|-------------------|
| $n_{k \rightarrow}$ | 1 | 2, 2 ₂ | 3, 3 ₂ 3 ₃ | 4, 4 ₁ 4 ₃ 4 ₂ | 5, 5 ₂ 5 ₃ 5 ₄ 5 ₅ | 6, 6 ₂ 6 ₃ 6 ₄ 6 ₅ 6 ₆ | 7, 7 ₂ |
| 1 H | 1 | | | | | | |
| 2 He | 2 | | | | | | |
| 3 Li | 2 | 1 | | | | | |
| 4 Be | 2 | 2 | | | | | |
| 5 B | 2 | 2 (1) | | | | | |
| 10 Ne | 2 | 4 | 4 | | | | |
| 11 Na | 2 | 4 | 4 | 1 | | | |
| 12 Mg | 2 | 4 | 4 | 2 | | | |
| 13 Al | 2 | 4 | 4 | 2 | 1 | | |
| 18 Ar | 2 | 4 | 4 | 4 | 4 | | |
| 19 K | 2 | 4 | 4 | 4 | 4 | 1 | |
| 20 Ca | 2 | 4 | 4 | 4 | 4 | 2 | |
| 21 Sc | 2 | 4 | 4 | 4 | 4 | 1 (2) | |
| 22 Ti | 2 | 4 | 4 | 4 | 4 | 2 (2) | |
| 29 Cu | 2 | 4 | 4 | 6 | 6 | 1 | |
| 30 Zn | 2 | 4 | 4 | 6 | 6 | 2 | |
| 31 Ga | 2 | 4 | 4 | 6 | 6 | 2 | 1 |
| 36 Kr | 2 | 4 | 4 | 6 | 6 | 4 | 4 |
| 37 Rb | 2 | 4 | 4 | 6 | 6 | 4 | 4 |
| 38 Sr | 2 | 4 | 4 | 6 | 6 | 4 | 4 |
| 39 Y | 2 | 4 | 4 | 6 | 6 | 4 | 4 |
| 40 Zr | 2 | 4 | 4 | 6 | 6 | 4 | 4 |
| 47 Hg | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 48 Cd | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 49 In | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 54 Xe | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 55 Cs | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 56 Ba | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 57 La | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 58 Ce | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 59 Pr | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 71 Lu | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 72 Hf | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 79 Au | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 80 Hg | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 81 Tl | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 86 Bi | 2 | 4 | 4 | 6 | 6 | 8 | 8 |
| 87 - | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 88 Ra | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 89 Ac | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 90 Th | 2 | 4 | 4 | 6 | 6 | 6 | 6 |
| 118 ? | 2 | 4 | 4 | 6 | 6 | 6 | 6 |

The former gives a diagrammatic scheme of the energy levels in the atom and the origin of the X-ray emission lines. Bohr's notation for the levels is used and for the emission lines, Siegbahn's notation as revised by Coster.

In the diagram, the horizontal lines represent the energy levels, each characterized by two quantum numbers n, k , and the vertical lines represent the various possible electron jumps between the different levels, the lettering on the lines indicating the particular emission lines resulting from these jumps. Though the diagram cannot be drawn to scale in the space available and at the same time show the sub-levels separately, yet it has been drawn to bring out the fact that the energy difference between two groups of levels is much greater than that between two sub-levels contained in the same group.

Figure XI gives Bohr's scheme of the structure of the atoms and the numbers of electrons describing orbits of the various n, k types.

The $M_{\underline{Y}}$ absorption limits have been measured spectroscopically for the elements uranium and thorium and Hjalmar has measured¹ the lines emitted when an electron falls from $P_{\underline{III}}$ to $M_{\underline{Y}}$ for these elements. The ν/R values

¹Hjalmar. Zeit. f. Phys. 15. 1923.

of these limits and lines are given in Table II, from which it can be seen that the $M_{\underline{V}}$ values are slightly greater than the $M_{\underline{V}}P_{\underline{III}}$ values.

Table II.

| Element. | $M_{\underline{V}}$. | $M_{\underline{V}}P_{\underline{III}}$. |
|----------|-----------------------|------------------------------------------|
| U. 92 | 261.0 | 259.3 |
| Th. 90 | 244.9 | 242.8 |

From this it is clear that the $M_{\underline{V}}$ absorption limit corresponds to the removal of an electron from the $M_{\underline{V}}$ level to a level a little further out than the $P_{\underline{III}}$ level. In this region of the periodic table, a level a little further out than the $P_{\underline{III}}$ level would certainly be included in the region of the most loosely attached electrons, and thus the fact that the $M_{\underline{V}}$ absorption limit corresponds to a transition to such a level supports the suggestion that the absorption limits in general represent removal of an electron to the periphery of the atom.

Table III gives the \sqrt{R} values of the emission line L_{β_5} which results when an electron falls from $O_{\underline{V}}$ to $L_{\underline{III}}$ and of the $L_{\underline{III}}$ absorption limit for certain elements lying between uranium ($z=92$) and tungsten ($z=74$).

It can be seen from the table that, with the exception of the value for lead, for those elements of higher atomic number than gold ($z=79$) the value of $L_{\underline{III}}$ is greater than that of L_{β_5} ($L_{\underline{III}} O_{\underline{V}}$) but that for gold,

Table III.

| Element. | $L_{\overline{III}}$. | L_{β_5} ($L_{\overline{III}}$ $O_{\overline{V}}$). |
|----------|------------------------|------------------------------------------------------------|
| U. 92 | 1263.2 | 1258.43 |
| Th. 90 | 1199.7 | 1194.93 |
| Bi. 83 | 988.79 | 987.98 |
| Pb. 82 | 959.53 | 959.72 |
| Tl. 81 | 932.15 | 931.4 |
| Au. 79 | 877.65 | 877.70 |
| Pt. 78 | 851.26 | 851.57 |
| W. 74 | 750.88 | 751.56 |

platinum and tungsten, the two values are almost the same. Coster says¹, with regard to the line L_{β_5} that it could not be measured for elements of atomic number lower than 73 and that for several of the rare earths and for barium ($Z=56$) and caesium ($Z=55$) he found the white absorption line $L_{\overline{III}}$ on the photographic plate in the position where the emission line L_{β_5} was to be expected. From this it is clear that in the region of the periodic table from gold ($Z=79$) down to caesium ($Z=55$) the absorption limit $L_{\overline{III}}$ corresponds to the removal of an electron to the $O_{\overline{V}}$ level, which for these elements comes within our definition of the periphery of the atom; but that for elements of higher atomic number than gold, the level to which an electron is removed on absorption is further out than the $O_{\overline{V}}$ level. This fact again supports the suggestion that the absorption

¹D. Coster. Phil. Mag. 1922.

limits correspond to the removal of an electron to the periphery of the atom.

It is to be noticed (see Fig. XI) that it is at the element gold that the $O_{\underline{V}}$ level has its full complement of six electrons for the first time. The level to which an electron is removed on absorption, for elements of higher atomic number than 73 is therefore necessarily further out than $O_{\underline{V}}$.

In Table IV are given certain ν/R values for elements lying between atomic numbers 67 and 73.

Table IV.

| Element. | $M_{\underline{V}}$. | M_{α} . | $(M_{\underline{V}} N_{\underline{VII}})$ | $L_{\alpha} + K_{\alpha}$ | $L_{\beta}, (L_{\underline{III}} O_{\underline{I}})$ |
|----------|-----------------------|----------------|-------------------------------------------|---------------------------|------------------------------------------------------|
| Ho. 67 | 100.0 | | 99.58 | 594.57 | - |
| Er. 68 | 104.2 | | 103.7 | 615.53 | 611.92 |
| Yb. 70 | 113.2 | | 112.2 | 658.59 | - |
| Lu. 71 | 117.9 | | 116.5 | 680.58 | 677.07 |
| Ta. 73 | 123.4 | | 123.9 | 726.10 | 723.30 |

It can be seen from Figure X that the value of $L_{\alpha} + M_{\alpha}$, corresponds to the energy difference of the $L_{\underline{III}}$ and $N_{\underline{VII}}$ levels.

From the table it can be seen that for holmium and erbium there is very little difference between $M_{\underline{V}}$ and M_{α} , but for the elements of higher atomic number $M_{\underline{V}}$ is appreciably larger than M_{α} . This means that for the first two elements there is very little difference in energy between the $N_{\underline{VII}}$ level and the level to which an electron

is removed from the $M_{\underline{V}}$ level at an absorption stage but that for the heavier elements the electron is removed to a level further out than $N_{\underline{VII}}$. This is to be expected from Bohr's theory, since it is in just about this region (at the element lutecium ($Z=71$)) that the $N_{\underline{VII}}$ level becomes full for the first time.

It is also seen from the table that for the elements erbium, lutecium and tantalum the ν/R value of $L_{\underline{III}} N_{\underline{VII}}$ is greater than that of $L_{\underline{III}} O_{\underline{I}}$. This means that the binding of the electrons in the $O_{\underline{I}}$ level is firmer than that of those in the $N_{\underline{VII}}$ level. This is also presumably true of the elements of lower atomic number than 68.

We see then, that for the rare earths the level $N_{\underline{VII}}$ as well as the level $O_{\underline{V}}$ is included in the term periphery.

In Table V are compared the ν/R values of the $L_{\underline{III}}$ absorption limit and of the line L_{β_2} , which is emitted when an electron falls from $M_{\underline{V}}$ to $L_{\underline{III}}$, for the elements of atomic number lying between 55 and 40. (The values of the $L_{\underline{III}}$ limit have been computed for elements of lower atomic number than silver ($Z=47$), which is the lightest element for which it has been observed spectroscopically.)

Table V.

| Element. | L_{III} . | $L_{\beta_2}(L_{III} N_V)$. |
|----------|-------------|------------------------------|
| Cs. 55 | 369.5 | 363.58 |
| J. 53 | 336.0 | 331.87 |
| Te. 52 | 320.1 | 316.84 |
| Sb. 51 | 304.3 | 302.09 |
| Ag. 47 | 247.3 | 246.7 |
| Rh. 45 | 220.9 | 221.07 |
| Mo. 42 | 186.2 | 183.62 |
| Nb. 41 | 174.4 | 174.4 |
| Zr. 40 | 163.5 | 163.5 |

It is seen from the table that the difference between the values in the two columns only becomes appreciable for elements of higher atomic number than silver ($Z=47$). Thus for elements lying below silver in the periodic table an electron at an absorption stage might be removed to the N_V level but at silver this level is full, as can be seen from Figure XI and the electron must necessarily be removed further out. For antimony ($Z=51$) it is possible to compare the ν/R values of the line $L\gamma_4$ ($L_I O_{II}$) and the L_I absorption limit and it is found that they are nearly equal. This means that at this stage in the periodic table, an electron is removed on absorption from the L_I level to the O_{II} level, which level is certainly included in our definition of the periphery of the atom.

For the elements of atomic number lower than zirconium ($Z=40$), we may compare the ν/R values of $K\beta$, ($K M_{III}$), $K\alpha$, + $L\alpha$, (which corresponds to the energy

difference between the K level and the $M_{\overline{V}}$ level), K_{β_2} (K $M_{\overline{IV}}$) and the K absorption limit as shown in Table VI.

The more recent values of the K absorption limit measured by Fricke, Duane, Blake and Hu are given and also some of the older measurements of de Broglie and Wagner.

The K_{β_1} line is emitted when an electron falls from the $M_{\overline{IV}}$ level to the K level and for the elements of lower atomic number than potassium ($Z=19$) the λ_R values of the K_{β_1} line and the K limit are very nearly the same as can be seen from the table.

This may mean that for these elements the $M_{\overline{IV}}$ level is to be included in the peripheral region. For the elements above potassium, however, the value of K_{β_1} is certainly less than that of the K limit and for these elements the electron from the K level is removed further out than the $M_{\overline{IV}}$ level when absorption occurs.

Table VI.

| Element. | K_{β_1} (K M_{III}) | $K\alpha_1 + L\alpha_1$ | K_{β_2} (K N_{II}) | K (Fricke, Duane) (Blake & Hu.) | K (de Broglie) and Wagner. |
|----------|---------------------------------|-------------------------|--------------------------------|---------------------------------------|-------------------------------------|
| Na. 11 | 78.62 | - | - | - | |
| Mg. 12 | 95.57 | - | - | 95.81 | |
| Al. 13 | 114.76 | - | - | 114.67 | |
| S. 16 | 181.48 | - | - | 181.81 | |
| K. 19 | 264.38 | - | - | 265.33 | |
| Ca. 20 | 295.51 | - | - | 297.48 | |
| Sc. 21 | 328.51 | - | - | 331.17 | |
| Ti. 22 | 363.20 | - | 365.42 | 365.43 | |
| V. 23 | 399.72 | - | 402.40 | 402.27 | |
| Cr. 24 | 438.00 | - | 440.86 | 441.14 | |
| Mn. 25 | 478.13 | - | 481.34 | 482.36 | |
| Fe. 26 | 519.90 | - | 523.54 | 524.34 | 523.71 (W). |
| Co. 27 | 563.51 | - | 567.63 | 568.90 | |
| Ni. 28 | 608.72 | - | 613.48 | 612.00 | 613.65 (W). |
| Cu. 29 | 655.91 | 661.22 | 661.30 | 661.06 | (662.74 (W). 656.53 (de B)). |
| Zn. 30 | 704.93 | 710.9 | 711.31 | 702.98 | |
| Ce. 32 | 808.94 | 815.75 | 819.58 | 817.57 | |
| As. 33 | 863.65 | 871.29 | - | 873.28 | |
| Se. 34 | 920.45 | 928.17 | 932.28 | 930.82 | |
| Rb. 37 | 1102.2 | 1111.4 | 1118.6 | 1119.1 | |
| Sr. 38 | 1166.7 | 1176.57 | 1185.4 | 1256.1 | |
| Zr. 40 | 1301.7 | 1312.68 | 1324.4 | 1326.1 | |

From the values of $K\alpha_1 + L\alpha_1$ and K_{β_2} we can compare the binding of the electrons in the M_{III} (3_3) level and in the N_{II} (4_1) level. For copper ($z=29$) and zinc ($z=30$) it is seen that the values are very much the same but for elements of higher atomic number than zinc the 3_3 electrons are bound more firmly than those in the 4_1 orbits (since the value of K_{β_2} is greater than that of $K\alpha_1 + L\alpha_1$).

From this it is clear that for copper and zinc the levels to be included in the periphery are M_{IV} and N_{III} .

The X-ray spectroscopic data are only available for these two elements of those investigated in this research but it is probable that the same will be true of the other elements studied since these two sub-levels are among those in which the last electrons are bound for all these elements.

It is to be noticed in Table VI that for the element vanadium ($z=23$) and for the elements from nickel ($z=28$) to selenium ($z=34$) the frequency of the line $K\beta_2$ ($K N_{\underline{II}}\underline{III}$) is actually greater than that of the K absorption limits most recently measured, though this is not the case for nickel and copper if Wagner's values of the absorption limit are used.

If the more recent measurements are correct, it would appear that the level to which a K electron is removed when absorption occurs is within the $N_{\underline{II}}\underline{III}$ level. However, as has been seen, the measurements of different observers give conflicting results and it is impossible to come to any definite conclusion on this point.

From the above arguments and comparisons it seems clear that an absorption limit corresponds to the removal of an electron from the level concerned to the periphery of the atom, i.e., to the region of the most loosely bound electrons, and that the levels which are to be included in the periphery will change as we progress down the periodic table.

An objection to this suggestion might be raised on the following grounds:-

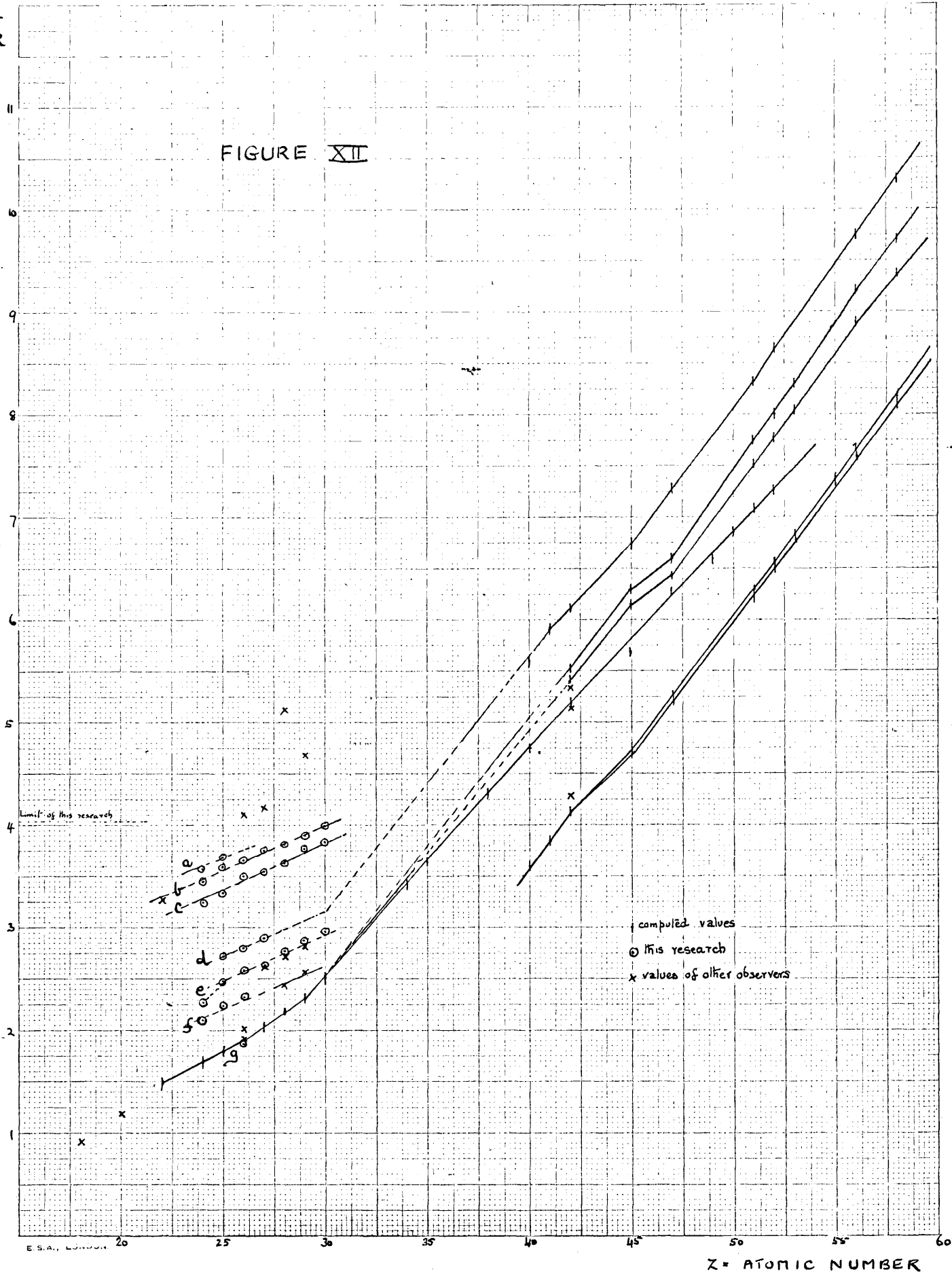
The Combination Principle, which relates emission lines and absorption limits and which has frequently been used in our discussion, if it is to hold rigorously, seems to imply that all the absorption limits for any given element must correspond to the removal of an electron from the different initial levels to the same final level. If an absorption limit is taken to correspond to the ionizing potential of the level concerned, this presents no difficulty.

However, if, as we have shown, an absorption limit must be taken to correspond to the removal of an electron from the initial level to a level in the periphery of the atom, it appears that this peripheral level must be the same for all absorption limits in the atom and several of the transitions involved would be prohibited by the selection principle. This difficulty, however, proves not to be a serious one for, as we have shown, the periphery of the atom includes, as a rule, several levels, all of about the same energy value and the combination principle will hold, to within the limits of experimental error, if one absorption limit corresponds to the removal of an electron to one of these peripheral levels and another absorption limit to another one.

There appears to be no reason why an absorption line should not be measured corresponding to the removal of

$\sqrt{Z/R}$

FIGURE XII



an electron to an incomplete level within the periphery. In fact certain absorption lines have been found by Fricke¹ for titanium, vanadium and chromium on the long wave-length side of the principal K absorption line, and have been explained by Coster as due to the removal of an electron from the K level to the incomplete M level.

The final level in these cases is presumably the M_{IIIII} level since the possibility of removal to the M_I level is ruled out by the selection principle and we have already shown that for these elements the other M sub-level, M_{IVV} is included in the periphery.

In order to show with which levels the critical potentials found for the different elements are to be associated, the points have been plotted on a Moseley diagram in Figure XII, where the values of the quantities $\sqrt{\nu/R}$ have been plotted as ordinates and the atomic numbers as abscissae. The lines corresponding to the M_I , M_{II} , M_{III} , M_{IV} and M_V absorption limits are also given in the Figure.

As has been mentioned before, all five of these limits have only been measured spectroscopically for uranium and thorium and three have been measured for bismuth. The values for elements of lower atomic number can however be

¹ Fricke. loc. cit.

computed from the frequency relations given below, in the cases where the limits and lines required for the computation have been measured.

$$\begin{aligned}
 M_{\underline{I}} &= L_{\underline{III}} - L_{\underline{\ell}} = L_{\underline{II}} - L_{\underline{\eta}} \\
 M_{\underline{II}} &= K - K_{\beta_3} = L_{\underline{I}} - L_{\beta_4} \\
 M_{\underline{III}} &= K - K_{\beta_1} = L_{\underline{I}} - L_{\beta_3} \\
 M_{\underline{IV}} &= L_{\underline{III}} - L_{\alpha_2} = L_{\underline{II}} - L_{\beta_1} \\
 M_{\underline{V}} &= L_{\underline{III}} - L_{\alpha_1}
 \end{aligned}$$

L critical absorption wave-lengths have been measured spectroscopically for twenty-two elements between uranium ($z=92$) and tin ($z=50$) and the necessary emission lines have been measured for most of these elements.

By using the frequency relations,

$$\begin{aligned}
 L_{\underline{II}} &= K - K_{\alpha_2} \\
 L_{\underline{III}} &= K - K_{\alpha_1}
 \end{aligned}$$

it is possible to compute the values of L critical absorption frequencies from observations of K absorption limits and K emission lines and by using the values of the L absorption limits thus computed, to calculate the values of $M_{\underline{I}}$, $M_{\underline{IV}}$ and $M_{\underline{V}}$ from the relations already given, even in cases where the L critical absorption wave-lengths have not been measured directly.

The quantities ν/R and also the square roots of these have been worked out down to $z=40$ by

Bohr and Coster¹ and by Nishina² and these values are plotted in figure XII. The values for the $M_{II,III}$ level for elements of lower atomic number than 40 can be calculated but they have not been marked in the figure on account of their being very irregularly situated. The accuracy of these computed values for elements of low atomic number seems doubtful for, as can be seen from Table IV, if the values obtained for the K absorption limit by different observers are employed, very different values of the M absorption limit result from the computation. The percentage error in the computed value resulting from a small error in the measurement of the K absorption limit or of $K\alpha_1$ or $K\alpha_2$ is very considerable because the two quantities whose difference has been taken are so nearly equal for low atomic numbers.

Measurements by other observers in the region from titanium to copper are also plotted in Figure XII and shown in the following table. The excitation potential method has been used by all the observers mentioned in the Table VIII except Robinson, who measured the energy of the photoelectrons emitted by the elements when exposed to monochromatic X-rays.

¹Bohr and Coster. loc. cit.

²Nishina. loc. cit.

(The points marked with an asterisk in the table cannot be distinguished from values found in this research).

Table VIII.

| Element. | Critical. | Potential. | Observer. |
|----------|-----------|---------------|-----------------------------------|
| | Volts. | $\frac{p}{R}$ | |
| Tl. 22 | 145 | 3.27 | Kurth ¹ |
| Cr. 24 | 60.8 | 2.12* | Levi ² |
| Mn. 25 | 67.7 | 2.23* | " |
| Fe. 26 | 50 | 1.92 | Kurth |
| | 227 | 4.10 | " |
| | 54.6 | 2.01 | Thomas ³ |
| | 228 | 4.10 | " |
| | 92.2 | 2.61 | Levi |
| Co. 27 | 235.6 | 4.17 | " |
| | 79.6 | 2.43 | " |
| Ni. 28 | 100.3 | 2.72 | " |
| | 354.8 | 5.12 | " |
| | 80 | 2.43 | Foote & Mohler ⁴ |
| Cu. 29 | 106 | 2.81 | Kurth |
| | 297 | 4.68 | " |
| | | 2.55 | Robinson ⁵ |
| Mo. 42 | 356 | 5.13 | Richardson & Bazzoni ⁶ |
| | | 4.28 | Robinson |
| | | 5.33 | " |

¹Kurth Phys. Rev. xviii. . 1921.

²Levi. Nature 113. 1924.

³Thomas. Phys. Rev. March 1925.

⁴Foote & Mohler. Origin of Spectra.

⁵Robinson. Proc. Roy. Soc. 104A. 1923.

⁶Richardson & Bazzoni. Phil. Mag. 42. 1921.

It is possible to calculate the energy difference between the $M_{\text{II III}}$ and $N_{\text{II III}}$ levels for the elements investigated from the difference of the lines K_{β_1} and K_{β_2} .

These \mathcal{D}/R values are shown in Table IX.

Table IX.

| Element. | K_{β_2} | K_{β_1} | $K_{\beta_2} - K_{\beta_1}$ | \mathcal{D}/R |
|----------|---------------|---------------|-----------------------------|-----------------|
| Cr. 24 | 440.86 | 438.00 | 2.86 | 4.43 |
| Mn. 25 | 481.34 | 478.13 | 3.21 | 5.02 |
| Fe. 26 | 523.54 | 519.90 | 3.64 | 3.47 |
| Co. 27 | 567.63 | 563.51 | 4.12 | 6.94 |
| Ni. 28 | 613.48 | 608.72 | 4.76 | 7.68 |
| Cu. 29 | 661.3 | 655.91 | 5.39 | 8.27 |
| Zn. 30 | 711.31 | 704.93 | 6.38 | 8.78 |

In the last column is given the \mathcal{D}/R value of the lowest critical potential found for each element. It may be seen from the table that only the point observed for iron in the present research is of the same order as the value for $K_{\beta_2} - K_{\beta_1}$. The difference between the measured and calculated values for this element is about 2 volts.

We will therefore assume that this value for iron is to be connected with the removal of an electron from the $M_{\text{II III}}$ level to the $N_{\text{II III}}$ level and that the lowest values for the other elements correspond to the removal of an electron from the $M_{\text{II III}}$ level to a level further out than the $N_{\text{II III}}$ level or to its removal from a different initial level, i.e., from the M_{I} level.

The $\sqrt{\nu/R}$ values of $K\beta_2 - K\beta_1$ have been calculated for the elements from titanium ($Z=22$), the lightest element for which $K\beta_2$ has been measured with certainty, to tellurium ($Z=52$), and have been plotted in Figure XII, against the atomic numbers. The Moseley line thus obtained has been prolonged to pass through a point for calcium ($Z=20$) corresponding to a line measured by Millikan¹ and shown by him to represent an electron transition from $N_{\underline{I}}$ to $M_{\underline{II} \underline{III}}$. The line also passes through the point corresponding to the first radiation potential of argon ($Z=18$) found by Horton and Davies², which is associated with the removal of an electron from the $M_{\underline{II} \underline{III}}$ level to an N level.

It is seen, as was to be expected, that the iron point lies quite well on this line, and that if the $M_{\underline{II} \underline{III}}$ line is prolonged from atomic number 40, the lowest value which can reasonably be computed, the two lines merge together at about copper ($Z=29$).

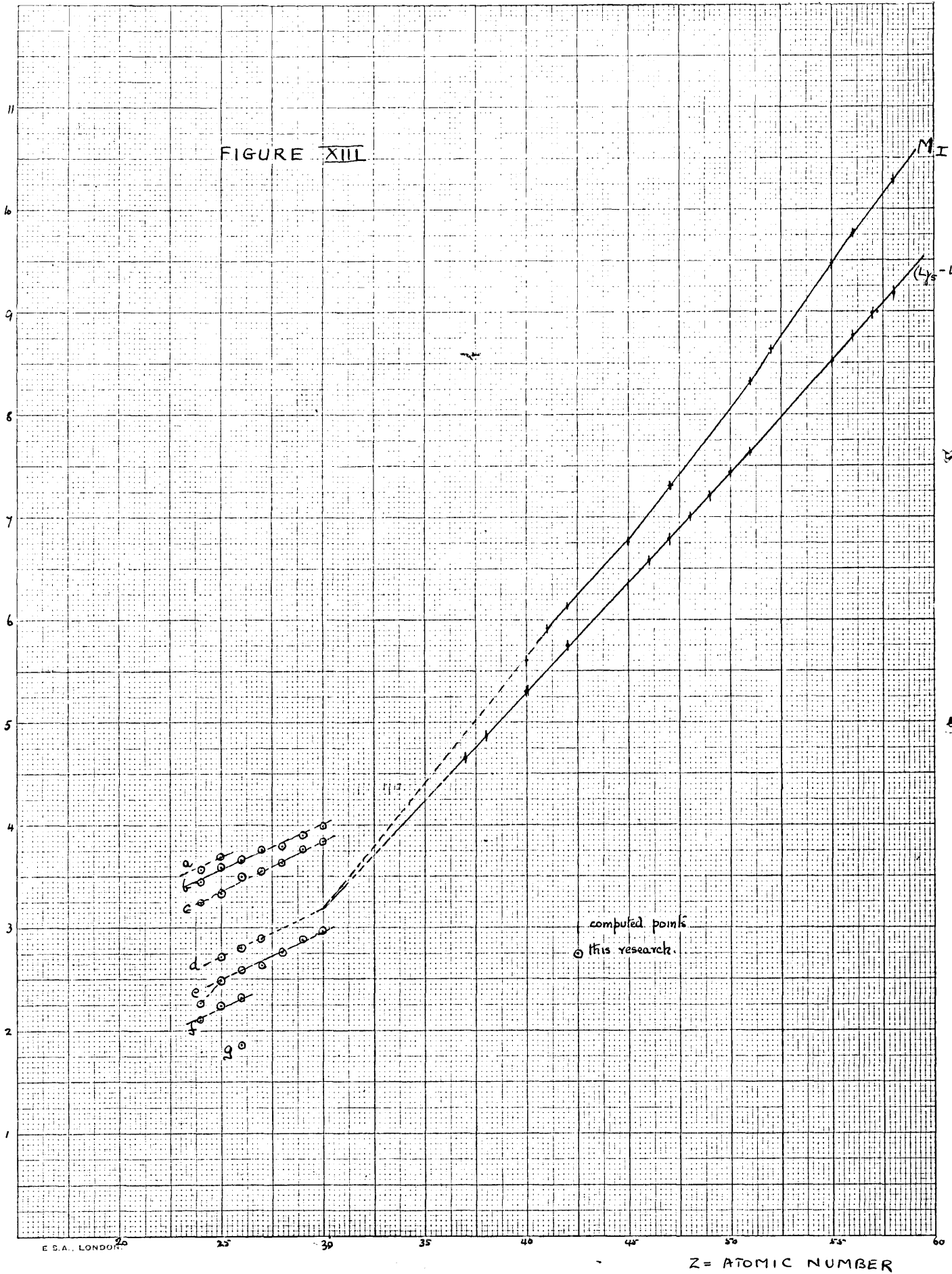
The electron transition from $M_{\underline{II} \underline{III}}$ to $N_{\underline{II} \underline{III}}$ is of course forbidden by the selection principle, because the azimuthal quantum numbers of the two levels are the same. This does not necessarily hold rigidly when the displacements

¹Millikan and Bowen. Phys. Rev. 23. 1924.

²Horton and Davies. Proc. Roy. Soc. 97A. 1920.

$$\sqrt{\nu/R}$$

FIGURE XIII



from the $M_{II} \overline{III}$ level occur under the influence of electronic bombardment, but, in any case, the energy differences between the $M_{II} \overline{III}$ level and all of the N sub-levels in this region cannot be very different, as can be seen from Table X, which gives the $\sqrt{\nu/R}$ values of these differences for the elements from $Z=40$ to $Z=50$.

Table X.

| Element. | $K\alpha_2 + L\gamma_3 - K\beta_1$ ($M_{II} \overline{III} - N_I$) | $L\gamma_2 - K\beta_1$ ($M_{II} \overline{III} - N_{II} \overline{III}$) | $K\alpha_2 + L\gamma_1 - K\beta_1$ ($M_{II} \overline{III} - N_{IV} \overline{IV}$) |
|----------|-------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Zr. 40 | 20.55 | 22.7 | 23.9 |
| Nb. 41 | - | 24.4 | 25.88 |
| Mo. 42 | 25.10 | 26.8 | 28.23 |
| Rh. 45 | 31.23 | 32.3 | 36.94 |
| Pd. 46 | 33.08 | 36.1 | 39.20 |
| Ag. 47 | 34.62 | 39.5 | 41.26 |
| Cd. 48 | 36.20 | 42.0 | 44.42 |
| In. 49 | 40.10 | 43.6 | 47.81 |
| Sn. 50 | 42.62 | 47.0 | 50.77 |

As can be seen, the differences in the values decrease as the atomic number decreases and if the $\sqrt{\nu/R}$ values are plotted in Figure XII and the lines prolonged to elements of lower atomic number, they can hardly be distinguished from one another for elements of atomic number lower than 30.

In the same way, the $\sqrt{\nu/R}$ values for $L\gamma_2 - L\eta$, which difference is equal to that of the M_{II} and N_{II} levels, have been calculated and plotted against atomic number. This line is shown, together with the Moseley line for the M_{II} level in Figure XIII. (A second figure has been plotted to avoid confusion). Values of the M_{II} -absorption limit can be computed

down to atomic number 37 but the values below atomic number 41 are very irregular. The Moseley line corresponding to $L\gamma_5 - L\eta$ can be plotted down to atomic number 37. It is seen that if the two Moseley lines are prolonged they meet at about atomic number 29 or 30 and it seems probable, from the general drift of the lines that the M_{II} line should be continued to pass through the three points for chromium, manganese and iron as shown.

To a first approximation, the frequency corresponding to the ionization of an atom by removal of an electron from an inner level is given by the formula

$$\nu = R (z - c)^2 \cdot \frac{1}{n^2}$$

where c is a constant which differs for different levels and n is the total quantum number. It can be seen from this equation that the Moseley graph of $\sqrt{\nu/R}$ against atomic number for any given level will be a straight line as long as c remains constant. The quantity c depends on the number and arrangement of the electrons in the various groups in the atom and an increase in the number of electrons in the groups within the level concerned or in the level concerned itself causes an increase in c . Hence, at any stage where an electron group is in the process of development, the quantity c will increase more rapidly with the atomic number and therefore the wave number will increase less rapidly with atomic number than at stages where the group is complete.

The Moseley line corresponding to the ionization of any given level should therefore show less steep portions where, according to Bohr's theory, the constitution of the group is undergoing a change. We should expect these changes of slope in the line corresponding to ionization of a level to be reflected in the line corresponding to removal of an electron from the level to the periphery, and it is seen in Figure XII that the $M_{\text{II}}^{\text{III}}$ line, which we have shown corresponds to removal of an electron to the periphery, is less steep between the elements titanium ($Z=22$) and copper ($Z=29$) than elsewhere, thus supporting the theory that a change in the constitution of the M group is in progress in this region.

The M_{I} line is also certainly less steep over the region from manganese ($Z=25$) to cobalt ($Z=27$) than in the extrapolated portion for elements of higher atomic number than zinc, again supporting the theory.

If the foregoing interpretation of the results is correct, it would appear that the upper points marked a, b and c in Figure XII might correspond to the removal of an electron from the M_{I} level and the points marked e and f to the removal of an electron from the $M_{\text{II}}^{\text{III}}$ level to virtual orbits outside the periphery of the atom.

Some further evidence in support of this suggestion can be obtained in another way.

In optical spectra, the frequency of any line can be expressed as a difference of two terms. In a spectral series, the first term is the same for all the lines of the series while the second term varies. On Bohr's theory the lines are emitted when an outer electron jumps between two orbits and a set of lines related similarly to the lines of an optical series is obtained if those lines are grouped together which correspond to electron jumps from different initial orbits to the same final orbit. Thus it is seen that the terms whose difference gives the frequency of an emission line must each be related to some quantity characteristic of one of the orbits between which the electron jumps. The first term of a series gives the limiting frequency of that series, that is to say, it corresponds to the ionized state of the atom. Therefore the quantity to which any term corresponds must be the frequency connected with the energy difference between the ionized state of the atom and the state associated with the term.

The frequency ν of an emission line of a series is given by an equation of the form

$$\nu = C - \frac{1}{(n+a)^2}$$

C being the constant term, n has successive integral values as the distance from the nucleus of the orbit

from which the electron jumps increases, and a is a constant for the series, depending on the azimuthal quantum number and the constants of the atomic field.

If W_1 and W_2 are the energies of the atom in two states, the frequency ν of the line emitted when an electron jumps from an orbit corresponding to the state 2 to an orbit corresponding to the state 1 is given by the relation:-

$$h\nu = W_2 - W_1$$

Thus the difference in the energies of the orbits in the case of the optical series is given by an expression of the form:-

$$h \left(C - \frac{1}{(n+a)^2} \right)$$

If the critical potentials observed are to be interpreted, as we have suggested as corresponding to the energies necessary to remove an electron from one level to different virtual levels beyond the periphery, we can see that they can be represented by an expression of the form:-

$$h (C_1 - C_2)$$

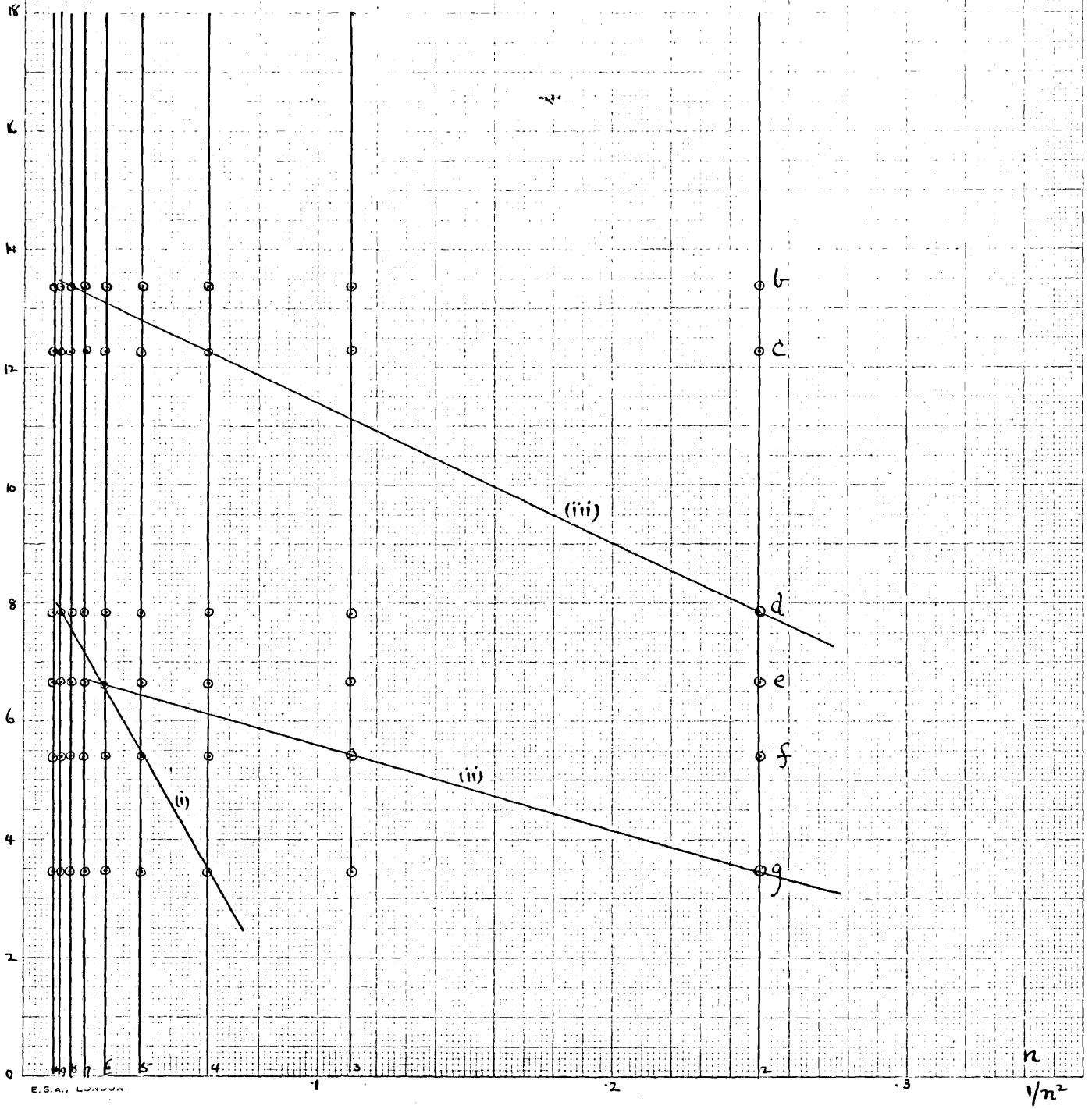
where C_1 and C_2 are two terms, one of which C_1 is constant and the other C_2 is of the form $\frac{1}{(n+a)^2}$ and varies in the same way as the second term in an optical series, provided that the orbits to which the electron is removed are further out than the normally occupied orbits.

The ν/R values of the observed potentials are therefore proportional to a quantity which can be expressed in the form:-

$$C - \frac{1}{(n+a)^2}$$

FIGURE XIV

γ/R



E.S.A., LONDON

The quantity $(n+a)$ is not integral, but part of it n has successive integral values as we pass outwards from the nucleus. Hence if the quantity a were known it should be possible, by plotting the observed values of ν/R for any element against suitable values of $(\frac{1}{n+a})^2$ to obtain a straight line, passing through the points associated with the removal of an electron from any given level to different outer levels. (It is obvious that the presence or absence of the constant C does not affect the linear relation between $\frac{\nu}{R}$ and $(\frac{1}{n+a})^2$).

As a is not known this cannot actually be done but some evidence as to the interpretation of the critical potentials can nevertheless be gained by plotting the observed values of $\frac{\nu}{R}$ against values of $1/n^2$ where n has successive integral values. This has been done for all the elements wherever possible and the figure for the element iron is given as an example in figure XIV.

The figure is drawn in the following way. Values of $\frac{\nu}{R}$ are taken as ordinates and values of $1/n^2$ as abscissae. Vertical lines are drawn corresponding to values of $1/n^2$ from $n = 2$ to $n = 10$. (The lines become too close together for higher values of n on the scale shown). The observed values of $\frac{\nu}{R}$ are then set on all the vertical lines as shown by the ringed points. Attempts are then made to draw a straight line passing through the ringed points such that

the larger values of \sqrt{R} correspond to the smaller values of $1/n^2$. Three such lines, (i), (ii) and (iii), are shown in the figure and it is obvious that several could be drawn but it is also clear that no line which passed through the four lower points d, e, f and g could also pass through the upper points b and c whatever values of $1/n^2$ are used. A line can be drawn, however, (see line (iii)) passing through b, c and d.

Thus it appears that the points b and c must be connected with removal of an electron from another level than the points e, f and g. The point g has already been shown to be associated with the $M_{\text{II}} \text{ III}$ level, so that the points b and c are presumably to be associated with the M_{I} level.

No definite conclusions can be drawn about the point d from figure XIV, for it can be seen that it may lie either on a line like (i) connecting d, e, f and g or on a line like (iii) connecting b, c and d. In the former case the point d corresponds to a much larger value of n than in the latter case.

However, it is very possible that the energy necessary to remove an electron from the M_{I} level to a level in the periphery or a little beyond it is very nearly equal to the energy necessary to remove an electron from

the $M_{II} \overline{III}$ level to a level considerably further out and that the critical potentials in the two cases could not be distinguished in the experiments.

The conclusions reached by this method as to the interpretation of the results, do therefore agree on the whole with the suggestions put forward before, that the points marked a, b, c and d, in figure XIII are to be associated with the removal of an electron from the M_I level and the points marked e, f and g with the removal of an electron from the $M_{II} \overline{III}$ level.

Bohr considers the question of the removal of an electron from an inner level when an absorption process occurs, and, in his third essay (The Theory of Spectra and Atomic Constitution) he shows that there are three possibilities,

These are (1) removal completely from the atom (2) removal to an incompleted group of electrons and (3) removal to an orbit where, during the greater part of its revolution, it moves at a distance from the nucleus large compared with the distance of the other electrons. He then goes on to say, "on account of the peculiar conditions of stability which control the occurrence of incomplete groups in the interior of the atom, the energy which is necessary to bring about a transition to such a group will in general differ very little from that required to remove

the particular electron completely from the atom. We must therefore assume that the energy levels corresponding to the absorption edges indicate to a first approximation the amount of work which is required to remove an electron in one of the inner groups completely from the atom."

The suggestions which we have put forward do not appear to agree with this view, which is supported by the experiments of Robinson¹; which have been mentioned before, but a closer examination of Robinson's results shows that the two ideas may not be incompatible.

In Robinson's experiments, the element under investigation was exposed to the $K\alpha$ rays of copper and the paths of the electrons liberated by photoelectric action were bent by a uniform magnetic field on to a photographic plate, the radius of the path depending on the velocity of the electron. A "line spectrum" of secondary corpuscular rays was produced, this "line spectrum" being composed of groups of electrons from different levels in the atoms of the target. The energy of the photoelectrons was calculated from the value of the magnetic field and the radius of the path and, assuming the energy in the incident copper rays, the energy of the levels from which the electrons came could be determined. The kinetic energy of the electron is given by

$$h\nu - W$$

where ν is the frequency of the incident radiation and W
I. Robinson. loc.cit.

the work required to free the electron from a level in the atom.

The conditions of these experiments are obviously quite different from those of experiments by other methods (spectroscopic and excitation potential methods) for determining critical absorption frequencies.

In the experiments described above, if an electron is removed to the periphery of the atom, there can be no indication of the occurrence on the photographic plate, and the frequencies determined from the positions of the lines on the plate must correspond to the ionization potentials of the levels.

An examination of the results shows that the agreement with measurements by other methods and with Bohr's and Coster's computed values is very much better for the more deeply seated levels in the atom than for those nearer to the surface. For instance, for the heaviest elements investigated, bismuth ($Z=83$) and lead ($Z=82$) the agreement is quite good for the M levels and for some of the N levels, but for the lighter elements (e.g. strontium ($Z=38$) and copper ($Z=29$)) the agreement is only good for the L levels.

It is to be noticed that in the results for the lightest elements, the agreement with Fricke's measurements for the K limit is not very good for the elements magnesium ($Z=12$), sodium ($Z=11$) and oxygen ($Z=8$) and that for

the elements calcium ($Z=20$), potassium ($Z=19$), sulphur ($Z=16$) and magnesium ($Z=12$) the L results are consistently higher than Fricke's measurements.

For these light elements, the L level is near the surface of the atom and it therefore appears, if any reliance is to be placed on these results, that for the levels nearer to the surface of the atom, definitely more energy is required for ionization than for removal of the electron to the periphery (Fricke's results being taken to represent the latter).

It certainly seems reasonable to suppose that the ratio of the energies corresponding to removal of an electron right outside the atom (ionization) and to its removal to the periphery should be greater for a level near the surface of the atom than for a level near the nucleus.

It has been suggested by various writers that the fine structure of the absorption limits observed spectroscopically might be accounted for by multiple ionization, but it is difficult to see how the results obtained in this research could reasonably be accounted for in this way.

The energy required to remove two electrons from a given level cannot surely be less than twice the amount required to remove one electron, and if the observed critical potentials are to correspond to multiple ionization of

a level, we should expect to find that the higher values observed are at least as great as the corresponding multiples of the lower values.

It can be seen that, on the contrary, the differences between the values which we have connected with the removal of an electron from the same initial level become successively smaller as the values of the critical potentials increase, which is what we should expect if the results are to be interpreted as we have suggested.

¹
Wentzel has suggested that the fine structure of an absorption discontinuity might be explained by successive ionization of the level concerned, but it seems that the probability of this occurring is so small that it is very unlikely that discontinuities due to effects of this kind would be detectable in the curves obtained.

From the general lines of the arguments which have been brought forward above, the conclusions reached are that the points a, b and c (see figure XII) correspond to the removal of an electron from the $M \underline{I}$ level to levels beyond the periphery of the atom and the points e and f correspond to the removal of an electron from the $M \underline{II} \underline{III}$ level to levels beyond the periphery. The point g, only observed for iron, is taken to correspond to removal to the periphery from the $M \underline{II} \underline{III}$ level i.e. to the $M \underline{II} \underline{III}$ absorption "limit" and the

1. Wentzel. Annalen d. Physik. lxvi 1921.

point d to correspond either to removal of the electron from the $M \underline{I}$ level to the periphery, i.e. to the $M \underline{I}$ absorption "limit" or to removal from the $M \underline{IV}$ level to a level considerably further out.

We have shown that the change of slope in the Moseley lines in this region indicates that the development of the whole M group is in progress at this stage in the periodic table, but it does not appear to be possible to make any further deductions as to the stages in the development of the sub-groups from the results obtained. There is no possibility of determining from the method of experiment, whether corresponding electron jumps will occur in all the elements, but it seems reasonable to suppose that this will probably take place and the general lie of the dotted lines in figure XII seems to suggest it.

If the points observed are plotted on a larger scale in a Moseley diagram the dotted lines show slight irregularities. Since we cannot be certain that the lines pass through corresponding points for all the elements, it does not seem reasonable to deduce anything from these irregularities. When the research was begun, it was thought that the ionization potentials of the levels would be measured. In this case, it is certain that points found for all the elements would have been corresponding ones and it might have been possible to deduce evidence as to the stages of

development of the M group from irregularities in the Moseley lines.

Bohr's theory shows that in the region of the rare earths, a similar kind of change in the development of an inner group is in progress. This is the N group and the change begins at atomic number 58 and all four groups are complete at atomic number 71.

Bohr and Coster, and more recently Nishina, have computed the values of the N absorption limits for the elements in this region, and they have shown that the Moseley lines corresponding to the inner N sub-groups 4_1 , 4_2 and 4_3 show a regular slope over this region, the slope being less steep between the elements which mark the beginning and end of the change in the constitution of the group, exactly as has been found in this research for the inner N sub-groups 3_1 and 3_2 .

If Bohr's view as to the numbers of electrons in the various sub-groups is accepted and if, as appears to be the case, the Moseley lines for the inner sub-groups are approximately straight over a region in which a change in the constitution of a group is occurring, then we can only conclude that it makes no appreciable difference to the alteration in the screening constant for a given sub-level, whether the electrons added to the group, while it is in the process of development, enter one sub-group or another.

Thus, while the experimental results obtained have not produced evidence supporting Bohr's view that the M group of electrons when complete consists of three subgroups containing six electrons each, they are not necessarily in conflict with it. They support equally well the view put forward by Stoner¹ that the development of the M group consists simply in the addition of ten electrons in orbits outside those of the electrons already bound in the group.

1. Stoner. Phil. Mag. Oct. 1924.