AN EXPERIMENTAL INVESTIGATION OF THE ENERGY IN THE CONTINUOUS X-RAY SPECTRA OF CERTAIN ELEMENTS.

By Clayton T. Ulrey.

IN the classical research of W. H. and W. L. Bragg[1] on the reflection of X-rays from crystals it was shown that besides the characteristic lines emitted by the target of the X-ray bulb there was always present a considerable amount of radiation in the neighborhood of the lines which could not be resolved into separate lines by the X-ray spectrometer. In photographs of X-ray spectra this continuous part of the spectrum manifests itself by the "fogged" background upon which the characteristic lines are superimposed.

The purpose of this investigation was:

(1) To obtain the energy-wave length distribution curves for the continuous spectra of various elements with the special object in view of determining the relation between the amount of energy radiated and the atomic number (or atomic weight) of the element, and

(2) To investigate the effect of a variation of voltage applied to the tube on the amount and distribution of energy in the spectrum.

Professor William Duane and F. L. Hunt[2] investigated the energy distribution in the continuous X-ray spectrum of tungsten and found that the short wave-length end of the spectrum has a very definite boundary whose wave-length is given by the relation

$$\lambda_0 = \frac{hc}{Ve},$$

where λ_0 = minimum wave-length excited, V = constant voltage applied to the tube, e = electron charge, h = Planck's radiation constant, and c = velocity of light. They showed that the energy, as measured by its ionizing effect, increases rapidly with increasing wave-length and soon reached a maximum value and then decreases less rapidly with a further increase of wave-length.

Similar radiation curves of tungsten have been obtained by Dr. A. W.

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[1] Royal Society, Proc., *A*, 88, July, 1913; and X-Rays and Crystal Structure, Chapter 6.

[2] Phys. Rev., VI:, Aug., 1915.

Hull[1] and by Dr. Hull and Miss Rice,[2] which show in a general way how the maximum is shifted toward the shorter wave-lengths as the voltage applied to the tube is increased. Dr. Hull[3] has also compared the radiation curves of tungsten and molybdenum obtained under identical conditions (at 45,000 volts). Inspection of these last curves shows that the intensities of the maxima are in the same ratio as the atomic numbers of the elements tungsten and molybdenum.

The problem of the dependence of the intensity of X-radiation upon the atomic weight of the element emitting the radiation has been investigated in a number of researches, among which may be mentioned those of G. W. C. Kaye,[4] of R. Whiddington,[5] of R. T. Beatty,[6] and of C. S. Brainin.[7] They all agree that there is no definite relation existing between the *total emission* and the atomic weight. Kaye, however, obtained an approximate proportionality between intensity and atomic weight when he interposed a sheet of aluminum of several millimeters' thickness between the X-ray tube and ionization chamber. The explanation given for this effect of the aluminum is that it absorbed most of the characteristic radiation from the elements of low atomic weight where the characteristic constitutes a large percentage of the total radiation. If this be the correct explanation we may expect to find the true relation only when the characteristic radiation is entirely eliminated. Analysis of the spectrum by the X-ray spectrometer is a suitable method for making this elimination. It is not improbable that a comparison of the intensities of corresponding characteristic radiations of different elements may also reveal valuable information in regard to this same problem.

Description of Apparatus and Method.

For these experiments a special X-ray tube was constructed, with a steel anticathode in the form of a hexagonal prism upon each face of which was mounted a sheet of one of the metals, chromium, nickel, molybdenum, palladium, tungsten and platinum. To the base of the prism and in line with its axis was attached a steel tube whose inside diameter was just sufficient to allow it to slip down over a steel rod mounted vertically in the bulb and acting as one electrode. Thus the anticathode was free to rotate about a vertical axis so that each of its faces could be brought

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[1] American Journal of Roentgenology, II., Dec., 1915.

[2] Proceedings National Academy of Science, II., May, 1916.

[3] Curves published by Bergen Davis, Phys. Rev., IX., Jan., 1917.

[4] Phil. Trans. Roy. Soc., *A*, 209, 1908–9.

[5] Proc. Roy. Soc., *A*, 85, 1911.

[6] Proc. Roy. Soc., *A*, 89, 1913–14.

[7] Phys. Rev., X., Nov., 1917.

into position to be bombarded by the cathode stream. The rotation was accomplished by use of an electromagnet outside the bulb acting upon a bar of soft iron fastened at right angles to the steel tube and as far below the prism as possible.

A Coolidge cathode obtained from the General Electric Co. was sealed into one side of the X-ray bulb in a horizontal position. The bulb was exhausted by means of a mercury diffusion pump in connection with a Gaede rotary pump for producing the fore-vacuum. In order to prevent mercury vapor from reaching the X-ray tube a condensation chamber was sealed between the bulb and pump. During the operation of the pumps this chamber was surrounded by a Dewar flask containing slush of carbon dioxide snow and ether. By this means a vacuum was attained which was high enough to prevent any trace of a gas discharge at 50,000 volts.

A step-up transformer was used to obtain high voltages. Energy was supplied to the transformer by a 5-kilowatt, 500-cycle generator whose speed was maintained constant by use of an auxiliary synchronous motor. The voltage was regulated by adjustment of a variable resistance in the generator field circuit which was separately excited by a storage battery of 120 volts. The current from the transformer was rectified by the use of two kenotrons, one connected to each terminal of the secondary of the transformer. In order to reduce the voltage fluctuations in the high-voltage circuit to a minimum, a resistance and a specially designed high-voltage condenser of .016 microfarad capacity were inserted after the manner suggested by Dr. A. W. Hull,[1] of the General Electric Co.

The voltage applied to the X-ray tube was measured by an electrostatic voltmeter designed by Professor Davis. It was essentially a Coulomb's balance in which a pair of movable spheres were *repelled* by a pair of stationary ones. A mirror attached to the suspension of the movable spheres reflected a beam of light upon a scale at a distance of approximately one meter. The instrument was calibrated by means of a spark gap between spheres of 12.5 centimeters' diameter.

The filament of the cathode was heated by a current from a storage battery. The electron current through the X-ray bulb was read by means of a milliammeter placed next to the bulb, so that it would indicate only the current through the bulb and not the leaks along the line.

The X-ray bulb was completely surrounded by a lead shield of .6 centimeter thickness with a narrow aperture on the side facing the spectrometer. The beam of X-rays after passing through this aperture and the first slit of the spectrometer was reflected from the (100) face of a crystal of calcite for which the distance between reflecting planes is

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[1] Phys. Rev., VII., March, 1916.

3.030×10^{-8} cm. The reflected beam passed through the second spectrometer slit and a thin mica window into the ionization chamber. The crystal used in these experiments was finally selected as being the most nearly perfect out of a large number which were tested by examination of the photographs obtained when the crystal was used as a reflector for a narrow band of general X-radiation.

The ionization chamber consisted of a hollow steel cylinder 75 cm. long and 7.5 cm. diameter, in which was supported a small steel rod insulated from the chamber and parallel to the axis of the chamber, but decentered far enough to prevent any X-rays from impinging upon it. The chamber itself was earthed and the insulated electrode was charged to a potential of 400 volts. A gold leaf attached to the end of this insulated electrode was viewed by means of a low power microscope with a scale in the eyepiece. The rate of leak was determined by observing the time required for the image of the leaf to move over a certain part of the scale (10 divisions). The sensitivity was about 5 divisions per volt

In order to increase both the absorption and the ionization, ethyl bromide (C_2H_5Br) vapor was used in the ionization chamber. At a temperature of 20° C. the absorption in a mixture of air and saturated ethyl-bromide vapor is approximately 2.4 times that in air, since the pressure of the vapor is 387 mm. and its density relative to air is 3.78. Hence the absorption in this mixture was equivalent to that in a chamber 180 cm. long if filled with air alone.

Discussion of Results.

I. *Comparison of the Energy Distribution Curves at Constant Voltage.*

In Figs. 1 and 2 are shown the radiation curves of the six metals investigated. The data for these curves were obtained under identical conditions with a potential difference of 35,000 volts applied to the X-ray tube, a current of 1 milliampere, and a slit width of .4 millimeter. The ordinates represent intensities, as measured by ionization, and the abscissas wave-lengths calculated from Bragg's formula, $\lambda = 2d \sin \theta$. After the maximum of the tungsten curve had been located and its intensity measured, this was chosen as a standard and readings were taken for this setting of the spectrometer during the observations for each of the other metals. This procedure was necessary in order to make corrections for variations in the sensitivity of the electrometer from day to day. The only other correction was made for the natural leak and scattered radiation from the crystal and other sources. These two errors were corrected at the same time observing the rate of leak whenby the X-ray tube was in operation but the crystal and ionization chamber slightly out of step. The curves are extended only to .9 Å.U. since beyond this limit the broad characteristic bands of the L series of platinum and tunsgten appear and also the absorption of ethyl bromide undergoes a sharp change in this region which corresponds to the edge of the K series absorption band of bromine. These curves have practically the same form except where they are modified by the presence of the characteristic radiation and the accompanying absorption in that region.

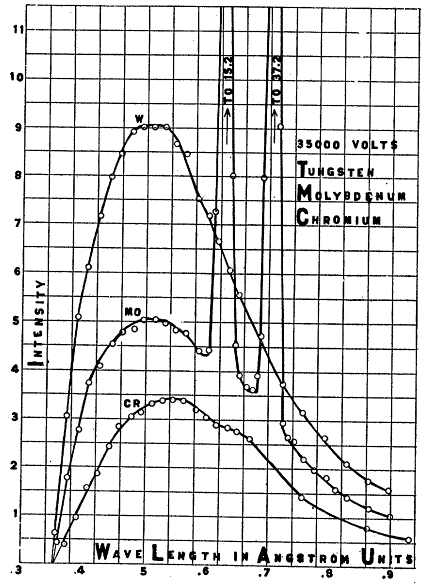

Fig. 1.

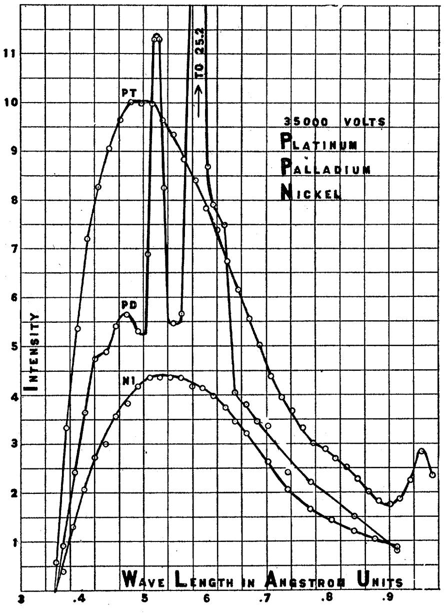

Fig. 2.

X-radiation curves of different metals.

There is a shift of the position of the maximum toward shorter wavelengths with increasing atomic weight. The shift is small and there does not appear to be any simple relation between the position of the maximum and the atomic weight.

The total energy which an element can emit in the form of radiation is given by:

$$\text{Energy} = \int_{\lambda_0}^{\infty} \epsilon_\lambda d\lambda$$

and the area under the radiation curve is proportional to this integral. The curves shown above do not represent the true radiation curves since they have not been corrected for the reflecting power of the crystal or the absorption in the glass of the X-ray bulb, both of which vary with the wave-length. However, since the curves extend over the same range of wave-lengths, their areas will still give the *relative* values of the energy emitted by the various elements. The areas were obtained by means of a planimeter and are given in Table I. The areas due to the characteristic radiation were not included in the integration. When these areas are plotted against atomic weights or atomic numbers of the radiating elements the relation appears to vary in a periodic manner, the periodicity coinciding with that of the chemical periodic system. For convenience of reference the arrangement of these elements in the periodic table is shown in Table II. The numbers are the atomic numbers and atomic weights. The same phenomenon is shown in a more striking manner when the intensities of the maxima are plotted against atomic numbers, as in Fig. 3.

Table I.

Element.	Atomic Weight.	Atomic Number.	Area of Radiation Curve.	Intensity of Maximum.
Platinum..........	195.2	78	100.0	100.0
Tungsten.........	184.0	74	90.0	89.9
Palladium.........	106.7	46	60.3	58.6
Molybdenum......	96.0	42	54.3	50.1
Nickel............	58.7	28	45.7	43.7
Chromium........	52.0	24	34.6	33.9

Table II.

Series.	Group VI.	Group VIII.
3	24 Cr. 52	28 Ni. 58.7
5	42 Mo. 96	46 Pd. 106.7
8?	74 W. 184	78 Pt. 195.2

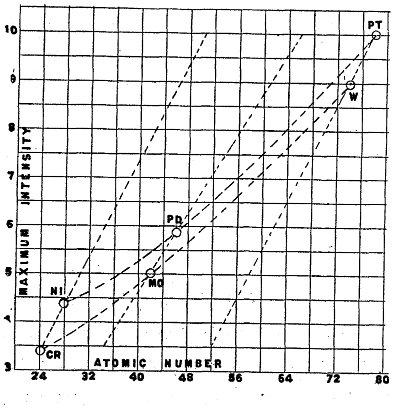

Fig. 3.

The values of the intensities shown here are averages of a number of observations (4–6) taken on the different elements in succession, except in the case of palladium where the characteristic radiation falls on the maximum. The value in this case was determined indirectly by finding its relative intensity for a wave-length slightly shorter than that of the maximum. The straight lines drawn through the points corresponding to the members of the same series are nearly parallel. The same periodicity was found when different voltages were used and also when the intensities of a wave-length greater than that of the maximum were compared.

It would be desirable to have similar data for a large number of elements before any definite conclusions in regard to this phenomenon be drawn, but it seems probable from these results that the number of radiating electrons which are active in producing the continuous X-ray spectrum, or the amplitude of their vibrations (or both) is a periodic function of the atomic number, *i. e.*, of the nuclear charge of the radiating element.

II. *Effect of Voltage Upon the Energy Distribution Curves.*

Fig. 4 shows the radiation curves of tungsten for voltages of 20, 25, 30, 35, 40, and 50 kilovolts. A Coolidge X-ray tube was used in this case

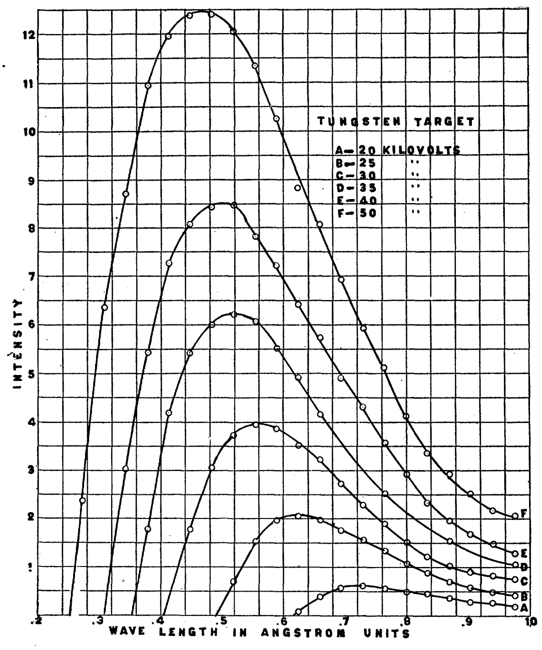

Fig. 4.

Tungsten X-radiation curves.

as it could be operated more easily and at higher voltages than the one previously used. The power supplied to the tube was maintained constant at 35 watts and the results reduced to intensity per milliampere. This was necessary in order to prevent shifting of the focal spot due to expansion of the metal rod supporting the target. The same corrections were made as in Part I.

The similarity between these curves and those of the radiation from a "black body" suggests comparison. Temperature in the "black body" radiation curves corresponds to voltage in the X-radiation curves. To test the apparent similarity quantitatively we must determine how the frequency of the maximum varies with voltage, *i. e.*, we must determine the displacement law for the X-ray curves. In order for the similarity to be complete we should have $\lambda_{\max} V =$ const. corresponding to Wien's displacement law, $\lambda_{\max} T =$ const. or what amounts to the same thing, we should have the ratio, $\lambda_{\max}/\lambda_0 =$ const. since $\lambda_0 V =$ const. as has been proved experimentally by Hull[1] for voltages up to 100 kilovolts.

In Table III. are given the experimental values of the minimum wave-length, λ_0, the wave-length of the maximum energy, $\lambda_{\max}$, and the ratio, $\lambda_{\max}/\lambda_0$ for the various voltages used.

TABLE III.

Volts.	Area of Radiation Curve.	λ_0.	$\lambda_{\max}$.	$\frac{\lambda_{\max}}{\lambda_0}$.	$\lambda_0 V$.	$\lambda_{\max} V^{\frac{1}{2}}$.
					$\times 10^{-7}$	
20,000	0.46	.615 Å.U.	.710 Å.U.	1.15	1,230	100.4
25,000	1.85	.490	.620	1.26	1,225	98.0
30,000	3.96	.405	.555	1.37	1,215	96.1
35,000	6.78	.355	.520	1.47	1,243	97.3
40,000	10.06	.310	.500	1.61	1,240	100.0
50,000	16.34	.250	.470	1.88	1,250	105.1

From these results it is clear that the ratio $\lambda_{\max}/\lambda_0$ increases with the voltage and shows no tendency toward a maximum value within this range of voltage. When the values of this ratio are plotted against the square root of the voltage, the relation is found to be nearly linear.

Hence

$$\frac{\lambda_{\max}}{\lambda_0} = k V^{\frac{1}{2}} + \text{const.}$$

or

$$\lambda_{\max} V^{\frac{1}{2}} = \text{const.}$$

The last column in the table shows how nearly this relation holds. It is probable that if corrections for absorption in the walls of the X-ray tube and in the crystal could be made, the variation in the ratio $\lambda_{\max}/\lambda_0$ would be less. This latter correction would involve a knowledge of the

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[1] PHYS. REV., VII., Jan., 1916.

variation of reflecting power of the crystal with wave-length, which, unfortunately, has not yet been determined.

The sixth column in the table shows $\lambda_0 V$ to be constant which is in agreement with the results of other observers who used the spectrometer method to measure λ_0. The value of h calculated from the average value of this constant is 6.54×10^{-27}.

The fact that $\lambda_{\text{max}}/\lambda_0$ increases with voltage means that the *maximum frequency*, ν_0, increases at a greater rate than the *frequency of the maximum*, ν_{max}. This would account for the deviation from a straight line which was obtained by R. Ledoux-Lebard and A. Dauvillier[1] when they plotted maximum frequency against voltage, since they determined the frequency by observing the position of the short wave-length limit of the continuous spectrum from photographs. Since the intensity falls rapidly from λ_{max} to zero at λ_0, they probably chose as the limit of the spectrum, a point nearer to λ_{max} than λ_0.

An estimate of the relative energy radiated at the different voltages may be obtained in two ways:

1. Since the radiation curves in Fig. 4 are similar and vary continuously with the voltage, the equation of such a curve may be deduced and when integrated this will give a measure of the energy. The equation of such a curve has been deduced from theoretical considerations by Professor Davis.[2]

2. The integration of the experimental curves may be performed directly by obtaining their areas with the planimeter. The latter method was used here and the areas were plotted against the square of the voltage in Fig. 5.

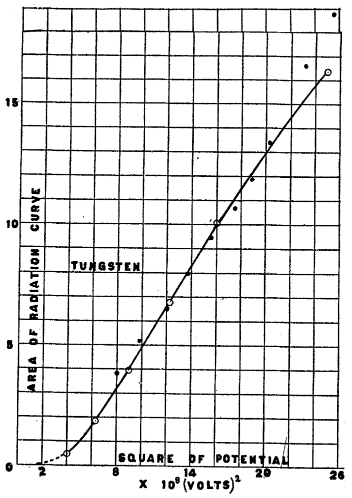

Fig. 5.

Assuming that the areas are proportional to the energy radiated, this method shows a linear relation between the energy in this part of the X-ray spectrum and the square of the voltage, between 25 and 40 kilovolts. For both higher and lower voltages there are deviations from the straight line relation. The errors previously cited may be even more serious here, since the radiation curves extend over different ranges of wave-length.

The curvature in the lower part of the graph is partially due to the

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[1] Comptes Rendu, Dec., 1916.

[2] Phys. Rev., IX., Jan., 1917.

fact that a greater percentage of the total radiation is absorbed in the walls of the tube and in the crystal for the lower voltages than the higher, since the absorption coefficient is greater for the longer wave-lengths. The low value of the energy for 50 kilovolts may be due to the fact that at this voltage radiation is present which is too penetrating to be completely absorbed in the ionization chamber. The graph does not pass through the origin since the integration extended only to a wave-length of .975 Å.U. which is excited at a voltage of 12.66 kilovolts. For lower voltages than this the only radiation excited would have wave-lengths greater than .975 Å.U. and therefore would not be included in the above measurements. This also contributes to the curvature in the lower part of the graph since, obviously, a greater percentage of the total energy is neglected at the lower voltages.

For the sake of comparison of methods, the data for the total X-ray energy emitted by a Coolidge tube and measured by means of a bolometer by P. T. Weeks[1] are shown in Fig. 5 by the dots. The fact that his measurements included the effect of the characteristic L radiation would account for the greater rate of increase of energy with voltage which he found.

SUMMARY.

The continuous X-ray spectra of platinum, tungsten, palladium, molybdenum, nickel and chromium have been investigated by the X-ray spectrometer method.

By comparison of the areas and maximum ordinates of the radiation curves of the different elements, it appears that the energy emitted in the form of X-radiation in this part of the spectrum is not directly proportional to the atomic weight or the atomic number, but is a periodic function of either, the periodicity coinciding with that of the chemical periodic system.

The continuous spectrum of tungsten has been investigated over a range of voltage from 20 to 50 kilovolts. Within this range the following relation between the wave-length of maximum energy, $\lambda_{\max}$, and the voltage is found to hold

$$\lambda_{\max} V^{\frac{1}{2}} = \text{const.}$$

The areas under the tungsten radiation curves are proportional to the square of the voltage between 25 and 40 kilovolts.

In conclusion I wish to acknowledge my indebtedness to Professor Bergen Davis who suggested this work and whose development of the X-ray laboratory made it possible.

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[1] PHYS. REV., X., Nov., 1917.