ATOMIC THEORY AND LOW-VOLTAGE ARCS IN CÆSIUM VAPOR

By Paul D. Foote and W. F. Meggers

CONTENTS

		Page
I.	Theoretical	309
II.	Experimental	316
III.	Results	320
IV.	Summary	324

I. THEORETICAL

The spectrum of cæsium is characterized by the principal doublet series 1.5 $s-m\ p_{\frac{1}{2}}$ where $m=2$, 3, 4, etc., the first subordinate series 2 $p_1-m\ d$ and 2 $p_2-m\ d'$ where $m=3$, 4, 5, etc., the second subordinate series 2 $p_{\frac{1}{2}}-m\ s$ where $m=2.5$, 3.5, 4.5,

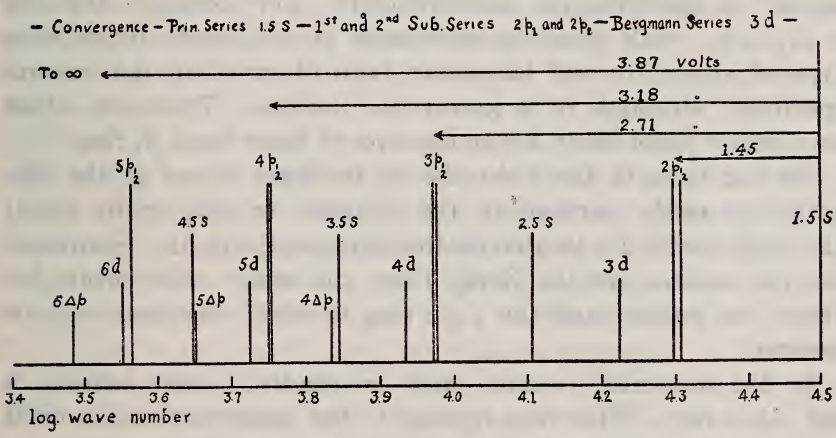

FIG. 1.—*Schematic representation of cæsium atom*

etc., the Bergmann series 3 $d-m\Delta p$ and 3 $d'-m\Delta p$ where $m=4$, 5, 6, etc., satellites to the first subordinate series and certain combination lines, those known lying in the far infrared. The above notation is that employed by Dunz in his tables except that, for convenience, we have used $p_{\frac{1}{2}}$ when both p_1 and p_2 are referred to.

The spectroscopic data are sufficient to permit a schematic representation of the cæsium atom, as illustrated in Fig. 1. This method was suggested to the writers by Dr. Raymond T. Birge,

and, regardless of the theory of atomic structure, it affords a precise picture of the possible series lines in the spectrum of an element, a much clearer picture than may be gained by one unfamiliar with series notation from an examination of the series formulas. The first doublet of the principal series may be represented by electrons falling from the 2 p_1 and 2 p_2 rings into the 1.5 s ring, thus emitting the lines 1.5 $s-2p_{\frac{1}{2}}$. The second doublet of this series is represented by electrons falling from the 3 p_1 and 3 p_2 rings into the 1.5 s ring, giving rise to the lines 1.5 $s-3\ p_{\frac{1}{2}}$, and so on. The lines of the first subordinate series are represented by electrons falling from the $m\ d$ rings into the 2 p_1 and 2 p_2 rings; the lines of the second subordinate series by electrons falling from the $m\ s$ rings into the 2 p_1 and 2 p_2 rings; the lines of the Bergmann series by electrons falling from the $m\ \Delta\ p$ rings into the d rings. Combination lines are represented in the same manner. Thus the line 2.5 $s-3\ p_1$ arises from an electron falling from the 3 p_1 ring into the 2.5 s ring. Few of the possible combination lines are probable enough to appear in spectroscopic measurements. For example, the line 2 $p_1-4\ p_1$, while possible, represents an extremely improbable type of transition and has never been observed in the cæsium spectrum, although it is known for sodium. There are other ways much more likely for an electron to leave the 4 p_1 ring.

On the basis of the Bohr theory the lines shown in the diagram are really portions of the elliptical or ring orbits about the nucleus which is located off the figure on the right. Surrounding the nucleus are the X-ray rings and many other orbits between the nucleus and the 1.5 s ring in which electrons may be present.

In the unexcited cæsium atom no electrons exist outside of the 1.5 s ring. This ring represents the outermost stable orbit and the innermost unstable orbit of the normal atom, and the diameter of this orbit should give the diameter of the normal cæsium atom. The evidence for this is fairly conclusive. That there are electrons in this ring is shown by the existence of the principal series, which converges at 1.5 s. That it represents the innermost unstable orbit for any ordinary method of excitation is shown by the fact that no spectroscopic series of cæsium converges at a higher frequency than 1.5 s, nor is any line of higher frequency known. That it represents the outermost stable orbit is evidenced by determinations of the ionization

potential for which Foote, Rognley, and Mohler[1] observed the value 3.9 volts. On the basis of the quantum relation, $h\nu = eV$, an electron falling through 3.877 volts possesses just sufficient energy to eject an electron from the 1.5 s ring to infinity, in excellent agreement with the experimentally determined value of 3.9 volts. Thus the ionization of the normal cæsium atom is produced by ejecting an electron from the 1.5 s ring. If the outermost stable orbit were the 2 p rings the ionization potential would be 2.4 volts, unless we make the improbable (see later) assumption that electrons colliding with an atom could not displace an electron from the 2 p ring.

Thus it is safe to conclude that any displacement of an electron from its orbit in the stable condition of the atom takes place from the 1.5 s ring. The question arises as to what type of displacements may occur in electronic-atomic impact. Inelastic collisions take place when the impacting electron has the energy eV where V is the ionization potential, this kinetic energy being just sufficient to account for the increase in total energy of the ionized atom. Another type of inelastic impact has been observed in which the colliding electron has the energy eV where V is the resonance potential,[2] this kinetic energy being just sufficient to account for the increase in total energy of the atom arising from a displacement of an electron from the 1.5 s ring to the 2 p ring. The displaced electron being then in an unstable orbit falls to the 1.5 s ring, giving up the quantum of energy received from the collision, eV, as a quantum of energy $h\nu$ of radiation of frequency ν, as is shown by the experiments described later. Thus inelastic impacts are known when the colliding electron has sufficient energy to eject an electron from the 1.5 s ring to infinity or to the 2 p rings. In the former case the electron returning to the atom causes the emission of various lines, and with many electrons in different ionized atoms returning by various paths we obtain the complicated line spectra in which the intensities of the lines represent to some degree the probabilities of each particular type of transition from orbit to orbit.

Suppose the colliding electron possessed just sufficient energy to eject an electron to some ring intermediate to ∞ and 2 p. Could the normal atom absorb the entire kinetic energy of the impacting electron? The only known series converging at 1.5 s is the principal series $1.5\,s - m\,p_{\frac{1}{2}}$. Hence it is extremely probable

[1] Phys. Rev., 13, p. 59: 1919.

[2] Foote, Rognley, and Mohler, see footnote 1.

that if a displaced electron falls into the 1.5 s orbit it comes from one of the p rings. Accordingly, it is reasonable to assume that in the original displacement from the 1.5 s ring the electron is ejected to some p ring. Thus inelastic impacts might occur when the colliding electron had fallen through any of the following potential differences, the kinetic energy being in each case equal to the increase in total energy of the atom corresponding to displacements to the 2 p, 3 p, ... to ∞ p rings.

Displacement from 1.5 s to m p_1

m	Volts
2	1.448
3	2.709
4	3.184
5	3.417
6	3.549
.	.
.	.
.	.
∞	3.877

The first and last of these values are readily observable, as above mentioned. That the values corresponding to $m=3$, 4, etc., have not been observed may be due to the fact that such displacements are very much less probable than the displacement corresponding to $m=2$ and the method of detection accordingly insufficiently sensitive. This is supported by the fact that the probability of a transition from the m p ring to the 1.5 s ring decreases as m increases, evidence for which lies in the relative intensities of the lines of any series. The displacement to the ∞ ring may take place in an infinite number of ways and hence is readily produced. The value 2.709 is nearly double the value 1.448 and accordingly might be mistaken for two successive collisions with different atoms, each resulting in a displacement to the 2 p_1 ring, the probability of which is quite high under ordinary experimental conditions.

Suppose that the inelastic impact resulted in a displacement to the 3 p ring. The electron may return to the 1.5 s ring directly, resulting in an emission of the line 1.5 $s-3$ p, or it might fall to the 3 d ring, giving the line 3 $d-3$ p, then to the 2 p ring, giving 2 $p-3$ d, and finally to the 1.5 s ring, giving 1.5 $s-2$ p, the total value of all the quanta being equal to the increase in total energy arising from the original displacement to the 3 p orbit. Other

modes of transition from ring to ring are possible. Hence, when a large number of atoms are considered, a certain group of spectral lines may result from a displacement of the type considered. The important point on the basis of Bohr's theory is that for the collision mentioned, lines resulting in displacements from rings beyond 3 p could not exist although the size of the quantum involved might be many times less. Thus an electronic impact of 2.7 volts could not excite the visually intense line λ 6973 ($2\ p_1 - 5\ d$), although the quantum involved requires but 1.8 volts. The energy (4.3×10^{-12} ergs) is sufficient to produce this line (2.9×10^{-12} ergs), but is not sufficient to displace the electron to the 5 d ring (5.1×10^{-12} ergs), a condition necessary for its excitation.

The above conception is in agreement with fluorescence phenomena observed in sodium vapor. Thus D light is absorbed by sodium vapor, and for each quantum absorbed an electron is displaced from the 1.5 s to the 2 p ring in an atom. The electron in falling back to the 1.5 s ring emits the D line ($1.5\ s - 2\ p$), which may be observed at right angles to the beam of incident radiation. Recently, Strutt[3] has found that the sodium line λ 3303 ($1.5\ s - 3\ p_{\frac{1}{2}}$) similarly stimulates both $1.5\ s - 3\ p_{\frac{1}{2}}$ and $1.5\ s - 2\ p_{\frac{1}{2}}$. Thus, after absorbing a quantum of frequency $1.5\ s - 3\ p_{\frac{1}{2}}$ an electron is displaced to the $3\ p_{\frac{1}{2}}$ orbit. In returning to equilibrium it may fall directly to the 1.5 s ring, in which case the line λ 3303 is emitted, or it may fall to the $2\ p_{\frac{1}{2}}$ ring and then to the 1.5 s ring, the second step involving an emission of the D lines. This leaves a quantum of frequency $2\ p_{\frac{1}{2}} - 3\ p_{\frac{1}{2}}$ (λ 7519) looked for, but not observed, by Strutt. However, this line represents a very improbable type of orbital transition, as is evidenced by the fact that the frequency is never observed in any sodium spectrum. A more probable method of falling from $3\ p_{\frac{1}{2}}$ to $2\ p_{\frac{1}{2}}$ is first to the 3 d ring and then to the 2 p ring, giving rise to the lines λ 8196, 8184, 9048, and 9085, or from the $3\ p_{\frac{1}{2}}$ ring to the 2.5 s ring and then to the $2\ p_{\frac{1}{2}}$ ring. In both cases the quantum relations are correct, and the lines are well known; but, lying in the infra-red, they would not have been observed by Strutt.

The fact that an atom can absorb radiation of frequency $1.5\ s - m\ p$ (absorption has been observed[4] for $m = 2$ to 60 in the case of sodium), thus resulting in displacement of an electron to the $m\ p$ ring, for each absorbing atom suggests that similar dis-

[3] Proc. Roy. Soc., 96, p. 282; 1919. [4] Wood and Fortrat, Astrophys. Jour., 43, p. 73; 1916.

placements may be produced by electronic collision. On the other hand, the failure to detect such displacements is not an argument against the Bohr theory. It is possible that the impacting electron must have the correct velocity as well as energy to produce any displacement at all. Thus, while the mass of an electron happens to be such that when its velocity is that obtained by falling through 1.45 or 3.88 volts, a collision with a cæsium atom is inelastic, resulting in a displacement of a bound electron to the 2 p_1 and ∞p rings, respectively, at other voltages such as 3.18, the velocity condition is not fulfilled. This assumption, as far as displacement from the 1.5 s ring is concerned, is, however, scarcely justifiable, since the range between 1.45 and 3.88 volts is small, and, since it appears that when the electron possesses 3.18 volts velocity 1.45 volts velocity may be absorbed at the impact, this going into increased total energy of the atom and the remainder into kinetic energy of the colliding electron. Also ionization is believed to occur from the 2 p_1 ring, since arcs may be operated below the ionization potential. At some stage, however, the mass of the colliding particle is effective, since the quantum relations do not appear to hold for low-speed positive or negative ions. Indeed, it is questionable whether a definite ionization potential for ions exists.

An electron of 1.45 volts velocity colliding with a cæsium atom ejects an electron from the 1.5 s ring to the 2 p_1 ring. In returning to equilibrium the atom emits the frequency 1.5 $s-2$ p_1. This radiation, however, is capable of being absorbed by a neighboring atom (resonance radiation effect), resulting in a displacement of an electron to the 2 p_1 ring. Hence in an electron tube there may be a building up of the number of electrons in the 2 p_1 ring, and, if all radiation emitted were absorbed, every atom might have electrons in this ring. Thus further collision with 1.45-volt electrons would result in an ejection of an electron to an extreme outer ring. A collision with a 2.4-volt electron would ionize the atom. Van der Bijl [5] has suggested as an explanation of low-voltage arcs operated below the ionization potential a theory of successive impact. The atom collides with an electron, causing a displacement of a bound electron to the 2 p_1 ring. Before it is able to return to the 1.5 s ring it collides again with a second electron, and the atom is ionized. The probability of a second collision under such conditions is, however, very small. The above

[5] Phys. Rev., 10, p. 546; 1917.

suggestion of the absorption of radiation which was first proposed by Compton [6] is a much more plausible explanation of arcs below the ionization potential. In fact, one must consider how ionization could take place otherwise than from the 2 p_1 ring. It must be accordingly necessary that only a small proportion of the radiation emitted when electrons fall from the 2 p_1 to 1.5 s ring is absorbed by the vapor. This is a reasonable assumption, for a large amount of radiation escapes from the tube. Thus with sodium at 2.2 volts the D lines are visibly intense and with cæsium at 1.5 volts, the infra-red lines λ 8943 and 8521 may be readily photographed with properly sensitized plates. The ionization of a vapor below its ionization potential is observed when the vapor and electron densities are high. This fact substantiates the present hypothesis, for more collisions occur, more radiation is emitted, and more is absorbed when the electron current and the vapor pressure are increased. Thus, as pointed out by Compton, in the operation of the mercury arc at 5 volts and high current density electrons are maintained in the 2 p_2 ring, partly by electronic impact, but mainly by absorption of radiation of the frequency 1.5 $s-2$ p_2, and a 5-volt impact is sufficient to ionize from the 2 p_2 ring.

An extension of this hypothesis leads to interesting conclusions in the case of absorption of radiation. The lines of the principal series of the alkali metals are all absorption lines, the energy absorbed increasing the total energy of the atom by a displacement of the electron from the 1.5 s ring to some p ring. If, however, the vapor is excited by electronic impact (or radiation) corresponding to $Ve=h\nu$, where $\nu=1.5\ s-2\ p$, electrons normally in the 1.5 s ring are driven to the 2 p ring and are no longer capable of absorbing 1.5 $s-m$ p, but rather series lines which converge at 2 p. Hence if the excitation is sufficient (i. e., electron current very dense) the principal series should show less absorption, and the first and second subordinate series should tend to become the prominent absorption lines.

It appears from the above that the general impression of the existence of a single-line spectrum at a certain low voltage, and an abrupt transition to the many-line spectrum as the voltage is increased to the ionization potential is scarcely justified a priori on any theoretical basis. If a mechanical theory is accepted, it is quite conceivable in spite of Stokes's law that the lines of higher

[6] K. Compton, Chicago Meeting Am. Phys. Soc., 1919, Phys. Rev.; 1920.

frequency may be excited by resonance when a fundamental line is produced. We have analogies to this effect in the relation between transverse and longitudinal vibrations of a rod, or in the "tripling" of the frequency of alternating current, etc. Thus instead of a single line, a single series might appear, the fundamental frequency and its harmonics—a view held by certain spectroscopists.

On the basis of the Bohr theory various groups of lines may appear as the excitation is increased. There is no experimental evidence on this question. In all previous work on single-line spectra, the observations would not have showed the presence of other lines had they existed. Thus the observed single-line spectrum of mercury is λ 2537, but the second line of the series λ 1436 might be present, and, lying in the extreme ultra-violet, it could not have been detected by the methods employed.

II. EXPERIMENTAL

The present work was undertaken with the object of obtaining information as to the existence of single-line spectra, single-

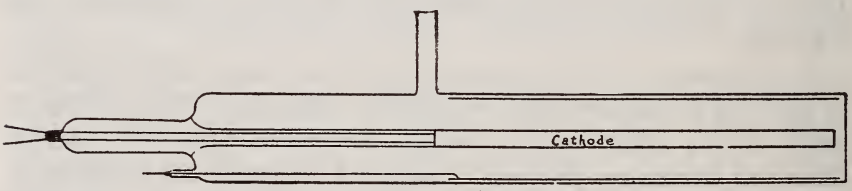

FIG. 2.—*Ionization tube*

series spectra, and group spectra. Cæsium appeared to be a desirable material, since all of its spectral lines, except certain combination lines in the far infra-red, may be photographed by properly sensitized plates. The apparatus is shown in Fig. 2. The ionization chamber consisted of a pyrex glass tube having an optically ground pyrex plate fused to one end, through which the arc was viewed. The anode was a nickel cylinder and the cathode a lime-coated platinum cylinder about 5 mm in diameter, heated by a small heating coil inside. The cathode was thus made an equipotential surface, and because of its large area the current was high (150 milliamperes at 6 volts), even though the temperature was maintained at 500° C. It is quite desirable to operate the cathode considerably below a red heat, as otherwise, on long exposure, stray reflection of the emitted light and heat may obscure the cæsium lines in the range λ 6500 to λ 9000.

All lead-wire seals were tungsten in Corning G 702 P glass. The ionization tube was evacuated and maintained at about 0.0001 mm of mercury-gas pressure, and heated to 200° C, thus giving a considerable vapor pressure. The radiation emitted near the anode where the electrons had gained their maximum velocity was photographed.

The spectrum photographs were made on Seed 23 plates stained with dicyanin. A few of the plates were sensitized with Hoechst dicyanin, but most of them were prepared with dicyanin made by the Bureau of Chemistry, Department of Agriculture, since these American dyes appear to be equal or superior to the German ones in photosensitizing action. The process of staining has been described several times, and it has been used almost continuously in spectroscopic investigations at the Bureau of Standards for the past four years. This experience in staining has made it possible to reproduce sensitized plates which are remarkably similar, so that very nearly the same spectral sensitivity is shown by different plates. This uniformity is of importance in the comparison of spectroscopic data obtained from different plates.

The spectrograph was made by Carl Zeiss and has a large flint prism of 10 cm base length and 60° angle. The collimator and camera lenses have 5 cm aperture and 26 cm focal length. On account of the very low intensity of the low-voltage arc a spectrograph with the highest attainable light efficiency is advantageous. About 30 lines with wave lengths from 4555 A to 8943 A were recorded with an exposure of 1 minute to the 6-volt cæsium arc. An exposure of 5 minutes showed additional lines and extended the spectrum from 3878 A to 9208 A. The exposures were much longer when the arc was operated at 3 volts or less. Most of these averaged about 15 hours, although in some cases exposures of 40 to 60 hours were employed.

The length of the spectrum on the photographic plate was about 40 mm between 3878 A and 9208 A, and the dispersion in this range was sufficient to separate all of the important doublets in the various spectral series even when a relatively large slit width (0.2 mm) was used.

Fig. 3 shows a photograph of several typical exposures at different voltages. Lower-voltage exposures were made, but were not suitable for reproduction, although the original negatives were measurable. It appears from visual observation that the first

doublet of the principal series alone appears below the applied potential of 2.4 volts; but this fact, as has been heretofore, with other elements, assumed conclusive, should not be accepted as proof of the existence of a single-line spectrum. If the plates possessed a constant sensitivity to light of various wave lengths, the line λ 8521 could be made to appear alone on very short exposure, even in a high-voltage arc, because in absolute energy it is the most intense line of the spectrum. The sensitivity of the plate, however, varies with the wave length, as shown by Fig. 4, so that on short exposure the line λ 6973 may appear alone. With ordinary blue sensitive plates the line λ 4555 is the most strongly reproduced. It is, however, possible to draw some conclusions by visually comparing various negatives. Thus, if the density of λ 8521 with a high-voltage arc is the same as that with a low-voltage arc and in the latter case no other lines appear, while in the former case the entire spectrum is shown, an argument is obtained for the single-line spectrum. However, it is desirable to eliminate the plate sensitivity from the data and reduce all measurements to the same scale of intensity of the lines in the arc. To do this the densities of all the lines photographed were carefully measured by a disappearing filament microphotometer.[7] This instrument is essentially the micropyrometer described by Burgess,[8] except that a microscope of higher power is employed. The photographic plate was mounted immediately below the objective of the microscope on a horizontal bed movable with a graduated screw and was illuminated beneath by an intense beam of light from a tungsten-ribbon lamp. Light transmitted by the portion of the plate, the image of which was adjacent to that of the photometer lamp filament, was matched against the filament brightness by adjusting the current through the lamp. The current readings are readily translated into measurements of photographic density, correcting, of course, for the "fog" of the gelatin films.

Several series of exposures from 2 to 300 seconds were made at different times on the 6-volt cæsium arc, and density measurements of the spectral lines showed that the dicyanin-stained plates have approximately the same development factor (gamma = 1.45) for all wave lengths from 4555 A to 8521 A. To calibrate the plates in terms of absolute intensity of the source, series of exposures of different durations were made by sighting on a black body, the temperature of which was measured by an optical pyrometer.

[7] This simple and effective instrument is described by the writers in a separate paper.

[8] Burgess, B. S. Sci. Paper No. 198.

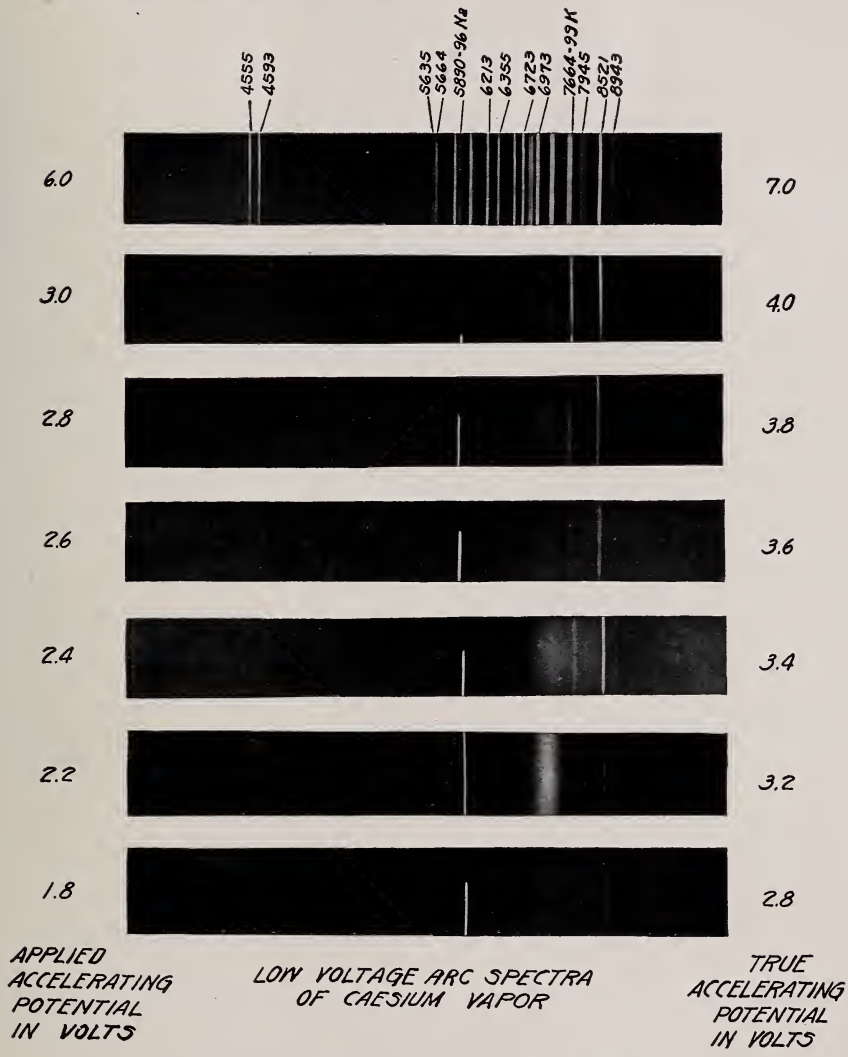

FIG. 3.—*Low voltage arc spectra of caesium vapor*

The *D* lines of sodium were superposed on each spectrum as fiducial marks. The densities of the plates for various wave lengths were measured with the microphotometer, and from the "characteristic curves" of the plates and the computed distribution of energy in the spectrum of the black body, the photographic density as a function of wave length was corrected for an equal energy distribution in the spectrum, a typical curve thus obtained being illustrated by Fig. 4. With the general characteristics of dicyanin-

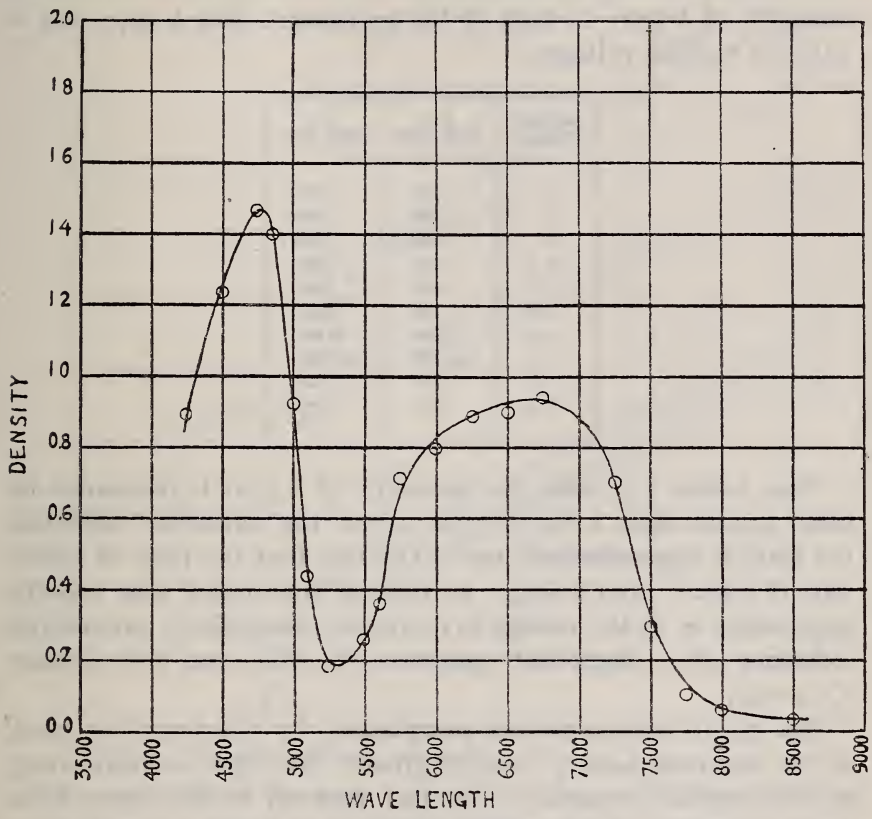

FIG. 4.—*Sensitivity of dicyanian stained plates to equal energy spectrum*

stained plates thus determined the relative absolute intensities of lines in the cæsium-arc spectra were obtained from their measured photographic densities and the durations of exposure. Since relatively long exposures were required to photograph the spectra of the low-intensity arcs, the reciprocity law of the photographic plate (density = function of intensity × time) was corrected[9] by giving the exposure time an exponent of 0.8.

[9] Schwarzschild, Photographische Correspondenz 1899, p. 109.

III. RESULTS

Fig. 5 shows the logarithms of the actual intensities of various lines emitted in the cæsium arc plotted against applied accelerating potential. At slightly below 3 volts the entire line spectrum appears, only a few of the lines of which are shown in the figure. It is noted that the intensity of the lines λ 8521 and λ 8943 persist at voltages below which the intensity of all other lines vanishes. This is more clearly illustrated by the following table of ratio of intensity of λ 8521 to that of the prominent lines λ 6973 and λ 4555 for various voltages.

Applied voltage	$\frac{J}{8521}\div\frac{J}{6973}$	$\frac{J}{8521}\div\frac{J}{4555}$
6	105	350
5	(130)	(400)
4	(200)	(600)
3	560	2100
2.8	1100	8300
2.6	620	3400
2.4	3600	10 500
2.2	>10 000	>10 000
1.8	≐∞	≐∞
1.5	≐∞	≐∞

Thus below 2.4 volts the intensity of λ 8521 is thousands of times greater than λ 6973, while above the ionization potential the ratio is approximately 100. The fact that the ratio of intensity of λ 8521 (and λ 8943) to that of any other line rapidly approaches ∞ as the voltage is decreased conclusively proves the existence of a single-line spectrum, in this case the doublet $1.5\ s-2p_{\frac{1}{2}}$.

The results are somewhat complicated by the fact that most of the electrons have a velocity greater than that corresponding to the applied potential. The fact that all of the series lines begin to appear at the applied potential of about 2.5 volts indicates the presence of ionization, which should normally occur at 3.9 volts. This is again shown by Fig. 6, which represents the current reaching the anode as a function of the applied accelerating potential. A marked break point, indicating ionization, occurs at 2.9 volts. This ionization might be explained on the assumption of ejection of electrons from the 2 *p* rings, which requires but 2.4 volts velocity; but such is not the case. If a 3-electrode tube is employed, it can be shown that most of the electrons possess an initial velocity of about 1 volt. Thus

Foote, Rognley, and Mohler [10] using a 3-electrode tube found the initial potential to be 1.3 volts in rubidium, and 1.0 volt in cæsium, and Tate and Foote [11] observed similarly high initial potentials in sodium and potassium. These high-velocity electrons are not produced photo-electrically, because they appear at accelerating voltages below which any radiation is excited. Thus in cæsium the first resonance collision occurs at about 0.5 volt applied potential and the second at about 2.0 volts, instead of 1.5

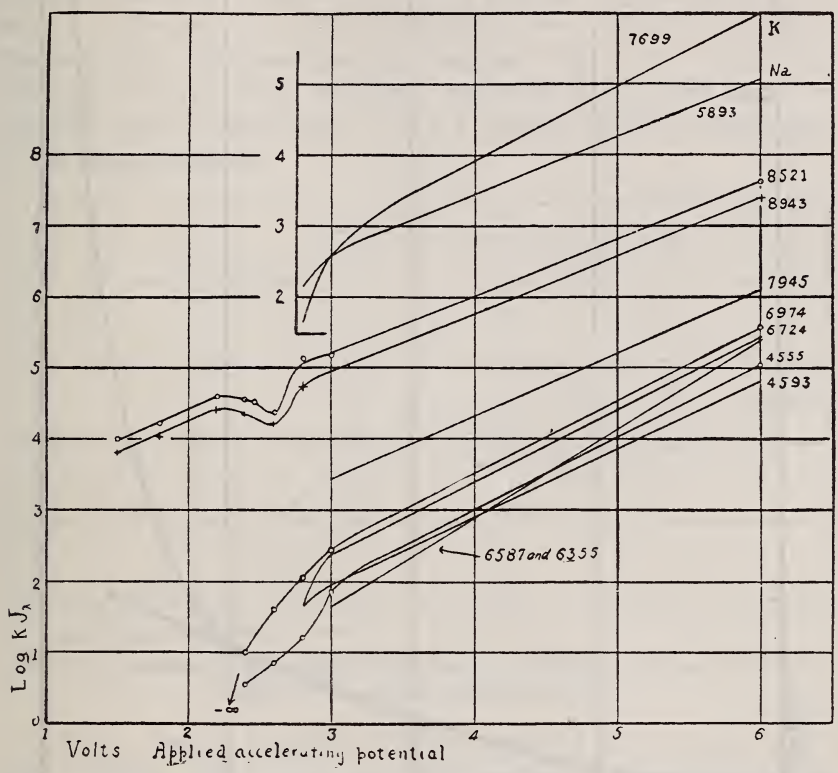

FIG. 5.—*Logarithm of intensity of various cæsium lines as a function of the applied exciting voltage*

volts and 3.0 volts. Neither can they be accounted for by velocity distribution due to temperature of the cathode. Thus the fractional number F of emitted electrons having a velocity greater by V_0 volts than the applied potential V, on the basis of the Maxwell distribution of velocities, is

$$F = erf\chi + \frac{2}{\sqrt{\pi}} \times e^{-\chi^2} \text{ where } \chi^2 = 11600V_0/T$$

[10] Loc. cit.

[11] Phil. Mag., 36, p. 64; 1918.

and T = absolute temperature of the cathode. In the present case but 3 electrons per thousand could have a velocity 0.5 volt greater than the applied voltage and but 5 per 10 000 000 a velocity 1.0 volt greater. The intensities of the lines are thousands of times too great at the applied potential 2.9 volts to be explained by the presence of 5 electrons per 10 000 000 with velocities sufficient to ionize. The high-speed electrons are,

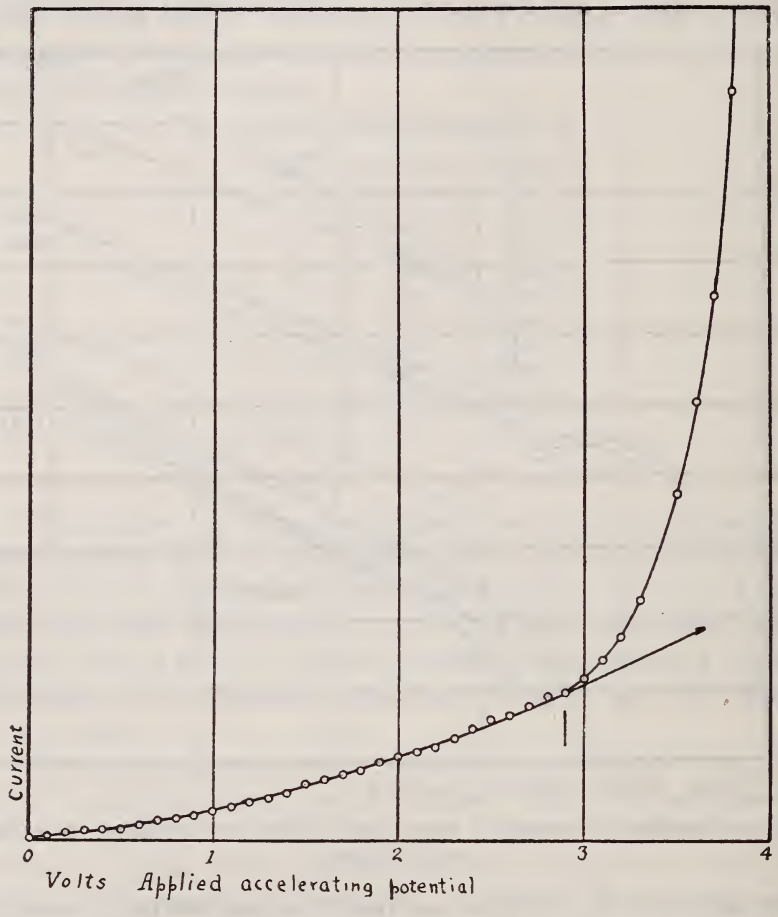

FIG. 6.—*Current reaching anode as a function of the applied accelerating voltage*

however, present. Possibly their initial velocities are due to contact potentials occasioned by the presence of an alkali metal. Accordingly, the curves of Fig. 5 should be corrected by adding to each abscissa the initial potential 1.0 volt, determined from the total current curve shown in Fig. 6.

It is noted that the intensity of λ 8521 and λ 8943 begins to decrease at 3.3 volts true potential, reaching a minimum at 3.6

volts. This would follow directly from Bohr's theory. Thus when the true accelerating voltage exceeds 1.45 volts the lines $1.5\,s-2\,p_{\frac{1}{2}}$ are excited by electronic impact and these lines continue to be produced until the ionization potential is reached. Above this latter voltage, however, electrons which at a slightly lower velocity would have given rise to $1.5\,s-2\,p_{\frac{1}{2}}$ now produce ionization and the complete series spectrum. Any line of the principal series, for which $m > 2$, is excited at a sacrifice in intensity of λ 8521 and λ 8943, since each line of this series requires that electrons fall from the $m\,p$ ring into the $1.5\,s$ ring. The subordinate series lines, however, converge at $2\,p$, and hence do not affect the intensity of $1.5\,s-2\,p$, which may be still excited at the same collision.

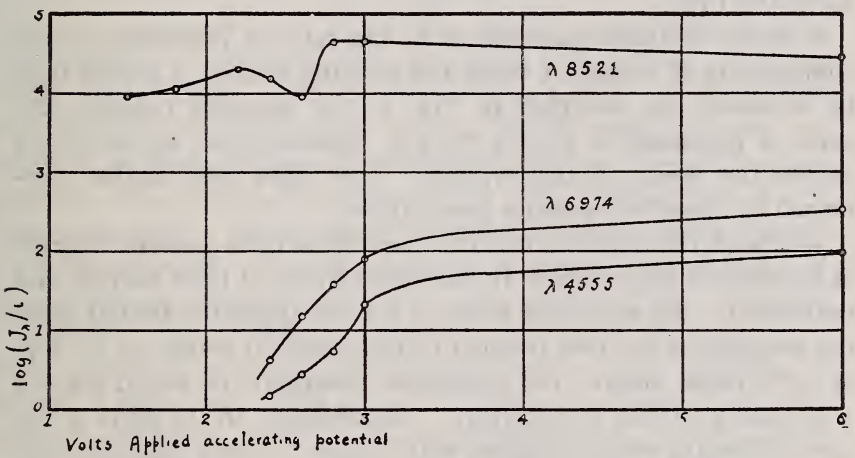

FIG. 7.—*Logarithm of intensity per unit number of electrons reaching anode as a function of the applied accelerating voltage*

In Fig. 7 we have plotted the logarithm of the intensity for λ 8521, λ 6973, and λ 4555 per unit number of electrons reaching the outer cylinder, as the accelerating voltage is increased. At higher voltages this ratio becomes a constant for each line in agreement with the work of Jolly,[12] who observed that in discharge through hydrogen "the radiation is proportional to the current density both for the whole spectrum and for any portion of it." This follows (approximately) directly from the quantum theory. Above a certain minimum voltage the number of electronic atomic collisions, and hence the number of quanta of any particular frequency produced is proportional to the number of electrons present. The existence of $1.5\,s-2\,p_{\frac{1}{2}}$ when the intensity of all

[12] Phil. Mag., 26, p. 801; 1913.

other lines has dropped to zero is well illustrated in this plot. The above law is not rigorously applicable in the present case, since some of the electrons reaching the anode have been produced by ionization and in general would not be able to accumulate sufficient velocity to cause radiation upon further collision.

An interesting phenomenon was observed in the operation of the cæsium arc at 120 volts. It was found that after once being started the arc operated with either electrode as cathode and that no rectification of alternating current was observable. This phenomenon is well known in certain types of mercury arc. With the outer cylinder as a cathode a quiet, dazzling glow discharge is obtained, while with the small, hot cathode the arc forms streams of brilliant discharge which flicker back and forth along the tube.

A much-discussed question as to the ratio of intensities of the components of a doublet when the exciting voltage is varied may be answered by referring to Fig. 5. In absolute measure the ratio of intensities λ 8521/λ 8943 is constant and equal to 1.5 within the errors of observation. This value was further confirmed by observations on a 120-volt arc.

Although the cæsium employed was made from cæsium chloride of supposedly high purity, it contained traces of both sodium and potassium. All exposures above 2.2 volts applied potential show the presence of the first doublet of the principal series $1.5\ s-2\ p_{\frac{1}{2}}$ of both these metals, the ionization potentials of which are 5.1 volts and 4.3 volts, respectively. Accordingly, in the light of the more extensive work described with cæsium, we may conclude that the doublet $1.5\ s-2\ p_{\frac{1}{2}}$ are the single-line spectra of sodium and potassium.

IV. SUMMARY

THEORETICAL

On the basis of several possible theories of atomic structure it is shown that the *normal* operation of an arc below ionization might result in the excitation of a single-line spectrum, a single-series spectrum, or a group spectrum consisting of certain lines of different series. This latter conclusion follows from an extension of Bohr's theory. Thus, if inelastic electronic-atomic impact occurred resulting in the ejection of an electron to the pth ring, the electron in returning to the nth ring, or equilibrium, may produce any combination of lines represented by interorbit transitions within this range, the single-line spectrum being a special case where $p=n+1$.

A simple explanation is offered of fluorescence phenomena in vapors of the alkali metals.

A mechanism of absorption of radiation is described and the theory proposed by K. Compton, that the ionization of an atom below the ionization potential may be explained by absorption of radiation arising in other atoms from electronic-atomic impact of insufficient energy to ionize, is further discussed. This hypothesis suggests that vapors of the alkali metals may be so stimulated that the first and second subordinate series lines, instead of the principal series, tend to become absorption lines.

EXPERIMENTAL

The cæsium spectrum was photographed for various accelerating voltages from λ 3878 to λ 9208 by use of dicyanin-stained plates. The sensitivity of the plates was investigated by density measurements of the spectrum of a black body having a known energy distribution. The general characteristics of the plates were determined and all lines of the cæsium spectrum were reduced to an absolute scale of intensity by means of density measurements made with a microphotometer and consideration of the plate sensitivity. No evidence of group or single-series spectra could be obtained. Thus the ratio of intensities of the first and second lines of the principal series, both of which should appear in a single-series spectrum, or above 2.7 volts in a group spectrum, rapidly approaches infinity as the accelerating potential in the arc is decreased. This ratio is 350 in a 7-volt arc, 2100 at 4 volts, 10 500 at 3.4 volts, and as near infinity as can be measured at 2.8 volts. Similarly, the intensity ratio of either $1.5\,s-2\,p_1$ or $1.5\,s-2\,p_2$ to any other line approaches infinity at low voltage, proving for the first time the existence of a single-line spectrum rather than a single-series or group spectrum; in the case of cæsium the doublet λ 8521 and λ 8943.

The doublet $1.5\,s-2\,p_{\frac{1}{2}}$ is alone produced under excitation of 1.5 to 3.9 volts accelerating field. The intensity of both of these lines gradually increases approximately proportional to the total number of electrons reaching the anode until the ionization potential is reached. At this point a pronounced decrease in intensity of these two lines occurs, amounting to the factor one-third.

This decrease takes place at the voltage at which the complete-line spectrum is produced and is readily explainable on the basis of Bohr's theory; in fact it affords a strong argument for this

theory. Thus the lines $1.5\ s-2\ p_{\frac{1}{2}}$ are the result of inelastic collision with electrons having velocities between 1.45 and 3.9 volts, but as the latter voltage is exceeded electrons, which at a slightly lower velocity would have given rise to $1.5\ s-2\ p_{\frac{1}{2}}$, now produce the complete-series spectrum; and any line of the series $1.5\ s-m\ p_{\frac{1}{2}}$ where $m>2$ is necessarily excited at the sacrifice of $1.5\ s-2\ p_{\frac{1}{2}}$.

Above a certain voltage the intensity of any line per unit number of electrons reaching the anode attains a saturation value in agreement with the quantum hypothesis, which requires that the number of quanta radiated be proportional to the number of collisions, and hence (approximately) to the number of electrons present.

Curves are given showing the relative intensities of the prominent cæsium lines at various voltages. The ratio of intensities of the components of the first doublet of the principal series λ 8521/λ 8943 is constant and equal to 1.5 from 1.5 volts to 120 volts.

The cæsium arc of the type employed does not rectify alternating current of 120 volts.

Sodium and potassium occurring as an impurity of the cæsium similarly exhibited the single-line or doublet spectrum $1.5\ s-2\ p_{\frac{1}{2}}$ below their respective ionization potentials.

Only two types of inelastic impact between electrons and atoms of the alkali-metal vapors occur, at potentials known as the resonance and ionization potentials and given by the quantum relation $h\nu=eV$ where $\nu=1.5\ s-2\ p_1$ and $\nu=1.5\ s$, respectively.

WASHINGTON, January 14, 1920.