PHOTOMETRIC STUDY OF THE APPEARANCE OF SPECTRAL LINES IN A CONDENSED SPARK

By H. V. Knorr
Mendenhall Laboratory of Physics, Ohio State University
(Received May 4, 1931)

Abstract

The time interval between the time of appearance in a condensed spark discharge of the arc lines 4678A, 4722A, 4811A ($2^3P_{012}-2^3S_1$) of zinc, 4680A, 4800A, 5086A ($2^3P_{012}-2^3S_1$) of cadmium, the air lines 4347A, 4631A and 5001A was measured visually, using the Kerr cell method developed by Beams. A photographic method was developed whereby it was possible to determine from photometric measurements the variation of the intensity of an individual line with the time after the beginning of the spark. The time of first appearance, or zero intensity, is inferred from the extrapolation of the curves showing the intensity as a function of the time. The arc lines of zinc appear simultaneously. The arc lines of cadmium appear simultaneously but definitely earlier than the zinc arc lines. The air lines appear simultaneously but earlier than the arc lines. The spark lines appear simultaneously but earlier than the arc lines and later than the air lines of the respective elements. The results of the visual and photographic methods do not agree. Neither method gives information that in the case of zinc or cadmium, an electron remains in the 2^3S_1 state for a longer time before dropping to the 2^3P_0 state than before dropping to the 2^3P_1 or the 2^3P_2 state.

Introduction

In 1925 Beams and Brown,[1] making use of a modified form of the electro-optical shutter of Abraham and Lemoine,[2] measured the time intervals between the appearance of spectral lines in the spectra of condensed discharges. This early work indicated that in the elements examined, the spark lines appeared before the arc lines. Since the appearance of this first paper, several experimenters[3,4] have extended the work to other elements. In the elements that were examined in common by various investigators the numerical values for the time difference between the appearance of individual lines did not agree and in some cases the observed order was different. In the case of multiplets, Beams found different lines of the same multiplet appeared at different times, while Locher found that members of a given multiplet appeared simultaneously within the limits of error of the experiment in all cases examined except in the case of the arc triplet of zinc.

The actual existence of these time lags in the appearance of spectral lines has since been questioned by Gaviola.[5] He believes that the basic assumptions made by the experimenters, namely, that the Kerr cell discharges in-

[1] Beams and Brown, J.O.S.A. & R.S.I. **11,** 11 (1925).
[2] Abraham and Lemoine, Comptes Rendus **130,** 245 (1900).
[3] J. W. Beams, Phys. Rev. **28,** 475 (1926).
[4] Gordon Locher, J.O.S.A. & R.S.I. **17,** 91 (1928).
[5] Gaviola, Phys. Rev. **33,** 1023 (1929).

stantaneously a certain time after the beginning of the spark, that oscillations, if present, have no appreciable effect on the operation of the shutter, and that the capacity in parallel with the spark gap does not modify the time at which the Kerr cell discharges, are incorrect and measurements based on them unreliable.

The purpose of this investigation was to make a comparison of the results obtained by the use of a visual method similar to that employed by other experimenters[3,4] and the results obtained by use of a photographic method, in which the order of appearance of the spectral lines is inferred from the observations on the way in which the intensity of the individual spectral line

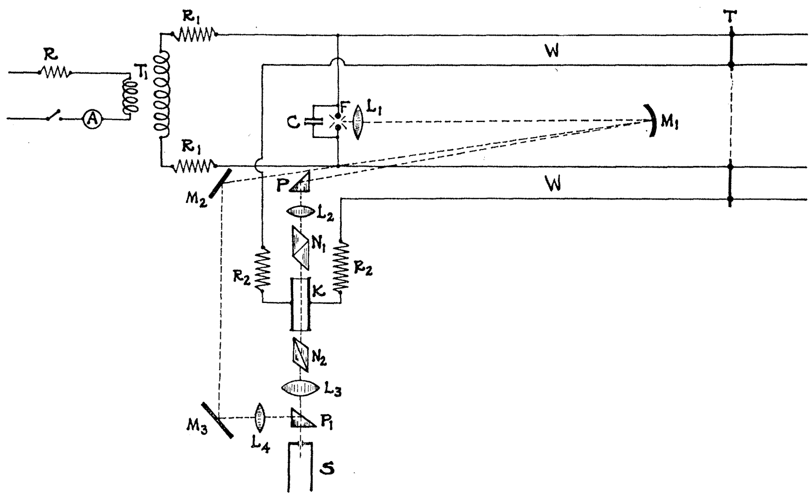

Fig. 1. Diagram of apparatus.

varies with time. By use of the latter method it is possible to eliminate the sensitivity of the eye which is a controlling factor in the visual method. In order that the results might have a possible interpretation as atomic phenomena, the spectral lines, 4678 $2^3P_0-2^3S_1$, 4800 $2^3P_1-2^3S_1$, 5086 $2^3P_2-2^3S_1$, of cadmium and 4680 $2^3P_0-2^3S_1$, 4722 $2^3P_1-2^3S_1$, 4811 $2^3P_2-2^3S_1$, of zinc were selected for the major part of this investigation. In the above triplets the transitions are from the same upper level to different lower levels, so the difference in the length of time that an electron remains in the 2^3S_1 state before the transition takes place to the 2^3P_0, the 2^3P_1 or the 2^3P_2 state could be measured. In addition to the above lines the spark doublet 5337 $3^2D_{3/2}-4^2F_{5/2}$, 5378 $3^2D_{5/2}-4^2F_{7/2}$ of cadmium, the spark doublet 4912 $3^2D_{3/2}-4^2F_{5/2}$, 4924 $3^2D_{5/2}-4^2F_{7/2}$ of zinc and the air lines which were excited when the discharge takes place between metallic electrodes in air at atmospheric pressure, were investigated.

Apparatus and Experimental Methods

Fig. 1 gives a diagrammatic representation of the apparatus used in the present experiment. It is essentially the same as that used by previous investigators. A fixed light path of 14.69 meters was used. A spark gap F with a capacity in parallel was connected across a source of high voltage T_1. The electro-optical shutter consisting of the two Nicol prisms N_1 and N_2 and the Kerr cell K, was placed between the spark gap and the spectrograph. The source of high voltage was a 25,000 volt 1 KW transformer. Electrodes of various shapes were tried in the spark gap, the shape finally selected being that of the frustrum of a cone, so that the discharge was actually taking place between two circular parallel faces. This type of electrode gave very steady spark conditions over quite long periods of time. The Kerr cell consisted of two parallel brass plates 12 cm long, 1 cm wide and separated at a distance of 3 mm, immersed in carbon disulphide which had been carefully purified. The shutter ordinarily was closed except when sufficient potential was applied to the Kerr cell, then the liquid became doubly refracting and light could pass it.

The circuit FC in Fig. 1 contains the condenser C, a certain amount of inductance in the lead wires, and the spark gap F, hence the discharge of the condenser C through the gap will be oscillatory. The circuit KF contains the Kerr cell, the trolley wires W and the spark gap F, this circuit being directly connected to the circuit FC, so oscillations are undoubtedly present in it. These oscillations if of sufficient amplitude, would reopen the shutter after having closed when the original voltage had fallen to so low a value as to make the shutter inoperative. The discharge of the Kerr cell will not be as sudden as was originally supposed, but its rate of discharge will be determined somewhat from the superposition of the oscillations in the two circuits. The oscillations can be critically damped by insertion of the resistance R_1, this reducing the rate of fall of voltage on the Kerr cell. Nevertheless it is possible to damp sufficiently these oscillations without delaying the closing time of the shutter appreciably, since it is well established that the relative difference in phase in the components of the ray vibrating parallel and perpendicular to the electric field is given by

$$\theta = 2\pi BlE^2$$

where B is the Kerr constant and θ the phase difference. Now the amount of light passing the prism N_2 at any given instant will be

$$I = A \sin^2 \theta/2 = A \sin^2 (\pi BlE^2).$$

Since the intensity of the light passing the shutter is proportional to the fourth power of the voltage, it is thus possible to damp sufficiently these oscillations and yet not delay the closing time of the shutter. The value of R_2 was found experimentally using a method employed by Lawrence,[6] that of observing the smallest distances of migration of the metallic vapor from the electrodes. The value of the damping resistance thus found was 2800 ohms (1400 ohms being placed in each lead from the spark gap to the Kerr cell). The effect of this damping resistance was quite evident, for when values of several hundred ohms less than 2800 ohms were used, oscillations were pres-

[6] Lawrence and Dunnington, Phys. Rev. **35**, 396 (1930).

ent, when values of several hundred ohms greater than 2800 ohms were used, a noticeable decrease in the rate of closing of the shutter was observed.

In Fig. 1 the light from the spark gap was rendered approximately parallel by the lens L_1 and was reflected from the concave mirror M_1, whose focal length was 7 meters, this converging beam was reflected by the right angle prism P through the lens L_2, the Nicol prism N_1 and focused between the plates of the Kerr cell. The lens L_3 focused the beam after passing through the Nicol prism N_2 on the slit of a constant deviation Gaertner spectrometer, so that the length of the spark was parallel to the slit. A number of diaphragms were placed along the light path and at each end of the Kerr cell so that only light which passed through the Kerr cell between the plates was focused on the slit.

An important modification in the optical path was the introduction of the auxiliary light path $PM_2M_3L_4P_1$, in order to adapt the apparatus to the photographic method. The part of the converging beam which passed the prism P was reflected by the plane mirrors M_2 and M_3 and the right angle prism P_1 and was focused on the slit of the spectrograph by means of the lens L_4. It was thus possible to have two spectra formed on the plate one directly above the other, the one formed by light which had passed through the Kerr cell and the other formed from the light which came directly from the spark gap. This modification was of utmost importance in the intensity measurements for it was thus possible to determine whether or not the spark conditions had changed appreciably during the time that was necessary to obtain a complete set of exposures.

Visual method. In the visual method in which a fixed light path was used, the time of closing the electro-optical shutter was regulated by changing the effective lengths of the four parallel wires which connect the spark gap with the Kerr cell, by sliding the trolley T along them by means of a string passing over a rather complicated pulley system and operated from the observer's position. When the trolley T is adjusted so that the effective length of wire path is as long as possible the intensity of the line under investigation is at a maximum for this particular time of closing of the shutter. If the position of the trolley is now adjusted so that the length of the wire path is decreased, finally a position is reached where the spectral line is no longer visible; this position of the trolley is noted. In a similar manner when the direction of motion of the trolley is reversed, a point of first appearance of the spectral line is located, which will differ slightly from the first position. The mean of the two positions is taken as the position of first appearance of the line, where the appearance of the line as used here means the position at which the line has become visible through the observing apparatus. The fall of potential produced by the passage of the spark is propagated along the wire to the Kerr cell at approximately the velocity of light,[7] so that the difference between the times of appearance of two lines is approximately the difference between the lengths of wire as determined above, divided by the velocity of light.

[7] Fred Allison, Phys. Rev. **30**, 66 (1927).

Photographic method. In the photographic method the observing telescope was replaced by a camera attachment converting the spectrometer into a spectrograph. The optical path was modified as previously described. The exposures on the plate were obtained by setting the trolley at a definite position and taking an exposure, then moving the trolley a known distance and taking a second exposure, and so on until five or more exposures had been obtained on each plate. Since the lengths of trolley wire between the spark gap and the Kerr cell correspond to lengths of time after the break down of the

TABLE I. *Zinc, cadmium and nitrogen.*

The nitrogen lines were obtained by a discharge between zinc electrodes in air. The zinc and cadmium lines were obtained from discharges between electrodes made from the chemically pure metals.

Element	Wave-length	Classification	Interval $\times 10^8$ sec.	Limit of error $\times 10^8$ sec.
Zn	4912	$3^2D_{1\frac{1}{2}}-4^2F_{2\frac{1}{2}}$		
	&			
Zn	4924	$3^2D_{2\frac{1}{2}}-4^2F_{3\frac{1}{2}}$		
			0.5	.06
Zn	4680	$2^3P_0-2^3S_1$		
			1.14	.04
Zn	4722	$2^3P_1-2^3S_1$		
			0.75	.04
Zn	4811	$2^3P_2-2^3S_1$		
Cd	5337	$3^2D_{1\frac{1}{2}}-4^2F_{2\frac{1}{2}}$		
	&			
Cd	5378	$3^2D_{2\frac{1}{2}}-4^2F_{3\frac{1}{2}}$		
			0.43	.05
Cd	5086	$2^3P_2-2^3S_1$		
			0.97	.12
Cd	4800	$2^3P_1-2^3S_1$		
			0.37	.08
Cd	4678	$2^3P_0-2^3S_1$		
N_2	5001	$1^3D_1'-1^3F_3'$		
	5005	$1^3D_3'-1^3F_4'$		
	5007	$1^3S_1'-1^3P_2'''$		
	5011	$1^3P_1'-1^3S_1'$		
			1.20	.15
N_2	4631	$1^3P_2'-2^3P_2$		
	&			
	4643	$1^3P_2'-2^3P_1$		
			1.92	.08
N_2	5676	$1^3P_0'-1^3D_1'$		
	&			
	5680	$1^3P_2'-1^3D_3'$		

gap, the position of the trolley can be plotted against the intensity of the spectral line and a curve obtained which will show how the intensity of an individual line varies with time. In the present experiment it was possible to obtain spectrograms of the light from the spark beginning at 3.9×10^{-11} seconds after the beginning of the spark to 1.4×10^{-7} seconds after the beginning of the spark, the range being limited by the lengths of wire in the set-up.

Each plate was carefully calibrated by the use of neutral screens.[8] The calibration curve was obtained by plotting the logarithm of the intensity of the light transmitted by these screens against the reciprocal of the photographic density upon the plate. The reciprocal of the density (the logarithm of the transmission of the plate) was determined from the microphotometer record which was secured from the spectrogram. A Moll microphotometer which records automatically was used. From the measured transmission of the metallic arc and spark lines and the air lines to be investigated, the intensity of the individual lines could be read directly from the calibration curves in arbitrary units.

Results

Results by the visual method. Table I contains the data obtained on the spectral lines which were examined in this experiment. In the case of zinc the order of appearance of the lines obtained in this experiment was the same as that reported by Beams.[3] The magnitude obtained for the interval between the first appearance of the spark lines 4912A, 4924A and the arc line 4680A is thirty times smaller than the value obtained by Beams. In cadmium the results for these corresponding lines differ by about the same amount, that is for the interval between the appearance of the spark lines 5337A, 5378A and the first arc line. However the order is not the same, for in this experiment 5086A was observed before 4800A, while Beams observed them in the reverse order. The time intervals between the appearance of the respective arc lines as measured by Beams show somewhat the same magnitude as those determined in this experiment, but the results are still far from agreement. Locher obtained no differences in the times of appearance of the cadmium arc lines.

Results by the photographic method. The data obtained for the arc triplet of zinc 4680A, 4722A, 4811A are plotted in Fig. 2. The intensity which is plotted as the ordinate is expressed in arbitrary units. The lengths of trolley wire, plotted as abscissa, are measured from an arbitrary reference point which corresponds to a time 5×10^{-11} sec., after the beginning of the spark. When the intensity curves for these lines are extrapolated backward they all intersect at a point on the time axis corresponding to a time 1.2×10^{-8} sec., after the beginning of the spark, indicating that the members of this arc triplet appear at the same time. Fig. 3 shows the data on the unresolved air lines 5001A, 5005A, 5007A and 5011A, 4631A, 4347A which were excited when the discharge occurred between zinc electrodes in air at atmospheric pressure. Here as in the case of the metallic arc lines of zinc, when the intensity curve for each of these lines is extrapolated backward to zero intensity, these curves meet at approximately the same point, corresponding to a time 5×10^{-11} sec. after the beginning of the spark. This would indicate that these lines appeared simultaneously, but at a time 1.19×10^{-8} sec. earlier than the metallic arc lines of zinc.

[8] G. R. Harrison, J.O.S.A. & R.S.I. **18,** 492 (1929).

Fig. 4 shows the curves plotted from the data obtained for the arc triplet of cadmium 4678A, 4800A, 5086A. The intensity curves meet at approximately the same point corresponding to a time 0.5×10^{-8} sec., after the beginning of the spark when extrapolated backward to zero intensity, indicating again that the members of this arc triplet all appear at the same time. The time of appearance of the cadmium triplet is 0.7×10^{-8} sec., earlier than the zinc triplet. Fig. 5 shows the data on the air lines 5001A, 5005A, 5007A, 5011A, 4631A, 4347A, which are excited when the discharge takes place between cadmium electrodes in air. When the intensity curve for each of these air lines is extrapolated backward to zero intensity these curves intersect at a point corresponding to the time 5×10^{-11} sec., after the beginning of the spark, which is the same as that obtained for these same air lines which were

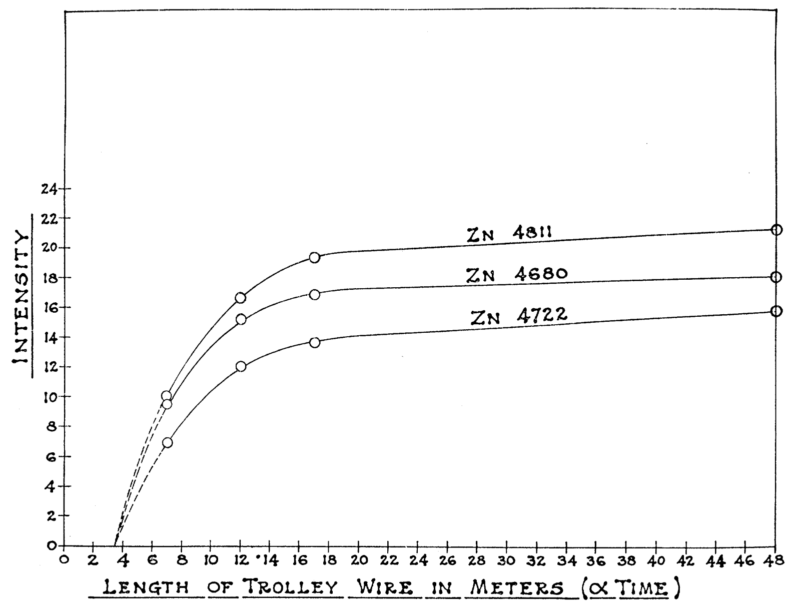

Fig. 2. Intensity of zinc arc triplet ($2^3P_{012}-2^3S_1$).

excited in the zinc spark. This indicates that these air lines just as in the case of zinc all appear at the same time.

In the upper part of Fig. 6 are plotted the data obtained for the unresolved zinc spark doublet 4912A and 4924A, and in the lower part are plotted the data obtained for the cadmium spark doublet 5337A and 5378A. The unresolved zinc doublet extrapolates backward to a point corresponding to 0.5×10^{-8} sec., after the beginning of the spark. The intensity curves for each of the lines of the cadmium doublet, when extrapolated to zero intensity, meet at a point corresponding to a time 0.32×10^{-8} sec., after the beginning of the spark, indicating that each of the members of this spark doublet appeared at the same time. The time of zero intensity or the time of first appearance of the spark lines is earlier than the arc lines of the same element, but is later than the air lines as shown in Figs. 2, 3, 4, and 5.

Discussion of Results

The photographic method in the case of the arc triplet of zinc 4680A, 4722A and 4811A, shows that all of these lines appear at the same time. The visual method when applied to this same triplet gives differences between the times of appearance of these same lines. Likewise in the case of the arc triplet of cadmium 4678A, 4800A and 5086A the photographic method gives the same time of appearance for each of these lines, but the visual method gives different times for each line, although the results of different observers using the visual method are not in agreement.

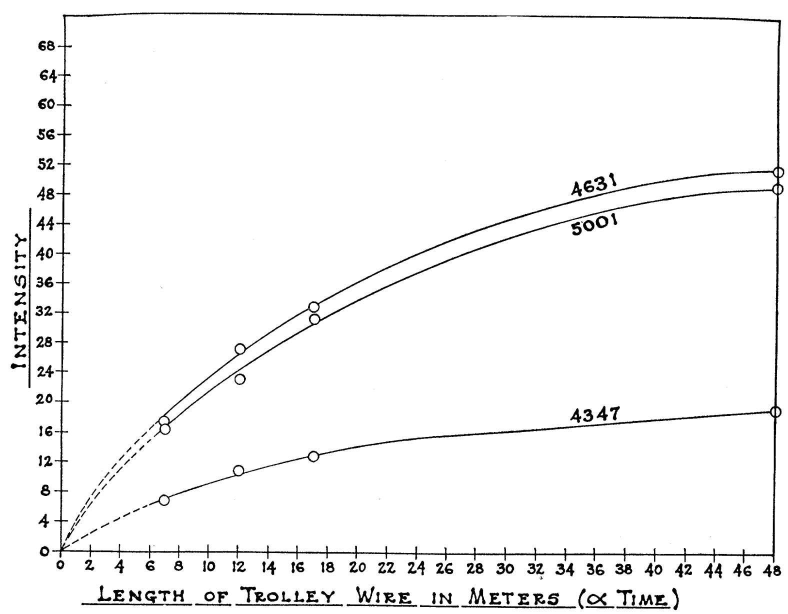

Fig. 3. Intensity of the air lines 5001A, 4631A, and 4347A with zinc spark gap.

The photographic method shows that the air lines 5001A, 5005A, 5007A, and 5011A, 4631A, 4347A whether excited in a zinc or cadmium spark, all appear at the same time, but at a time definitely earlier than the metallic arc lines of the respective element. The visual method on the other hand gives different times of appearance for the individual air lines and it also indicates that the air lines appear before the arc lines in the case of zinc and cadmium. Since in this case the observations were made on groups of lines rather than individual lines, the results are not as convincing as in the case where the observations are made on separate lines.

The photographic method shows that the members of the spark doublet of cadmium 5337A and 5378A appear at the same time and definitely earlier than the metallic arc lines of cadmium, but later than the air lines in the cadmium spark. The visual method gave no information on the separate spark lines as it was impossible to resolve them, so the observations were made probably on both lines, the times of appearance being earlier, however, than the arc lines. The result, indicating that the spark lines appeared before the arc lines, is the same for each method. The zinc doublet 4912A and 4924A was unresolved in both the photographic and visual methods so that the data obtained in each case are not satisfactory. However each method shows that this unresolved zinc doublet appears before the zinc arc triplet, hence again the two methods lead to the same result.

There is an evident disagreement between the results obtained by the visual method and those obtained by the photographic method. This diver-

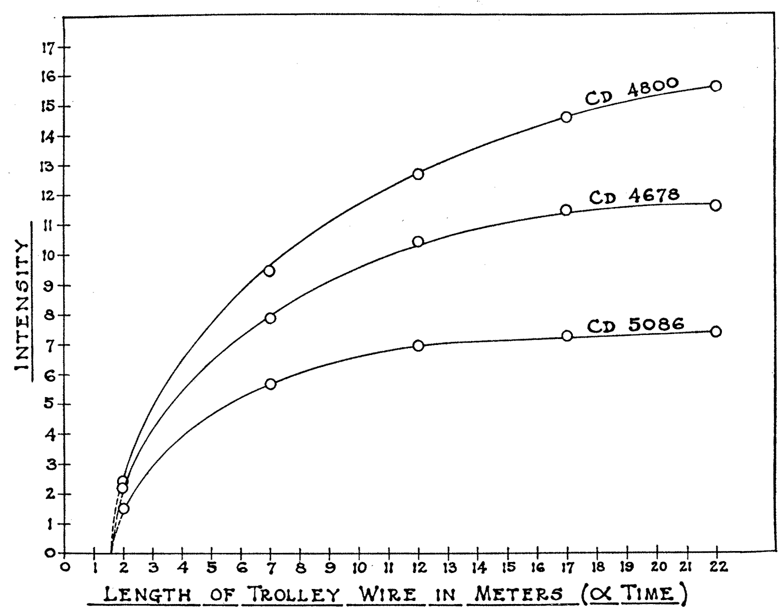

Fig. 4. Intensity of the cadmium arc triplet $(2^3P_{012}-2^3S_1)$.

gence of results is to be expected from the fact that the human eye is not equally sensitive to light of different colors, whereas the photographic plate when properly calibrated should give results on relative intensities which are independent of the sensitivity of the plate for light of different wave-lengths. Hence the zero of intensity inferred from the measurements on the photographic plate would be different from the threshold of visibility detected by the human eye. In reality what one does in the visual method is to observe the line at some intensity considerably above the zero intensity. Examination of the curves, showing the intensity as a function of the time after beginning of the spark, shows that the times when the different lines have the same intensity is variable. The critical intensity which the eye could first detect would be influenced by the sensitivity of the eye for the particular wave-length. The lines which were examined were located in a region of the spectrum where the sensitivity of the human eye changes quite rapidly with the wavelength. It would be impossible to extrapolate the intensity curves shown in Figs. 2, 3, 4, 5 and 6 in a reasonable manner and obtain values for the relative differences in the times of appearance that were obtained visually. The calibration of the photographic plate made the results obtained by the photographic method independent of the sensitivity of the plate for different colors. The fact that the air lines appeared before the spark and arc lines of the respective elements is probably a result of the natural sequence of events in breakdown of the spark gap. One might suppose as Gaviola[5] suggested, that the discharge was initiated by ionizing the air between the electrodes. This was followed by evaporation of the metal from the electrodes which was then ionized and excited by collisons. This observed difference between the

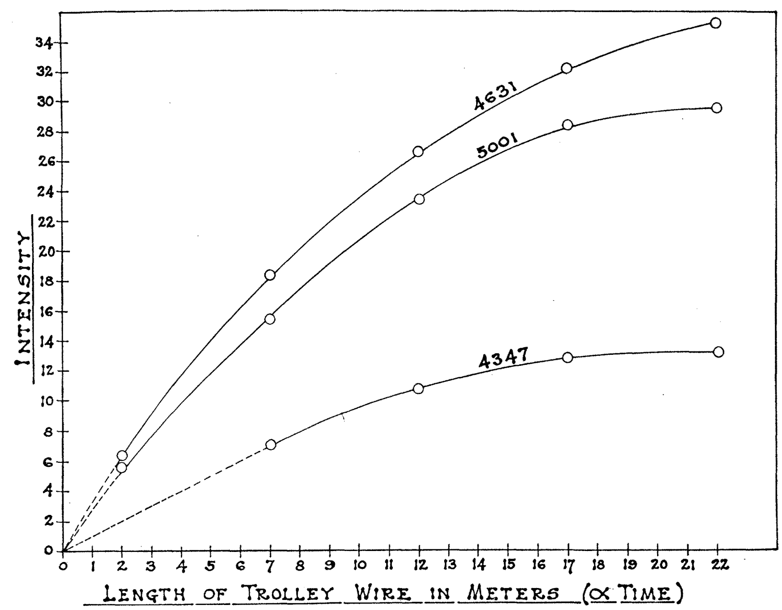

Fig. 5. Intensity of air lines 5001A, 4631A, and 4347A with cadmium spark gap.

times of first appearance of the air lines in the zinc and cadmium spark and the metallic arc lines of the same elements may be explained as a characteristic of the spark discharge. Hence if the results of the photographic method are accepted, the data obtained in this type of experiment give no evidence that an electron in the 2^3S_1 state of zinc or cadmium remains there a longer time before the transition takes place to the 2^3P_0 state, than to the 2^3P_1 or the 2^3P_2 state.

Conclusions

1. The results obtained by the visual and photographic methods are not in agreement.

2. The results obtained by the photographic method indicate that the members of the arc triplet of zinc appear simultaneously. They also indicate

that the members of this same triplet of cadmium appear simultaneously but not at the same time as the members of the arc triplet of zinc. These results therefore seem to verify Gaviola's contention that the apparent time difference between the appearance of spectral lines in such condensed discharges is not an atomic phenomenon.

3. The differences in times of appearance between the air lines which are excited in the spark gap, the spark lines of the element and the arc lines of

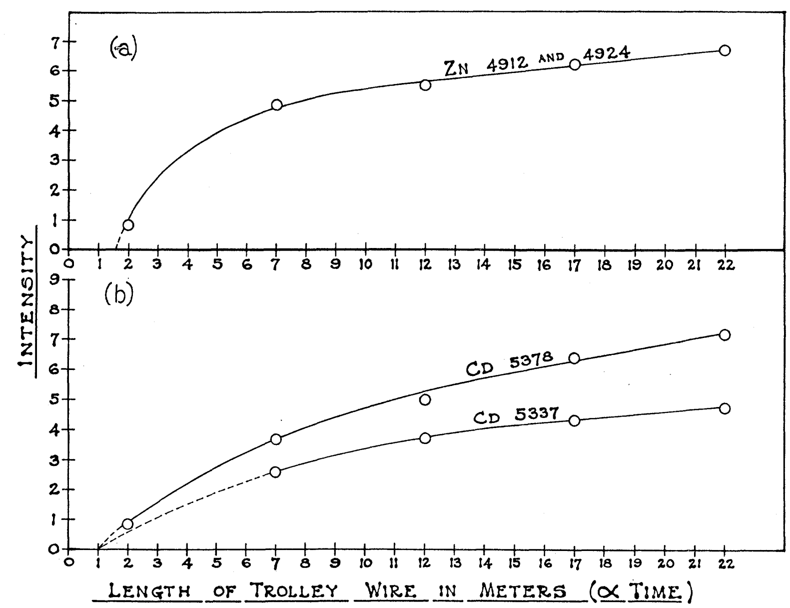

Fig. 6. (a) Intensity of unresolved zinc doublet $(3^2D_{3/2}-4^2F_{5/2})$ and $(3^2D_{5/2}-4^2F_{7/2})$.
(b) Intensity of cadmium doublet $(3^2D_{3/2}-4^2F_{5/2})$ and $(3^2D_{5/2}-4^2F_{7/2})$.

the same element, can probably be attributed to the way in which the discharge is formed in the spark gap, i.e. the manner in which the molecules of air or vapor of the element begin to be ionized.

The writer wishes at this time to express his appreciation of the constant help and encouragement he has received from Professor Alpheus W. Smith under whose direction this work was carried out and of the valuable suggestions and criticisms received from Dr. M. L. Pool during the course of this work.