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A METHOD FOR THE MEASUREMENT OF TIME INTERVALS OF THE ORDER OF MAGNITUDE OF 10^{-8} SECONDS AND ITS APPLICATION (1) TO THE MEASUREMENT OF THE TIME INTERVAL BETWEEN EXCITATION AND EMISSION IN FLUORESCENT SOLUTIONS; (2) TO THE DETERMINATION OF THE RELATIVE TIMES OF FIRST APPEARANCE OF SPECTRUM LINES.

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A METHOD FOR THE MEASUREMENT OF TIME INTERVALS OF THE ORDER OF MAGNITUDE OF 10^{-8} SECONDS AND ITS APPLICATION (1) TO THE MEASUREMENT OF THE TIME INTERVAL BETWEEN EXCITATION AND EMISSION IN FLUORESCENT SOLUTIONS; (2) TO THE DETERMINATION OF THE RELATIVE TIMES OF FIRST APPEARANCE OF SPECTRUM LINES.

HISTORY

The first accurate method for the measurement of short time intervals was used by Galileo[1] about 1638 in his investigations of the laws of falling bodies. He attached a small spout to the bottom of a water pail and caught the water escaping during the time the body traveled a certain distance; from the weight of the water he could calculate the time interval. Wheatstone[2] in 1834, Schenk[3] in 1901, and Milner[4] in 1909 determined the duration of the electric spark by the use of rotating mirrors. This idea was used by several investigators in the determination of the velocity of light, and was probably developed to its highest degree of perfection by Michelson[5] in 1924. In order to measure the time a phosphorescent substance continues to emit light after the exciting energy is cut off, Becquerel[6] invented his well-known phosphoroscope, by means of which

he could observe the substance one thousandth of a second after its illumination. Another method by which the time between excitation and fluorescent emission can be measured was applied by Wood[7] to the cases of mercury and sodium vapors. A unidirectional stream of say mercury vapor issuing from a properly designed nozzle is illuminated by a diaphragmed beam of radiation of wave-length λ2537. This same wave-length λ2537 is radiated by the moving vapor at a point in the stream displaced in the direction of the motion of the vapor. Then since the velocity of the vapor in the stream is known, the displacement gives a measure of the time between excitation and emission. Intervals of the order of magnitude of 10^{-6} seconds were measured by Wood in these experiments. Frank and Grotrian[8] have repeated these experiments with various modifications, and find that the displacement is too short to be measured for shorter times than those observed by Wood. They also show that the method is not sensitive enough to be applicable to the measurement of the time lag between excitation and emission of free atoms, since with low pressure in the absence of foreign gas no displacement of the illuminated spot could be detected, although the velocity of the vapor was increased. A method which has recently been developed by Pederson[9], and extended by Heymans and Frank[10], for measuring time intervals from 10^{-6} to 10^{-10} seconds, makes use of the relative position of "the Lichten-

berg figures which accompany the reflection of an electric impulse at the terminal of a conductor placed in a gaseous atmosphere capable of radiation". The calibration of this instrument presumably depends upon the velocity of electromagnetic waves along wires, which is probably not invariable and of which we have uncertain knowledge for the purpose in view. So far the method has found no application, but it is of interest for the possibilities which it holds. The most important method from the practical and theoretical standpoint for measuring time intervals of the order of magnitude of 10^{-6} to 10^{-10} seconds is that first used by Abraham and Lemoine[11]. This method makes use of the property of electric double refraction in liquids, discovered by Kerr[12] in 1875, and depends on the rate of decay of the double refraction while the electric field is falling. The lag of the fall of double refraction behind the fall of potential was found by Abraham and Lemoine (Loc. cit.), Rayleigh[13] and James[14] to be practically ~~infinite~~ very small, that is, far too ~~rapid~~ small to be detected even by means of a variable light path.

The original method used by Abraham and Lemoine, in which this electric double refraction of a liquid was first used for the purpose of measuring short time intervals, and which is essentially the method used by Rayleigh, James, Gottling and others, is that shown in Figure 1.

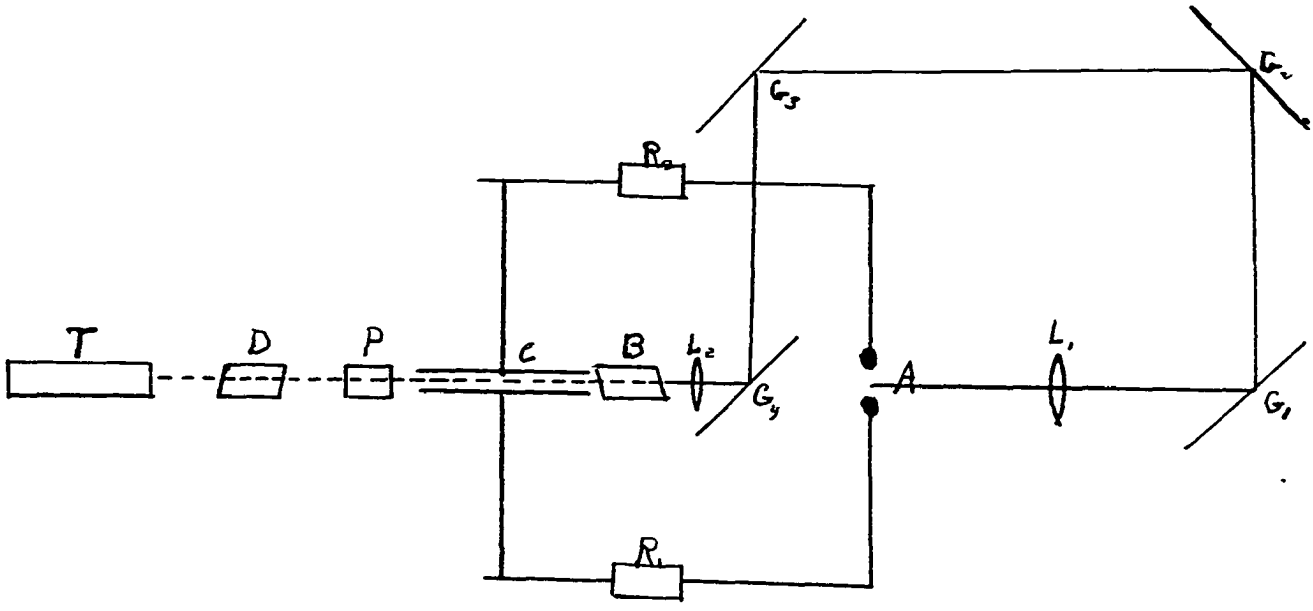

fig 1.

The Kerr cell, made by immersing two metallic plates in the doubly refracting liquid such as carbon disulphide or nitrobenzine, is connected in parallel with the spark gap A through high resistances R_1, R_2, which makes the circuit AR_1CR_2A non-oscillatory. The transformer M charges the Kerr cell C up to the potential where the spark passes at the gap A. Light from A is made parallel by L_1, is reflected by the movable mirrors G_1, G_2, to G_3, taken to G_4 and through the lens L_2 and Nicol prism B, which polarizes the light in a plane 45° with the plane of the plates of the Kerr cell C, and comes to focus at I. If the Kerr cell is uncharged, the polarization of the light is not affected, consequently the double-image prism may be turned so that only one image of I, which is plane polarized, reaches the Nicol prism D; then D may be rotated until no light reaches the telescope T. This point is marked as the zero position of D.

On the other hand, now suppose that the light from the spark at A, made plane polarized by the Nicol B, reaches the Kerr cell C before it is discharged; then the plane polarized light is made elliptically polarized by the double refraction of the carbon disulphide in C, and the double-image prism breaks it up into two images polarized in perpendicular planes, with one component of course in the same direction as in the previous case. This one is cut out by

the Nicol D, but the other can be viewed by the telescope at T. Now if D is turned say clockwise from the zero point, the two images appear in T, and a point may be found where they are of equal intensity. This is noted and D turned anticlockwise from the zero point until a second position is found where the intensity of the two images is again the same. The angle α between the two positions where the images are at equal intensity is a measure of the eccentricity of the elliptic polarization produced in the Kerr cell C. Since elliptical polarization in C is a function of the electrostatic potential across C, and since the electrostatic field across C is a function of the time after the discharge at the gap A, then within certain limits the angle α is a function of the time after the discharge at A.

Mathematical relations connecting α with the time after discharge at A have been worked out in detail by James (loc. cit.). Experimentally the relation between α and the time after discharge for the various resistances R_1, R_2 was determined by delaying the arrival of the light at C by moving the mirrors G_1, G_2. After thus finding this relation, Gottling (loc. cit.) focused the light from A on a fluorescent substance and measured the time between excitation and emission by viewing first the spark and then the fluorescent light. Gutton[15] in his measures of the ratio of the velocity of electromagnetic waves in wires to that of light removed

the resistances R_1, R_2 and the double-image prism P, thus giving a light shutter effect and an oscillatory circuit. He used a very high potential across A in order to obtain oscillations which he used as the basis of his measurements. In the present work this arrangement was again modified by adjusting the gap at A so that when once the Kerr cell discharges, its double refraction is not again affected by oscillations, and hence a complete light shutter is obtained. Also the time from the beginning of the closing of the shutter until it is completely closed is negligible in comparison to the time required for the electric drop of potential to travel from the spark gap A to the terminals of the Kerr cell C. This latter modification by which the drop in potential in the Kerr cell as explained above is considered instantaneous and the retardation brought about by increasing the wire in the leads of the Kerr cell differs essentially from the original method of Abraham and Lemoine (loc. cit.), which depends upon the rate of leak through a high resistance.

PURPOSE

The purpose of the present work is to develop a Kerr cell which will discharge in a time interval less than 10^{-9} seconds without oscillations great enough to render the carbon disulphide again doubly refracting; that is, to devel-

op a light shutter which will close in a definite interval of time of the order of magnitude of 10^{-8} seconds after an arbitrary fixed time. The need for such an instrument arises out of the necessity for definite knowledge concerning time intervals between excitation and emission, and duration of emission after excitation. Using the modern Quantum Theory, which postulates that energy can be absorbed or radiated only in whole multiples of a constant $h\nu$, whose dimensions are energy times time, Bohr[16] has constructed a theory of atomic structure which will quantitatively account for the spectral series of hydrogen and helium, whose atomic models have been fairly well worked out, and which serve as guides to the interpretation of the series of other elements for which definite models have not yet been found. His model of the atom consists of a nucleus which is in general composed of both positive charges and electrons with an excess of positive charges equal to the atomic number of the element. Around this nucleus, moving in various orbits or energy levels are electrons equal in number to the atomic number, so that the atom in its stable state is neutral.

The atom emits line series radiation when one or more electrons fall from one energy level to another, but as long as the electron remains in the same energy level no radiation is emitted. The possible energy levels in which an electron can move are finite in number, and are determined by

the quantum relation, i. e., when an electron jumps from one energy level to another the atom emits a spectrum line, the frequency ν of which is determined by the difference in energy W_1 and W_2 of the two energy levels by the relation

$$W_1 - W_2 = h\nu.$$

Consider for example the simplest conception of the hydrogen atom, as shown in Figure 2. This figure was taken from Sommerfeld's "Atombau und Spektrallinien", 4th edition, page 112.

In the stable or neutral hydrogen atom the electron is in the k orbit or energy level. Suppose it is removed say by electronic impact or absorption of radiation to the O level. According to the Bohr theory then there are seven ways of its return to the k level, with the possibility of emission of the following ten spectrum lines:

(1) The fourth member of the Lyman series.

(2) The third member of the Balmer series H_γ and first member of the Lyman series.

(3) The second line of the Paschen series and second line of the Lyman series.

(4) The second line of the Paschen series, H_α, and first line of the Lyman series.

(5) The first member of the Brackett series and third member of the Lyman series.

(6) The first member of the Brackett series, H_β, and first

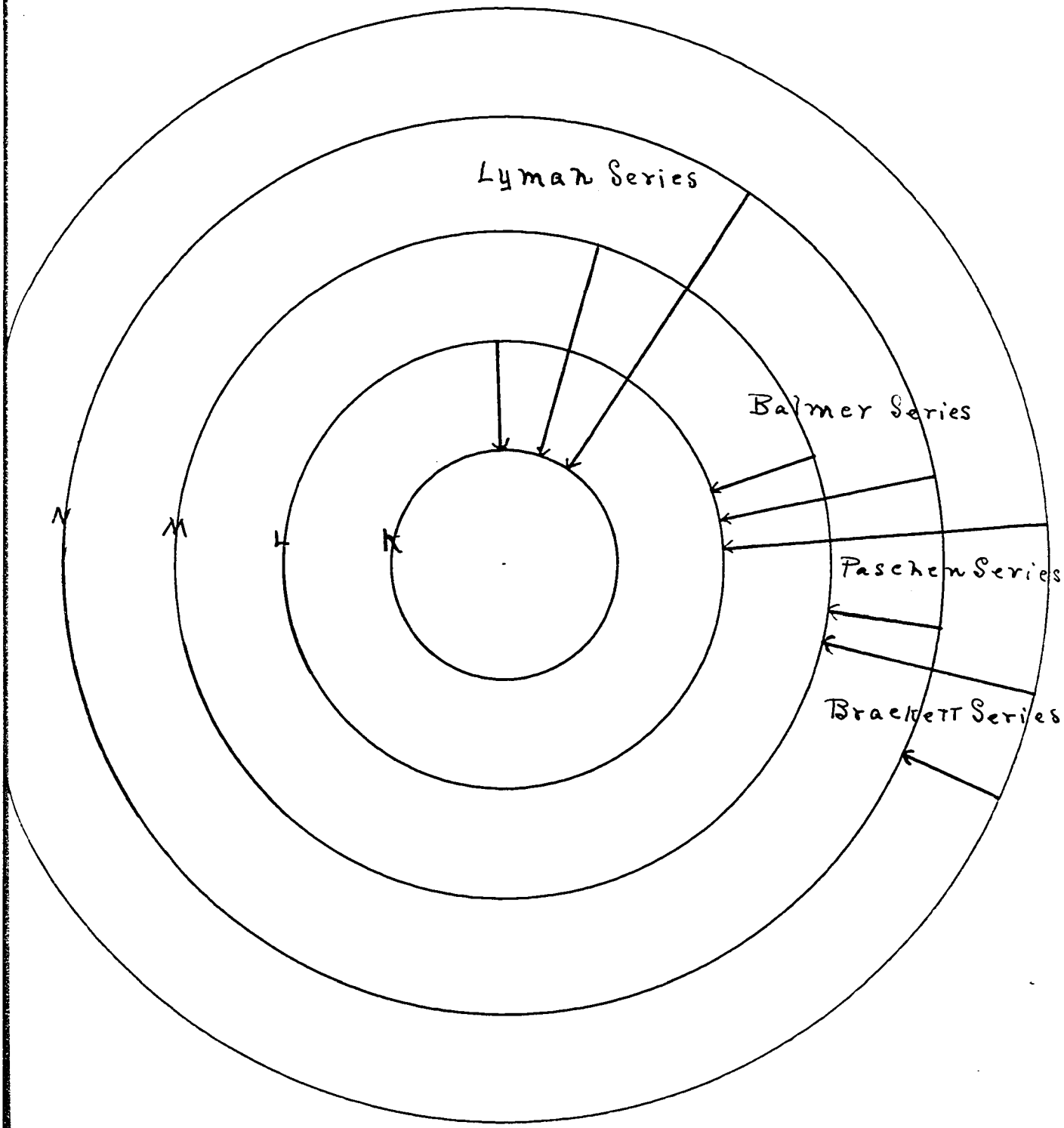

fig 2

member of the Lyman series.

(7) The first member of the Brackett series, first member of the Paschen series, H_α, and first member of the Lyman series.

Now since a single atom at a given instant can emit only a single line of the whole spectrum, the electron must remain a finite time in the orbits N, M, or L, or in each, if any line of the hydrogen spectrum is to be emitted other than the fourth line of the Lyman series. Therefore in order to explain the known experimental phenomena on the present theory it is necessary to assume that the electron remains a finite time in each of its orbits. From experiments of Wenn[17] and of Dempster[18] on the decay in luminosity in canal rays, and from theoretical predictions of Frank and Grotian (loc. cit.), Foote and Mohler[19], Tolman[20] and others based on indirect experimental evidence, we should expect these times to vary for different lines, and to be of the order of magnitude of 10^{-6} to 10^{-9} seconds. Another phenomenon which has attracted considerable interest and upon which there are at present many conflicting opinions is that of fluorescence. If the exciting light is a single line, the spectrum may be one of two types:

(1) That in which the fluorescence consists of a single line of the same wave-length as the exciting light. This is called resonance radiation, and is explained on the Bohr theory as follows: The electron in the ground orbit is just lifted to a higher orbit, from which it can fall only

back to the ground orbit and hence radiate only the line which it absorbs. The time which the electron remains in this outer orbit has been estimated in a few vapors by Frank and Grotian (loc. cit.) and others, but has been too short to measure except in the case of mercury vapor, for which Wood (loc. cit.) finds it to be 1/15000 second. (This value is probably due to another phenomenon as previously explained.

(2) That in which the fluorescent light is composed of the same wave-length as the exciting light, a few lines shorter than this wave-length, and a great number of longer wave-length. This is explained on the theory by assuming that the exciting light raises the electron out of its ground orbit to an orbit from which it may take several paths back to its ground orbit, thus giving rise to the wave-length of the exciting line and those on the long wave side of it. Now in this vapor at any time there will consequently be a large number of electrons in the various orbits besides the ground orbit which are in a position to absorb radiation. These will absorb the exciting energy or perhaps the radiated energy and be lifted to higher and higher levels, and in falling back give shorter wave-lengths than the exciting light, thus accounting for exceptions to Stokes's law.

A measure therefore of the time intervals at which these lines appear is of vital importance to the modern

theory of atomic structure.

The fluorescent spectrum which occurs when the substance is excited with several wave-lengths is very complicated and has not been satisfactorily explained. In the case of fluid solutions it seems to be most complicated and is usually attributed to chemical action. However, it is difficult to visualize, in view of the short time between excitation and emission, just how this could be. This time interval, as well as the interval the substance continues to fluoresce after the light is cut off, has remained too small to detect, with the exception of rhodamine in a solution of acetic acid and glycerine, where Gottling (loc. cit.) found the time interval between excitation and emission to be $(2.11 \pm 0.01) \times 10^{-8}$ seconds by the original Abraham and Lemoine method previously described. This value however must be subject to serious errors. In the first place he calibrated his apparatus at one time and made his readings at another; thus it is not certain that his apparatus remained in calibration. However, a more serious error must manifest itself in the two points which he takes as the beginning of excitation and as the beginning of emission. He matches two images of the spark as is previously explained in this paper, then focuses the light from the spark on the rhodamine and matches the two images of the fluorescent light. The difference in his two angles he assumes is a measure of the time

interval between excitation and emission. This would hold only if the lines of spectrum of the spark were emitted simultaneously and those of the fluorescent light appeared simultaneously. Schuster and Helmsaleck (loc. cit.), Schenk (loc. cit.), Milner (loc. cit.), and the present work have found that the lines of the spectrum do not all appear simultaneously, and that in the red region of the spectrum, where the absorption bands of rhodamine mostly fall, these bands appear last. This alone will probably introduce an error larger than the value he observed. Also there is reason to believe that the complete fluorescent spectrum does not appear simultaneously, which again complicates his values.

In view of the great need for some direct way of getting an accurate measure of the above time intervals, this work was undertaken.

APPARATUS

In the apparatus as shown in Figure 3 the Kerr cell C was constructed by anchoring in a glass tube, by means of sheet mica, two parallel plates of copper 12 cm. in length, 1.5 cm. in width, and placed 0.5 cm. apart. Each lead from the plates of the condenser passed out through a small glass tube sealed into the top of the main tube. The ends of the main tube were of optically inactive glass soldered on with a fusible alloy containing four parts each of bismuth and lead

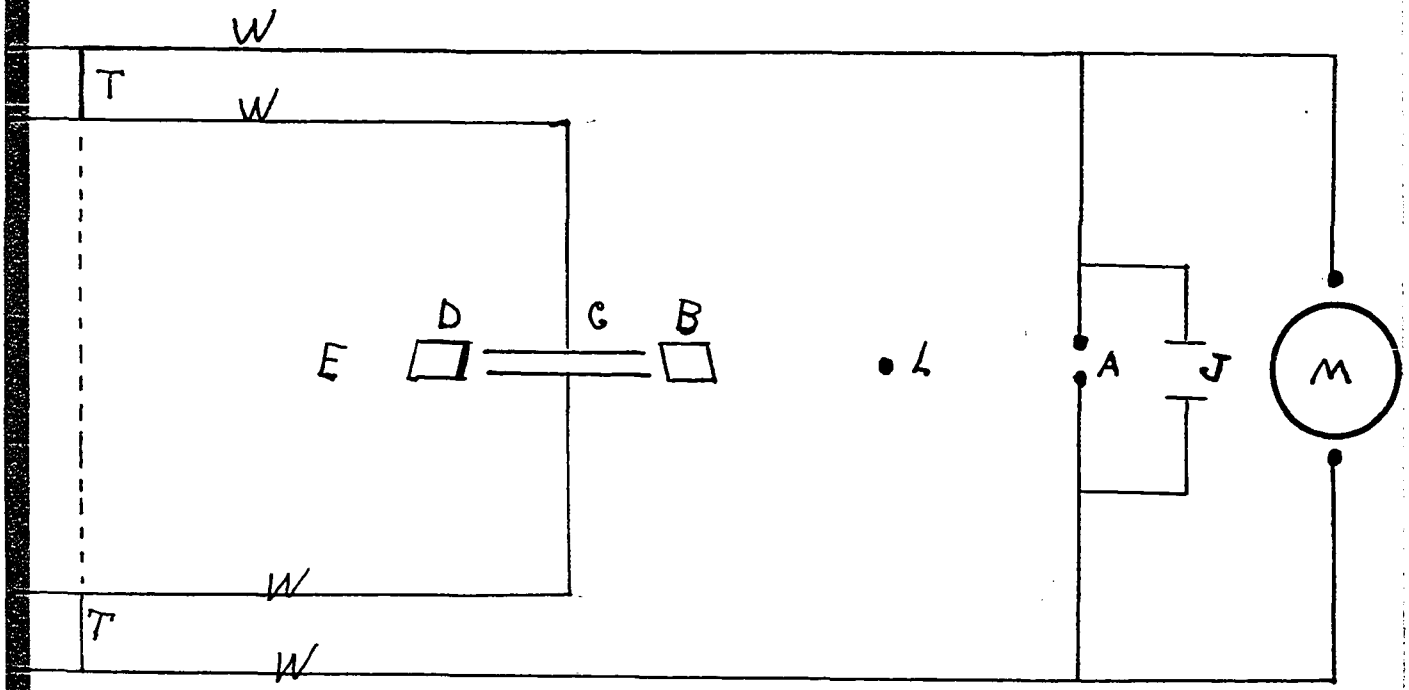

fig 3.

and two parts each of tin and cadmium. This alloy has the property of adhering very tightly to glass, and at the same time it makes a good seal. A thin coat of waterglass is usually placed over the alloy to give a more rigid construction. This seal can easily be removed by warming with a bunsen burner in case the condenser needs repair. The leads W W W W from the spark gap A to the condenser C are long parallel wires (B & S gauge No. 12 bare copper), placed approximately 20 cm. apart. These leads are lengthened or shortened symmetrically by a slider or trolley T T. The electrostatic potential was maintained by a motor-driven static machine without condensers, or by a 500-watt transformer with high non-inductive resistance in its high potential leads. This resistance is necessary to prevent an arc at the gap A. The electrostatic potential was regulated by the width of the spark gap A. B and D are two crossed Nicol prisms having their short diagonal 45^{0} with the plates of the condenser. J is a Leyden jar with 2×10^{-3} microfarads capacity and a period of 2×10^{-6} seconds. It is in parallel with C and the gap A, and merely serves to brighten the spark at A. L is an incandescent light used only for accurately crossing the Nicols and setting the correct potential.

METHOD

If in Figure 3 the electrostatic potential is gradually applied across the gap A by the static machine or transformer M, the Leyden jar and the Kerr cell C both become charged. When the Kerr cell reaches a certain limiting potential, an observer at E, On looking through D, C, B, can just see the incandescent light L. The spark gap is then adjusted so that a discharge will take place across it at this instant. When the condensar discharges, the light from L is extinguished. We shall refer to B C D as the cut-off. If now the light L is removed and the spark gap A itself aligned with the cut-off, the light from the gap A cannot be seen through the cut-off although it is but a few centimeters in front. If, however, the leads from the gap to the Kerr cell are lengthened to about three meters in each lead by moving T T, the light from A comes into view. If now the light from A is first reflected to a distant mirror and then returned (see Figure 4), it will reach the cut-off after it has closed. By moving T T farther back, the light from A is again brought into view. The time of retardation is not in general a linear function of the length of wire in the leads, but over limited ranges the retardation is proportional to the velocity of the electromagnetic waves along the wires. This velocity is also complicated by various constants of the circuit, but from measurements taken with the circuit shown in Figure 3 it can be said with certainty that the velocity

of these electromagnetic waves is less than the velocity of light. Hence from the above a lower limit to the time interval the exciting energy is imprisoned in the gases between the gap before the visible light appears is at least of the order of magnitude of 10^{-8} seconds.

TIME INTERVAL BETWEEN EXCITATION AND EMISSION IN FLUORESCENT SOLUTIONS

It has been shown that in some fluorescent substances the exciting energy enters the substance a definite measurable time before the fluorescent light appears. (R. W. Wood, loc. cit.; Gottling, loc. cit.)

It was decided to attempt to measure this interval by making use of the above cut-off. or shutter

During the progress of this work it was discovered that the spectrum lines appear at different times. Since this might add a correction to the measurements taken with the apparatus in use, the work was discontinued until the order of appearance of the spectrum lines could be investigated.

The apparatus was arranged as shown in Figure 4. The spark at the gap A is focused on the fluorescent substance S, passes through S and is made parallel by the lens F, is reflected by the movable mirror G through H to K, and brought to a focus at the point I. The image of the spark

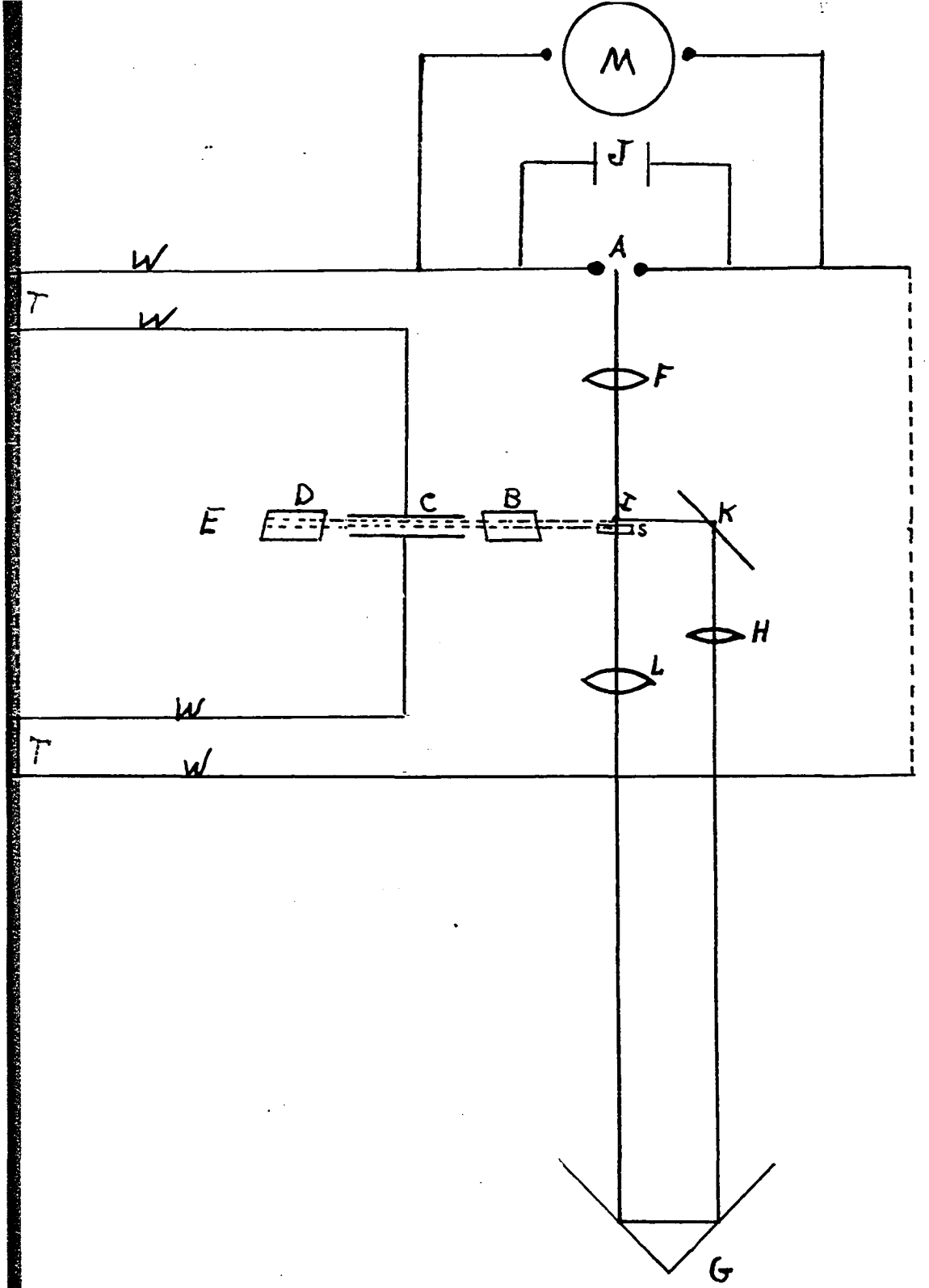

fig 4.

at I and the fluorescent light from S are viewed through the cut-off B C D. Then by adjusting the length of wire by moving T, and the light path by moving G, it was possible to find a point where the image of the spark and the fluorescent light as viewed side by side through the cut-off were extinguished together. Before each reading the mirror G was moved forward and backward to make sure that there were no oscillations in C great enough to let the light through the shutter after the initial discharge. The time interval between excitation and fluorescent emission is then equal to the time required for light to traverse the path S F G K I. This is true of course on the assumption that the lines of the spark spectrum that excite fluorescence are the same as those that arrive at I.

The fluorescent substances tried were dilute solutions of fluorescein and erythroscene in water. Both show brilliant fluorescence, so that the settings were not difficult to make. The time of traversal of the light path for fluorescein was found to be $(2.2 \pm 0.2) \times 10^{-8}$ seconds, and that for erythroscene $(5.1 \times 10^{-8}) \pm 0.3 \times 10^{-8}$ seconds.

These values are shorter than the time interval sought. For, in the case of fluorescein for example, the lines that excite fluorescence are absorbed, while the lines transmitted (and, therefore, traversing the said light path) excite little if any fluorescence. It is just these lines,

however, that are found to appear after the others. This second interval should be added to the first. However, accurate quantitative measurements of the latter are yet to be made.

In future work it is planned to use a slight modification that will not depend upon the sequence of the appearance of spectrum lines.

The above method of viewing simultaneously the fluorescent light and the image of the spark has the obvious advantage of eliminating errors arising from fluctuations in the constants of the electrical circuits as well as other changes that might occur in the course of the investigation.

THE DETERMINATION OF THE RELATIVE TIMES OF FIRST APPEARANCE OF THE SPECTRUM LINES

It has been found that the spectrum lines in the spark spectrum in some metals do not all appear simultaneously. Schuster and Helmsaleck (loc. cit.) observed in the case of calcium that the air lines appear first, followed by the H and K lines and then the arc lines. Schenk (loc. cit.) observed in the case of magnesium first the air lines, then the spark line 4481 A. U., and then the arc lines; because of the low sensitivity of their method they could not observe a sequence in the order of appearance of the air lines, arc lines and spark lines themselves. These have been found and measured by

means of the shutter previously described.

The apparatus used was the same as that in Figure 3, except that the light from the spark is viewed and photographed through a prism spectroscope and prism spectrograph, respectively, at the point E. The metal whose spectrum is to be studied is used as terminals for the spark gap A. The trolley T T was first adjusted so that the light from the spark reaches the shutter too late to get through. The trolley is then moved back and the various lines of the spectrum can be observed as they flash on in succession. Tests were always made before each reading to make sure that there were no oscillations in the circuit large enough to open the shutter after once it was closed.

The sequence in the appearance of a few of the bright lines of cadmium, magnesium and zinc was observed with a direct vision spectroscope, and photographed with a spectrograph using a 60° carbon disulphide prism. This spectrograph was assembled rather hastily for student use, but was pressed into service for this work for want of a better one. It will cover with fair definition the range 6600 to 3850 A. U. on the long dimension of a 4 by 5 " plate. However, the shutter used did not transmit wave-lengths less than 4200 A. U., so that it was not possible to reach anything outside the visual region. The photographs were taken on Wratten and Wainwright panchromatic plates hypersensitised with ammonia.

For cadmium the lines observed were the red line 6438, the spark doublet 5378 and 5337, and the first members of the sharp series 5086, 4800 and 4678. The air lines appeared first with from 3 to 5 meters of wire (B & S gauge No. 12 bare copper) in each lead. The two cadmium spark lines appeared next with about 16 meters of wire in each lead, and the arc lines appeared later with about 17.5 meters of wire. The spark was roughly one meter in front of the light shutter. Although the delay in seconds can be given only very approximately, there is no question as to the sequence. If to the photographic record are added the visual observations made by me, and also observed by members of the staff here, one would be inclined to place the order of appearance as follows: spark lines, followed by 4800, followed immediately by 5086 and 4678 together, last of all line 6438.

In the case of magnesium the only lines available are the spark doublet 4481 which Fowler[21] assigns to a combination type, and the first term of the sharp triplet series 5184, 5172 and 5167. Neither the doublet nor the triplet is resolved on the plates, for the lines of the doublet were too close together, and an air line at 5180 blurs the triplet. When the spark is viewed through the direct vision spectroscope, it is possible to adjust it so that the short air lines appear at the bottom of the field and the longer metallic lines extend beyond them into the upper part of the field; the

triplet is then resolved. Again, the air lines appeared first with from 3 to 5 meters of wire, the spark lines appeared with 15.5 meters, and the triplet with 17 meters. In the photographs the region about 5180 shows a great increase in brightness with anything over 17 meters of wire, and this is taken to confirm the appearance of the triplet at about that time. Due to the extreme brightness of the line 4481, the length of exposures (60 minutes), and the sensitiveness of the plates in this region, some stray light which does not traverse the condenser directly, but is reflected by the condenser plates, shows in all the exposures, but the line increases in density in no uncertain manner when the length of wire exceeds 15.5 meters, and to the eye when viewing the lines directly the flashing out of this bright line leaves no doubt as to the time of its appearance.

In the case of zinc the lines observed were the spark doublets at 4924 and 4912, which Salis[22] assigns to $4d_1 - 4f$ and $4d_2 - 4f$ respectively, and 6103 and 6021, which he assigns to $4p_1 - 5d_1$ and $5p_2 - 5d_2$ respectively; the first term of the sharp triplet series 4811, 4722 and 4680, and the first term of the diffuse series 6362.

The air lines as before appear first, followed by the spark pair 4924 and 4912, which were unresolved on the plate, at 18 meters of wire. Then the arc triplet 4811, 4722 and 4680 appear at about 19½ meters. 4680 appears first, followed very closely by 4722 and 4811 in succession. At about

21 meters the spark pair at 6103 and 6021 appear, and last of all the red line at 6362 A. U.

In the case of the air lines the only groups which show with sufficient intensity to give accurate determinations are those at 5002 - 16 (p - s), 4631 (p - p'), and 5667 - 80 (p - d), which are assigned by Fowler[23] to ionized nitrogen. The group 5002 - 16 (p - s) appear first, followed closely by 4631 (p - p'), and then 5667 - 80 (p - d). It will be observed that these are groups of lines, and it may be that certain members of each group appear later than the remaining members of the same group, also that certain members in the first two groups may appear after those in the last group. This point can only be settled by the use of higher resolving power, which was undesirable in the present instance because of the loss of light. The spectra of nitrogen, oxygen and cyanogen in vacuum discharge tubes have been examined and a sequence of the lines observed in each case. The discharge tubes were of the H type, and the positive column was viewed end on. The tube was connected in series with the Leyden jar and the spark gap A, but in parallel with the Kerr cell. A high non-inductive water resistance was shunted around the tube in order to provide a leak while the condenser was being charged. The sequence in the case of nitrogen is the same as that in air; however, a larger number of lines was observed. Several of the lines of the spectrum were observed to appear before the band spectrum or the continuous spectrum. This is

beautifully demonstrated in the case of cyanogen. It was also observed that some of these band spectra and continuous spectra appeared before a few of the line spectra. However, further experiments must be made before any definite conclusions can be drawn. Various other substances have been examined, including iron, bismuth, strontium, copper, aluminum, sodium, potassium, lithium, barium, calcium and lead; and each shows a sequence in the appearance of its spectrum lines.

A method for determining the actual time interval between the appearance of different lines has been developed. The preliminary arrangement, which has been in use until recently, was essentially the same as that to be described, with the exception that the movable mirror G was double instead of triple and was carried on a rolling table kept in alignment by guides nailed to the floor. It was also limited to light-path differences of only 20 meters. The new arrangement of the apparatus is shown in Figure 5. The movable mirror G is composed of three mirrors arranged on a trihedral angle which has its sides respectively perpendicular, so that a beam of light parallel to the line making equal angles with the sides of the trihedral angle, after three reflections will be returned parallel to its path. With this arrangement, any small rotation about, or slight displacement along, any axis of the mirror, does not affect the direction of the reflected beam. The triple mirror G is mounted on a wooden carriage which slides

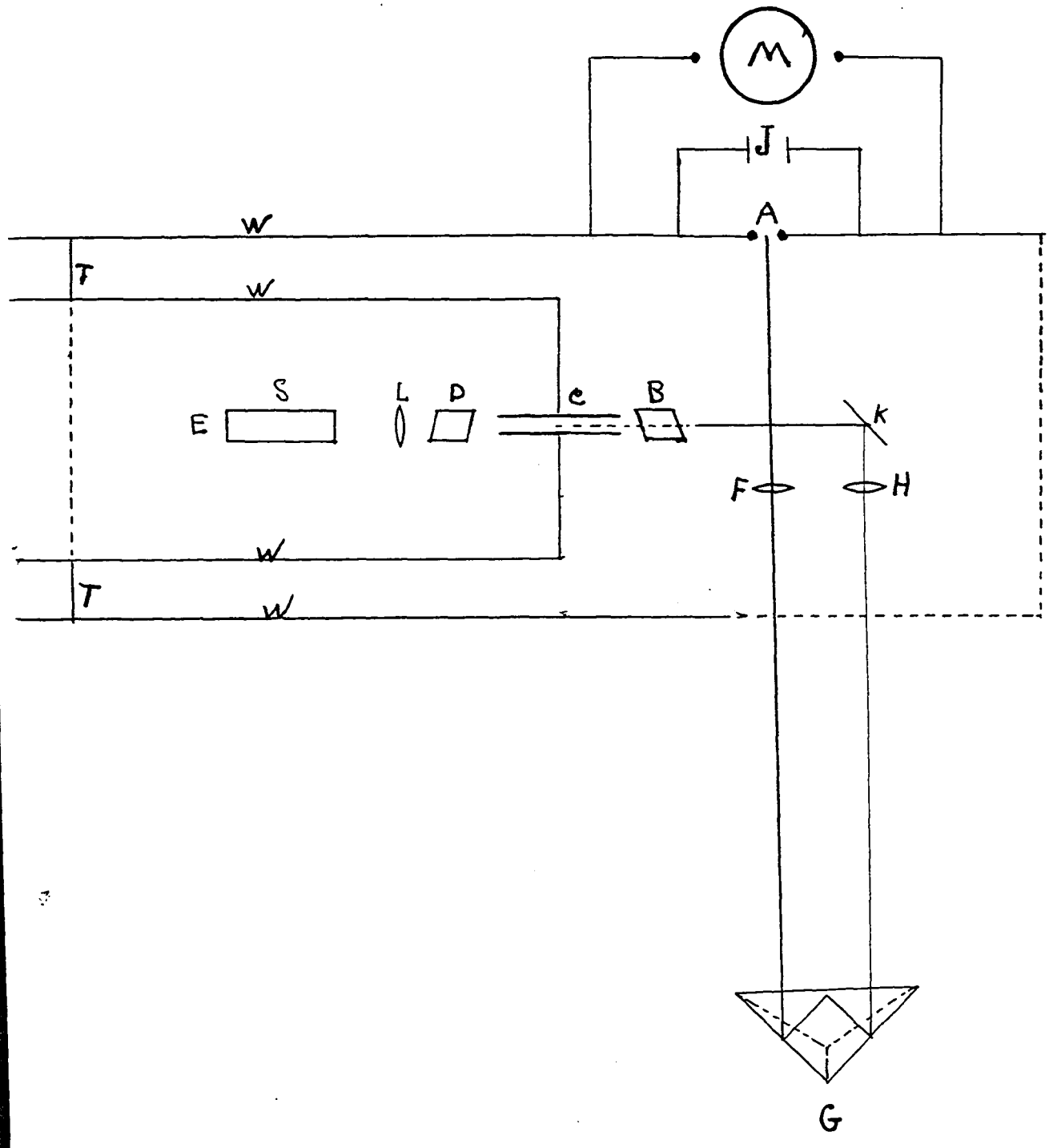

fig 5

on a level wooden track. The track is composed of two parallel wooden rails 80 ft. in length and 20 inches apart, anchored to the building. The carriage is moved along the track by the observer at E by means of a system of pulleys over which passes an endless wire cable fastened to the carriage. The long parallel wires W W W W are fastened at their ends by non-conducting cord, and the trolley T T sliding on these wires (as previously described) is also operated by the observer at E. The remainder of the apparatus has been previously described. Light from the gap at A is made parallel by the lens F, passes to the triple mirror G, and is returned in a beam parallel to the first, to the lens H; is reflected by the mirror through the shutter, and observed through the prism spectroscope S from the point E. Now by moving G forwards and backwards the observer at E can vary the time interval between the departure of the light from A and its arrival at the shutter by increasing or decreasing the distance traversed by the light from A to G.

To measure the delay of an arc line over a spark line, for example, the triple mirror G is moved in close to H. The trolley T T is then moved into such a position that the arc line just appears. Then the mirror G is moved back until the arc line just disappears, and this position of the mirror is noted. G is then moved farther back until the spark line just disappears and this point noted. The difference in light

path divided by the velocity of light will give the delay in seconds. The observations are checked in each case by noting the positions where the lines just appear; however, preliminary observations indicate that these readings should be given less weight than the former, probably because of the unequal brightness of the lines and the difficulties in focusing the eye when the line is not in the field of view. Accurate quantitative readings have not yet been made with the above method, but it was found with a preliminary arrangement that the lines could be made to appear and disappear by moving G, which is a good indication of the success of the method.

DISCUSSION OF RESULTS

The conditions in the spark discharge are very complicated. It is a well-known fact that change of capacity or of inductance alters the intensity of various lines. However, these effects are usually attributed by most investigators to conditions in the spark after the initial discharge. Since in the present work only the beginning of the spark was investigated, these phenomena are not effective. Then let us consider what probably takes place during the initial discharge. Electrons falling through a high accelerating potential collide with neutral atoms of the gases and vapors in the gap and remove one and sometimes more electrons, making the atoms po-

sitively charged. Each of these ions (in the case of the singly charged ions) "neutralizes the effect on the space charge of $4\sqrt{3680}$ M electrons" [24], where M is the atomic weight of the element, which, for example in the case of cadmium is about 27,000 electrons. This in turn increases the potential gradient and more singly charged ions become doubly charged. It is thus very probable that at the beginning of the emission of light by the gases and vapors in the gap a very large percentage of the ions are doubly ionized, especially in the case of nitrogen and metallic vapors.

The only spectrum which a doubly charged ion can emit (with a few isolated exceptions[25]) is the spark spectrum; i. e., an electron falling between the various orbits of a doubly charged ion produces the spark spectrum. When it reaches its ground orbit the doubly charged ion becomes singly charged; then if another electron falls between the various energy levels of the singly charged ion, the arc spectrum is emitted. Therefore if we start with all the atoms doubly ionized we should expect the spark lines to appear before the arc lines. Although it is reasonable to assume a large percentage of the ions doubly ionized (this is indicated by the intensity of the spark lines as they flash on in the above experiments), enough singly charged ions are probably present to give the arc lines with observable intensity. The appearance of the spark lines before the arc lines in the above experiments would therefore indicate that the greater

field of the doubly charged atom would attract an electron before that of the singly charged atom, or that the various virtual orbits of the doubly charged atom are less stable than those of the singly charged atom.

It is interesting to note an apparent exception to the above, however, in the case of zinc, where arc lines are observed to appear before spark lines.

The above gives an easy way of explaining the observed sequence of any particular element in the gap. It explains the sequence of the air lines and that of the metallic lines. It also would indicate that the air lines should appear before the metallic lines, since the ionization potential of the gases is greater than those of the metals. However from the difference in the ionization potentials of the ions of the gases and those of the metals we should not expect such a long period between the appearance of the air lines and those of the metals. There are at least two possible ways of explaining this. In the first place it may be that the first jump of the electron in nitrogen for instance gives rise to a line in the visual region while that of the metal gives rise to a line outside the visual region; that is, if in the case of the metal the electron must pass through several stationary states before it radiates a visual line and if in the case of nitrogen it radiates a visual line in the first jump, then we should expect the lines of nitrogen

to appear considerably before those of the metal. Unfortunately the series relations of the spark spectrum of the metals and those of the gases of the air are not yet worked out definitely enough to give sufficient information on this point. Also an extension of the present work to the ultraviolet is necessary to throw light upon the phenomenon. The other way of explaining this phenomenon is to assume that the positively charged ions of the metals form "metastable" chemical compounds with excited or neutral atoms of the gases or of the metal. These compounds due to their instability break down in a short time into their constituent parts. The ions are then free to radiate their energy. The longer life of these chemical compounds is then responsible for the long time interval between the appearance of the air lines and the metallic lines. This view would seem to find support in experiments of Wood (loc. cit.), Franck and Grotrian (loc. cit.) and others, who find evidences of these compounds under various conditions analogous to the conditions in the spark discharge.

It has been pointed out (26) in a letter from Dr. Foote that a possible explanation of the order of appearance of the various lines may be based on the "characteristics of the spark discharge rather than of the atom". However in a later letter after the results of zinc had been sent to him, he said" Of course, in many cases the nature of the discharge may have an influence; but when electrons have gotten into the 2s orbit of neutral zinc, it is hard to see how external

circumstances can influence the time interval τ which elapses before the atom passes to a lower energy level". That is, the field of the atom is so much stronger than the external field that its effect may be neglected in comparison with that of the atom. Also, if the external field in the spark is the determining factor, we should expect the order of appearance of the lines and certainly the time between the appearance of the various lines to change. If the field is changed by altering the capacity of the circuit, this should be true. It is found not to be the case within the limits investigated. Also in a spark gap containing magnesium and cadmium one should expect the spark lines of cadmium to appear before those of magnesium because of the greater excitation potential of the spark spectrum of cadmium. Experiments show just the opposite, so this view certainly cannot explain the results. However, a definite explanation of the phenomenon must await further experimental data.

SUMMARY OF RESULTS

The chief results of the work may be summarized as follows:

1. A method has been developed by which time intervals of the order of magnitude of 10^{-9} seconds may be measured.

2. A light shutter has been developed which will close a predetermined time (within certain limits) after a spark discharge.

3. The visible light from the spark was discovered to

appear a definite interval of time after the electric discharge and measured to be at least of the order of magnitude of 10^{-8} seconds.

4. The results of various previous experiments on the order of appearance of the groups of air lines, spark lines and arc lines in the spark spectrum have been definitely confirmed in the cases investigated in this work.

5. A sequence in the appearance of the air lines, spark lines and arc lines themselves has been discovered and their order observed.

6. The spectrum lines of a gas in vacuum tube discharge have been discovered to appear at different times.

7. Fluorescene and erythroscene were discovered to have a time lag between excitation and emission of their fluorescent light, and these times found to be greater than 2×10^{-8} seconds for fluorescene and 5×10^{-8} seconds for erythroscene.

8. A new valuable field of research has been opened which holds promise of throwing light on many important unsolved problems of atomic structure.

This work was suggested by Professor C. M. Sparrow, to whom I am indebted also for advice and encouragement during its progress. I wish also to thank Professor L. G. Hoxton for his many valuable suggestions, which have made possible the successful prosecution of the work, and for his continued interest and encouragement. I wish to acknowledge my indebtedness to Professor F. L. Brown, who measured the

spectrum plates, and to Mr. Carl Harris, who aided in the construction of apparatus; finally, I desire to thank Mr. A. J. Weed, Mechanician, for help and cooperation.

BIBLIOGRAPHY

1. Galileo, Cajori's History of Physics, p. 31.
2. Wheatstone, Cajori's History of Physics, p. 149.
3. Schenk, Astrophys. Jour., 14, 1901.
4. Milner, Phil. Trans., 209 A, p. 71, 1909.
5. Michelson, Nature, 114, p. 85, Dec. 6, 1924.
6. Becquerel, Preston's Theory of Light, 2d ed., p. 478.
7. Wood, Proc. Roy. Soc., 99, p. 362, 1921.
8. Frank and Grotrian, Zeitsch. f. Phys., 4, p. 89, 1921.
9. Pederson, Ann. d. Phys., 1921.
10. Heymans and Frank, Proc. Amer. Phys. Soc., Washington, 1924
11. Abraham and Lemoine, Comptes Rendus, 1899.
12. Kerr, Phil. Mag., 1, p. 337, 1875.
13. Rayleigh, Collected Papers, V.
14. James, Ann. d. Phys., 1904.
15. Gutton, Comptes Rendus, 152, p. 685, 1911.
16. Bohr, The Theory of Spectra and Atomic Constitution, 1922.
17. Wenn, Ann. d. Phys., 60, p. 597, 1919, and 66, p. 229, 1921.
18. Dempster, Phys. Rev., 15, p. 138, 1920.
19. Foote and Mohler, Origin of Spectra, p. 166.

20. Tolman, Phys. Rev., 23, No. 6, 1924.

21. Fowler, Report on Series in Line Spectra.

22. Salis, Ann. d. Phys., 76, Feb. 5, 1925.

23. Fowler, Proc. Roy. Soc., A, 107, p. 741, 1925.

24. Foote and Mohler, Origin of Spectra, p. 155.

25. Russell and Saunders, Astrophys. Jour., 61, p. 1, 1925.

26. Schuster and Hamsaleck Phil Trans, 193, P212, 1900

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June 1, 1925.

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Dr. J. C. Metcalf, Dean of the Graduate School,

University of Virginia,

University, Va.

My dear Dr. Metcalf:

With reference to the dissertation of Beams in connection with the printing of its title on the program for the conferring of degrees, I would suggest that the phrase "order of magnitude of 10^{-8} seconds" be translated by "order of magnitude of one hundred millionth of a second" or, if you prefer, "order of magnitude of ten billionths of a second".

Yours very truly,

L. G. Hoxton.