THE TIME INTERVAL BETWEEN THE APPEARANCE OF SPECTRUM LINES IN SPARK AND IN CONDENSED DISCHARGES*

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Abstract

The experimental method consisted essentially in a comparison of the time interval elapsing between the appearance of two spectrum lines with the time required for light to travel a measured distance. The time intervals between the appearance of the bright visible spectrum lines of cadmium, magnesium and zinc in the spark in air and nitrogen and hydrogen in condensed discharges at various pressures were measured. The results indicate that the time between the appearance of these lines is due to atomic phenomena, and emphasize the importance of the final energy levels as well as the initial energy levels in determining the average time between excitation and the beginning of emission.

IT has long been known that the spectrum lines in a spark between metallic electrodes in air do not all appear simultaneously. In previous work,[1] however, owing to the very short time interval between the appearance of most of the lines and to the low resolving power of the instruments used, many of the lines appeared simultaneously. Also since the rate of increase of intensity of different lines varies considerably the results might be somewhat in error due to the lack of sensitivity of the photographic plate. Recently[2] the sequence of the appearance of the visible spectrum lines of cadmium and magnesium have been investigated by a modification of a method first used by Abraham and Lemoine[3] for measuring short time intervals. This work has been continued and extended to the determination of the actual time intervals between the appearance of the various spectrum lines, and this paper gives the results for the visible region of cadmium, magnesium, zinc, nitrogen and hydrogen.

The experimental method has been considerably refined since it was first described,[2] making it necessary to outline it briefly here. K (Fig. 1a) is a so-called Kerr cell, made by immersing two parallel plates of copper in carbon disulphide. N_1 and N_2 are crossed Nicol prisms, the diagonals of N_1 making an angle of 45° with the plates of K. If an electric field is applied across the plates of K, light passes N_2; but no light passes N_2 if

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[1] See Baly, "Spectroscopy," p. 406 (1912).

[2] Brown and Beams, J.O.S.A. **11**, 11 (1925).

[3] Abraham and Lemoine, Comptes Rendus **129**, 206 (1899).

the field is relaxed.[4] If now the electric field in K is relaxed by a spark placed in front of N_1 and if the leads from K to the spark gap are very short, the field in K is relaxed before any visible light from the spark reaches it and no light passes N_2. If now the leads from the gap to K are lengthened, light passes N_2; if it is viewed in a spectroscope, the various spectrum lines are found to appear in a definite sequence. The arrangement N_1KN_2 then acts as a light shutter, the closing of which can be advanced or retarded with respect to a spark by simply lengthening or shortening the leads from the spark gap to K. The quick closing of this

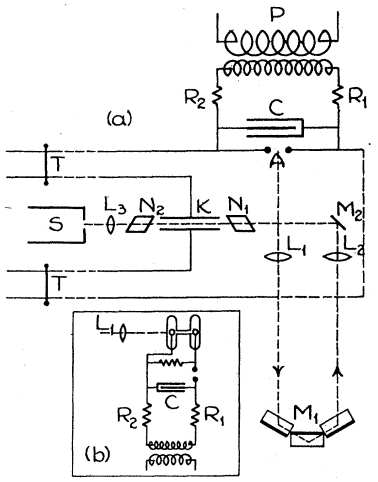

Fig. 1. Diagram of apparatus.

shutter results from the fact that the electric double refraction in K varies as the square of the voltage across the plates of K, and from the fact that the damping stops effective oscillations in K after the initial discharge. P is a sixty cycle ten thousand volt transformer, R_1 and R_2 non-inductive resistances, C a variable capacity which serves to brighten the spark at A. TT are cross wires which slide on the long leads from A to K. M_1 is a trihedral mirror system designed by Professor Hoxton, which is movable along a track parallel to the light path indicated and reflects the light from A accurately to the center of L_2 regardless of slight irregularities in the track upon which it slides. Both TT and M_1 are adjusted by the observer at S without the necessity of removing his eye from the position of observation. Several different spectroscopes, each with large light-gathering power, were used at S for the visual and photographic observa-

[4] Kerr, Phil. Mag. **1**, 337 (1875).

tions. The photographs were taken on Wratten and Wainwright panchromatic plates hypersensitized with ammonia.

The metal whose spectrum is to be studied is placed in the terminals of the spark gap A. Light from A, made parallel by the lens L_1, is reflected from the movable mirror system M_1 through the lens L_3 and comes to focus at the center of K. The lens L_3 collects the light on the slit of the spectroscope, where the light is either viewed visually or photographed. M_1 is first moved a considerable distance from A and the shutter retarded until light just passes N_2. This light is composed of only a single line of the spectrum. If now the mirror system is moved forward, thus shortening the optical path from spark to shutter, the other spectrum lines one by one come into view. If then the distance that M_1 is moved forward between the appearance of any two spectrum lines is noted, the time interval between their appearance can be found by dividing the difference in light path by the velocity of light.

In studying the spectrum of hydrogen, the spark was between brass electrodes in a large glass tube filled with hydrogen at atmospheric pressure, with steam or with water gas. These lines were broad but quite intense. At lower pressures in the case of both hydrogen and nitrogen a short discharge tube was placed in the position of the spark gap so that its capillary was viewed end on. The tube was connected as shown in Fig. 1b, with a non-inductive resistance across its terminals to eliminate flashing while the potential was being built up. The capillary was very short and the tube as nearly symmetrical as possible. This is necessary in an alternating current discharge because of the finite velocity of the propagation of luminosity from anode to cathode, which varies with the constants of the circuit.[5] (This phenomenon was hurriedly investigated, and the results were in agreement with those of other investigators.[6])

The values given in the table are probably the result of atomic phenomena, and independent of the conditions of excitation within the limits of experimental error.[7] These conditions were varied considerably by changing the capacity in parallel with K, by replacing the carbon disulphide in the Kerr cell by chloroform and by changing the pressure in the discharge tube in the case of hydrogen and nitrogen, but no change in the measured time intervals could be detected. The precision of the above results is at least 0.3×10^{-8} sec., but varies somewhat for different lines because the sensitivity of the eye and photographic plate is not

[5] J. J. Thomson, "Recent Researches in Electricity and Magnetism," p. 115 (1893).
[6] Whiddington, Nature **116,** 506 (1925)
[7] Beams, Phys. Rev. **27,** 805(A), 1926.

TABLE I

Time intervals between appearance of spectrum lines.

	Wave-length		Classification	Intensity	Interval (sec.$\times 10^8$)
			Magnesium spark		
1	4481	spark	$3d_{1,2}$—$4f$	10	
2	5184,73,67	arc	$2p_{1,2,3,}$—$2s$[8]	10	8.2
			Cadmium spark		
1	5337,78	spark	$(5d_1$—$4f_1)$ $(5d_2$—$4f_2)$[9]	10	
2	4800	arc	$2p_2$—$2s'$	9	12.
3	5086	arc	$2p_1$—$2s'$	9	1.3
4	4678	arc	$2p_3$—$2s'$	8	0.7
			Zinc spark		
1	4912,24	spark	$(4d_1$—$4f_1)$ $(4d_2$—$4f_2)$[10]	10	
2	4680	arc	$2p_3$—$2s$[8]	8	15.
3	4722	arc	$2p_2$—$2s$[8]	9	2.
4	4811	arc	$2p_1$—$2s$[8]	9	1.3
			Magnesium-cadmium and cadmium-zinc spark		
1	4481 Mg	spark	$3d_{1,2}$—$4f$		
2	5337,78 Cd	spark	$(5d_1$—$4f_1)$ $(5d_2$—$4f_2)$		7.5
3	4912,24 Zn	spark	$(4d_1$—$4f_1)$ $(4d_2$—$4f_2)$		9.6
			Hydrogen discharge tube and spark in hydrogen		
1	4861	H beta		10	
2	4340	H gamma		8	6.
3	6563	H alpha		10	13.3 (?)
			Nitrogen discharge tube and spark in hydrogen		
1	5011	p_2—s'[10]	N II	2	
	5008[11]			4	
	5005[11]			8	
	5003	p_3—s'[10]	N II	10	
					0.8
2	5045	p_1—s'[10]	N II	6	
					0.2
3	4643	p_1—p_2'[10]	N II	10	
	4641	enhanced[11]		8	
	4631	p_1—p_1'[10]	N II	10	
					0.6
4	4803	d_1—d_1'[10]	N II	9	
	4788	d_2—d_2'[10]	N II	8	
	4781	d_2—d_1'[10]	N II	7	
	4448	ordinary[12]		10	
	4433	ordinary[12]		8	
					0.3
5	4531	ordinary[12]		7	
	4515	enhanced[12]		6	
					0.8
6	5679	p_1—d_1[10]	N II	10	
	5676	p_3—d_3[10]	N II	6	
	5667	p_2—d_2[10]	N II	8	
					0.2
7	5942	p_1'—d_1'	N II	8	
	5932	p_2'—d_2'	N II	8	

[8] Revised Paschen notation.

[9] Salis, Ann. d. Physik **76,** 145 (1925).

[10] Fowler, Proc. Roy. Soc. **A107,** 31 (1925).

[11] Kayser, "Handbuch der Spectroscopie."

[12] Fowler, Monthly Notices **70,** 692 (1920).

uniform over the spectral region investigated. However, with the exception of the red region the sensitivity of the eye is greatest where that of the photographic plate is least, which gives a check upon intensity errors. The observations on hydrogen are less precise, because of the red color of H alpha.

It is easily seen from the table that the appearance of the lines is not in the order of increasing wave-lengths or in the order of integrated intensities, yet the value of the intensity of any given line usually varies over such wide ranges during the discharge that the integrated intensity is not a measure of its actual intensity at the time of observation. In the case of magnesium, cadmium and zinc, at least, the spark lines appear before the arc lines. In the sharp arc triplet of zinc the members appear in the order of increasing wave-lengths, while in the corresponding triplet in cadmium the sequence is different.

In the processes connected with the emission of each of the members of the above triplets the electron falls from the same $2s$ energy level to different $2p_{1,2,3}$ energy levels so that the sequence in the time of appearance of the lines of these triplets indicates definitely the importance of the final energy level ($2p_{1,2,3}$ in this case) in determining the average time between excitation and the beginning of emission.* The same kind of a result is also found in NII spectrum where the d—d' group appears before the p'—d' group. It will be noted that in the NII spectrum, the p—s group appears before the p—p' group and the latter before the p—d group. In the emission of these groups the electron falls from different initial energy levels to the same final energy levels so that this sequence illustrates the well known importance of the initial energy level in determining the time of the beginning of emission. Unfortunately the resolving power of the spectroscopes used was not sufficient to determine the time of appearance of the different members of the above groups of NII.

A photometric study of the rate of increase of intensity of the members of the zinc and cadmium triplets and an extension of the present work into the ultra-violet region are now in progress and promise to give more

* In emphasizing the importance of the final energy level in determining the time of the beginning of emission, the above results suggest, although they do not prove, that the electron might not remain in the initial energy level the total time between excitation and emission, but falls to the final energy level and remains a definite average time there before the energy is radiated.

information on the processes taking place between excitation and emission.

In conclusion I should like to express my thanks to Professors C. M. Sparrow, L. G. Hoxton and F. L. Brown for many valuable suggestions and criticisms, and to Mr. A. J. Weed, instrument maker, for help in the construction of apparatus.

ROUSS PHYSICAL LABORATORY,
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June 7, 1926.