THE ELECTRODELESS DISCHARGE IN CERTAIN VAPORS.

BY J. K. ROBERTSON.

SYNOPSIS.

Appearance and Spectrum of Electrodeless Discharge in Various Vapors.—The discharge was produced by electromagnetic induction, the bulbs containing the vapors being placed within a Tesla coil through which passed a high-frequency condenser discharge. The effect was found to *vary with vapor pressure*, controlled by the temperature, *and with electromotive force*, controlled by a spark gap. In general, for a certain range of pressure, an intense ring discharge was obtained which weakened to a faint luminosity for higher pressures. *Potassium* at temperatures of 250–300° C., gave a bright ring with a spectrum including seven or more members of each subordinate series. The bright yellow discharge in *sodium* above 300° C. showed the *D*-lines, four members of the diffuse series and three members of the sharp series. With *lithium* up to 500° C. only a feeble discharge due to impurities was obtained. In the case of *mercury*, the work of Kowalski was confirmed and extended. A dazzling white ring discharge appeared from 70 to 110° C. or higher depending on the spark gap; then became fainter, while a greenish glow whose spectrum showed a few lines superposed on a continuous band extending from the violet to the yellow, appeared for 110 to 115° C., *irrespective of the spark gap.* It is suggested that the glow may be associated with polyatomic molecules formed at the higher vapor pressures. In the case of *iodine*, the only diatomic vapor studied, at temperatures from − 5° to 5° C. a pale yellow ring showing a band spectrum changed to a green, pink-bordered ring with a line spectrum when the spark gap was increased; the higher the pressure, the greater the spark length necessary to excite the line spectrum. The change probably accompanies dissociation of the molecules into atoms.

Electrodeless Discharge as a Source of Sharp Lines should be of value in measuring wave-lengths and in analyzing, with an instrument of high dispersion, lines with components due to isotopes.

ALTHOUGH the subject of investigation by Sir J. J. Thomson as long ago as 1892, the electrodeless discharge has been utilized but little by spectroscopists. Some time ago it occurred to the writer that it might be worth while to try to obtain this type of discharge in the case of the more easily vaporized metals. Because of the comparatively simple conditions of discharge, combined with the absence of electrodes and the ease with which ordinary impurities can be avoided, it was thought that much valuable information might be gained from such a spectroscopic study. Circumstances have not made possible as yet an exhaustive investigation, but enough has been done to show that this type of discharge provides a most useful source for the study not only of the vacuum arc spectrum of such metals as sodium and potassium, but also, as in the case of the diatomic vapor of iodine, of the change in the spectrum brought about by dissociation. Since the investigation was undertaken, it has been noted that McLennan[1] made use of this type of discharge in his work on the spectral series of mercury, while Kowalski[2] examined the change in the appearance of the discharge in the same vapor with changing temperature. Hagenbach and Frey,[3] moreover, have made a preliminary report of a spectroscopic study of the discharge in many gases and vapors. It will be seen below, however, that these writers, in the case of sodium and of iodine, failed to obtain the proper discharge. Quite recently Dunoyer[4] has published a report on the spectrum of cæsium, obtained also from the discharge excited by electromagnetic induction.

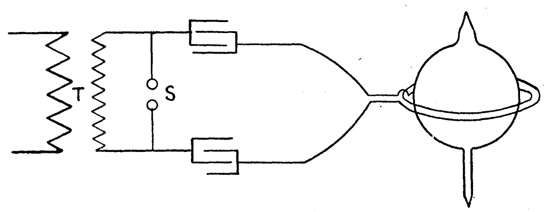

Fig. 1.

The experimental arrangement differed little from that first used by Sir J. J. Thomson. A bulb, some 12 cm. in diameter was suspended inside a coil of six co-planar turns of stout copper wire through which passed the high-frequency oscillatory discharge of two Leyden jars connected as shown in the diagram (capacity of each $5–7 \times 10^2$ absolute electrostatic units). A clearance of some two to four millimeters existed between the outside of the bulb and the innermost turn of the coil. The jars were charged in some cases by an induction coil but subsequently by means of a small interrupterless x-ray transformer T, while the spark gap S enabled one to control the intensity of the exciting field inside the bulb. It may be noted here that Bergen Davis[5] has shown that the mean value of the electrical intensity inside the bulb is directly proportional to the potential at the spark gap.

By means of a Langmuir condensation pump with auxiliary, the bulbs of pyrex glass were exhausted to a pressure of the order of 0.0002 mm. Hg., he flame of a large Meker burner being played over each of them for an hour during exhaustion. The vapor of the element to be used was then distilled over from a side tube, and the bulb finally sealed off both from the side arm and from the pumps. In the case of sodium,

[1] J. C. McLennan, Proc. Roy. Soc., A, 87, p. 256.
[2] J. Kowalski, Phys. Zeit., XV., No. 5, p. 249.
[3] Hagenbach and Frey, Phys. Zeit., XVIII., p. 544, 1917.
[4] M. L. Dunoyer, Comptes Rendus, Tome 175, No. 6, p. 350.
[5] Bergen Davis, Phys. Rev., Vol. XX., p. 129, 1905.

before sealing off from the pumps, the metal was "chased" about the bulb a number of times to drive off as much as possible occluded hydrogen.[1] The bulb to be used was then suspended within the primary coil, which in all cases so far studied except iodine, was inside an electric oven. In this way vapor pressures corresponding to temperatures as high as 500° C. could be obtained if necessary.

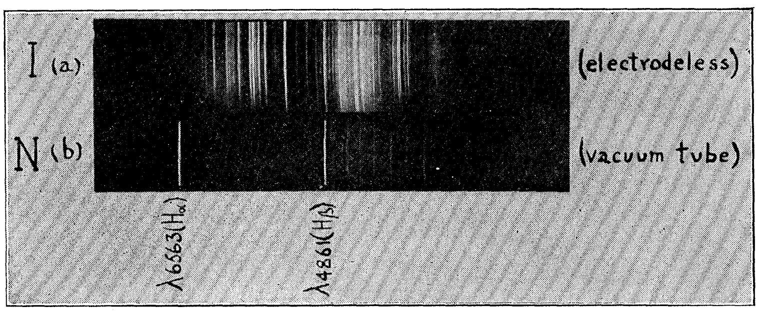

Fig. 2.

IODINE.

To obtain the discharge in iodine a projecting stem of the bulb was immersed in a vessel containing melting ice. It was found that two distinct types of ring discharge could be obtained. With a spark gap of the order of 1 mm., the ring had a pale yellow appearance, probably the same color as the chamois yellow which Wood[2] describes. Examination with a spectroscope of small dispersion showed a continuous band extending from red to green, then a wide absorption band, followed by a second apparently continuous band in the blue-violet. As the spark gap was increased in length, the appearance of the ring changed abruptly to a pale green ring with an inner pink border, the latter extending to a slightly greater distance above the plane of the coil than the green luminescence. The spectrum of this second type of discharge showed numerous bright lines, with faint continuous background in the red region. Photograph *a* in the accompanying plate is a photograph of the spectrum of the "green" discharge, made with a Hilger constant deviation spectrograph. The abrupt change in the appearance of the discharge is doubtless the result of dissociation, the pink border probably corresponding to the lesser degree of dissociation one might expect in the weaker electric field nearer the center of the bulb. It was at first thought that the pink luminosity might be due to nitrogen present as an impurity,

[1] R. W. Wood, Researches in Physical Optics, Part II., p. 178, 1919.

[2] R. W. Wood, Researches in Physical Optics, Part II., p. 53, 1919.

Wood[1] having observed that color in insufficiently exhausted iodine vacuum tubes. It will be seen from the plate, however, that there is no trace of nitrogen as far as one can judge from *b*, the comparison spectrum

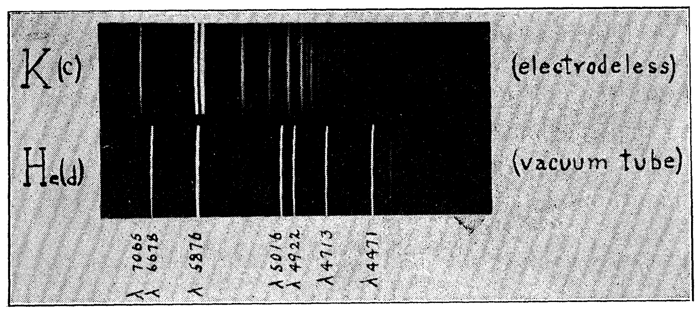

Fig. 3.

of a nitrogen vacuum tube (with hydrogen impurity). Observation with a small direct-vision spectroscope directed successively at the green and the pink portions of the ring showed that the lines in the pink were much feebler than in the green. This is what one would expect from a smaller degree of dissociation.

By varying the temperature of the bath in which the stem was immersed, it was shown that both types of ring discharge could be obtained at vapor pressures corresponding to temperatures lower than $-5°$ C. and higher than $+5°$ C. With increasing pressure, a longer gap was required to bring out the line discharge. This again is just what one would expect, because the higher the pressure, the shorter the free path of an electron or ion and so the greater the electric intensity necessary to give the electron the energy required to bring out the line spectrum.

As the pressure rises higher and higher, a stage is reached at which the discharge is accompanied by a general and comparatively feeble luminosity filling part or all of the bulb. It is not surprising that Hagenbach and Frey, who apparently worked with iodine only at room temperature, found the discharge in this case not brilliant.[2]

By slowly changing the spark gap, an attempt was made to see which line, if any, first became visible during the transition from the band to the line spectrum. A line approximately λ 4860 seemed to flash in first, although others followed so quickly that it was difficult to determine this conclusively. In this connection it is interesting to note that, if we apply the quantum relation, $eV = h\nu$, λ 4860 corresponds to a radiating poten-

[1] Researches in Physical Optics, Part II., p. 53, 1919.

[2] "Doch bildet sich die Ringentladung . . . nicht schön aus."—Hagenbach and Frey, loc. cit.

tial of 2.54 volts, while the value obtained for the resonance potential of iodine by direct experiment by Mohler and Foote[1] is 2.34 ± .2 volts. Moreover, Smyth and Compton,[2] in their work on the ionization of fluorescing iodine vapor, obtained 2.6 volts as a rough value for the quantum of absorbed radiant energy. This agreement, however, is probably purely accidental. Working with hydrogen, Franck[3] has shown that, in order to bring out the complete line spectrum, a voltage must be applied which is greater than the ionizing potential by an amount equal to the work of dissociation. It is probable, therefore, that in all diatomic gases the simple quantum relation cannot be applied without correction.

POTASSIUM.

At temperatures ranging from 250° to 300° C. no difficulty was experienced in obtaining a bright ring discharge in the case of potassium. The ring which is not so sharply defined as in the case of iodine, consists of a pale green portion, with an outer border of orange yellow. If the electrical intensity is great enough, a distinctly violet region is seen next the bulb. The spectrum shows the ordinary arc lines, as will be seen from photograph *c* in Fig. 3 where *d* is a comparison spectrum of helium. It was not possible with the small dispersion of the spectroscope to make any exact measurements of wave-lengths. Lines of the first and second subordinate series as far as λ 4805 were easily identified. Then followed a group of two or three faint lines, then λ 4757 (rough setting), then a group of seven or eight or more, until λ 4643 was read. This last is no doubt the combination pair 4642.17 and 4641.58 recently observed by Datta.[4] Further in the violet region lines were observed at values approximately λ 4607, λ 4506, λ 4390 and λ 4314. It would seem, therefore, that with this source one may obtain if anything higher members of the subordinate series than those measured by Datta.[5]

The sodium D lines always came out strongly, and at times the red sodium lines at λ 6161 were faintly visible. A few unidentified lines were visible, for the most part very faintly, although one at λ 5007 and another at λ 4831 were at times moderately intense.

As his source of light Datta used a potassium vapor lamp, similar in construction to the sodium lamp devised by Lord Rayleigh,[6] but much more troublesome to operate than the sodium. With the electrodeless

[1] Mohler and Foote, PHYS. REV., Vol. XV., No. 4, p. 321, 1920.
[2] H. D. Smyth and K. T. Compton, PHYS. REV., Vol. XVI., p. 501, 1920.
[3] J. Franck, Phys. Zeit., XXII., p. 468, 1921.
[4] S. Datta, Proc. Roy. Soc., A, 99, April, 1921.
[5] S. Datta, loc. cit.
[6] R. J. Strutt, Proc. Roy. Soc., A, 96, p. 272, 1919.

arrangement no difficulty whatever was experienced, and it was found that observations could be extended over a series of days. Indeed, a bulb which has been used on four or five different occasions, is only slightly discolored and may still be used for further observations.

Such a source, moreover, because of the low vapor pressure at which the luminous discharge occurs, should be suitable for a study of the structure of single lines. If potassium is a mixture of two isotopes, as recently shown by Aston, one might expect each line of a doublet to be made up of two components. It might be well worth while, therefore, to examine the structure of some of the potassium lines from the above source with a sufficiently high resolving power. Making use of the difference in wave-lengths obtained by Merton[1] for different specimens of lead (0.002 Å.u.–0.005 Å.u.) one might expect for potassium lines a separation of possible components approximately (0.002–0.005) × 207/40 or (0.01 Å.u.–0.025 Å.u.). The echelon at the disposal of the writer, however, has not a resolving power sufficiently high to detect a difference of that order.

Sodium.

In the case of sodium at temperatures above 300° C. a brilliant yellow discharge filling almost the whole bulb was obtained. In addition to the D lines, the first four doublets of the diffuse series were identified, as well as the first three of the sharp series. The Balmer lines of hydrogen, the most likely impurity, were not visible. Hagenbach and Frey[2] observed only the D lines in the immediate neighborhood of a piece of the metal placed in the bulb, although they obtained a ring discharge showing mercury, nitrogen and carbon dioxide. Apparently their bulb was not exhausted thoroughly, nor was the sodium sufficiently vaporized.

With sodium an induction coil was used for charging the Leyden jars. With excitation similar to that used in the case of potassium and iodine, and at a temperature considerably above 300° C., it is highly probable that more and stronger lines would be brought out. As a matter of fact, evidence has been obtained of a more brilliant discharge in the case of a bulb excited in this way, but unfortunately because of a "short" which developed between the primary coil and the oven no observations were possible.

Lithium.

By courtesy of the Metallurgical Department of Queen's University, a small quantity of lithium of unknown purity was obtained, and a bulb prepared. By using an iron capsule in the side tube a small quantity of

[1] Merton, Proc. Roy. Soc., A, 679, p. 388, 1920.

[2] Hagenbach and Frey, loc. cit.

metal was vaporized and deposited in the bulb, but although the oven was heated as high as 500° C., nothing but a feeble discharge due to impurities was obtained.

MERCURY.

In common with Kowalski,[1] the writer observed with mercury, two distinct types of discharge—the first a dazzling white ring, the second a diffuse greenish glow which filled the whole bulb. The ring discharge showed numerous lines, the number increasing with increasing spark gap. One set of visual observations showed some 24 lines ranging from λ 6234 to λ 4339, twenty of which were identified with standard mercury lines belonging to the triplet, single line and combination series. Unidentified lines were observed at approximately $\lambda\lambda$ 6122, 5026, 4959. The spectrum of the greenish glow showed a continuous band upon which λ 5461 was superimposed, as well as λ 4959 and λ 4355, if the intensity was great enough. The continuous band seemed to end abruptly towards the red end at the two yellow lines.

The brilliant white discharge could be obtained at temperatures ranging from 70° to 110° C. or higher, the exact temperature at which it disappeared increasing with increasing spark gap. On the other hand, observations made with spark gap 1 mm., 2 mm., 4 mm. and 6 mm. in length indicated that the temperature at which the glow begins (110°–115°) is *independent* of the electrical intensity. The origin of the continuous spectrum, therefore, is probably closely connected with the density of the vapor. Very recently R. W. Wood [2] has made the statement that mercury vapor can be made to fluoresce only when freshly liberated from the fluid metal, and suggests that the formation of diatomic molecules is necessary for the phenomenon of fluorescence. That such a grouping of atoms is possible is evident from the work of Sir J. J. Thomson on Positive Rays, in the course of which he showed that even at the low pressures obtaining in his discharge tubes, it was possible to have clusters of four mercury atoms with a single positive charge. As such groupings would occur much more readily at vapor densities corresponding to temperatures over 100° C., it would seem that the "radiators" of the continuous spectrum are to be found in such clusters, an idea which has been previously suggested by more than one writer.[3]

With the temperature of the vapor approximately constant (at say 90° C.), observations were made at various spark lengths. It was found that below a minimum gap length (of the order of 0.5 mm.), the bright

[1] J. Kowalski, Physik. Zeit., 15, 225, 1914.
[2] R. W. Wood, Proc. Roy. Soc., A, 700, p. 362, 1921.
[3] C. D. Child, Science, Sept. 10, 1921. Horton, Phil. Mag., Vol. 22, p. 214, 1911.

white discharge gave place to a faint white luminosity whose intensity was greater in the plane of the coil, while above this length, the ring discharge appeared. At the critical stage, when the ring flashed in intermittently, the spectrum showed the five lines λλ 5791, 5770, 5461, 4916 and 4358. On increasing the gap, other lines quickly made their appearance.

In conclusion, the writer would like to emphasize the difference in the behavior of a diatomic vapor like iodine compared with that of monatomic vapors. It would seem that useful information concerning the spectra of diatomic gases, such as hydrogen, might be gained by a study of their electrodeless discharge, and it is planned to make such a study in the near future. The work planned includes an examination of the discharge in CO_2 and N_2O, to see if there is any similarity in the spectra of these two gases, whose molecules on the cubical atom theory of Lewis and Langmuir have almost identical electron structures.

Queen's University,
Kingston, Ont.,
October, 1921.

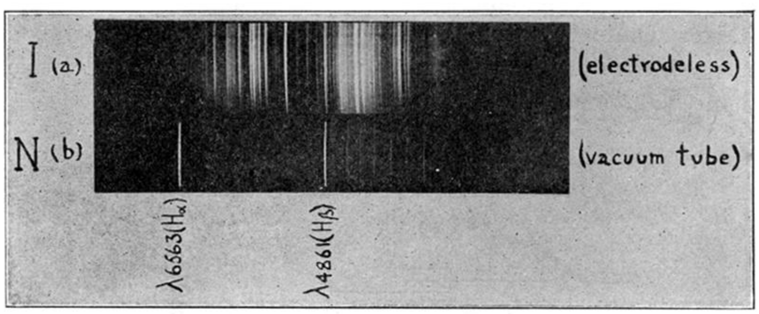

Fig. 2.

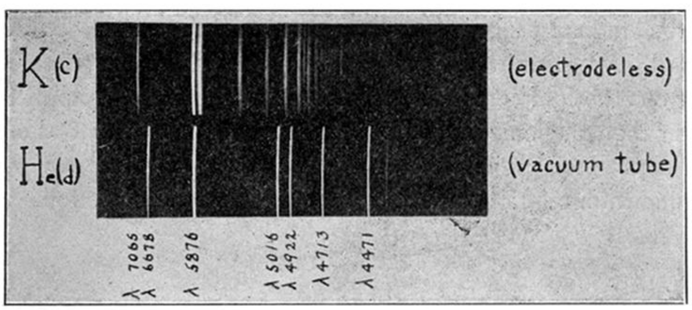
K (c)
(electrodeless)
He (d)
(vacuum tube)
λ 7065
λ 6678
λ 5876
λ 5016
λ 4922
λ 4713
λ 4471

Fig. 3.