



## LXIX. On the spectra of the electrodeless ring discharge in certain gases

H. Donaldson B.A. B.Sc.

**To cite this article:** H. Donaldson B.A. B.Sc. (1911) LXIX. On the spectra of the electrodeless ring discharge in certain gases , Philosophical Magazine Series 6, 22:131, 720-727, DOI: [10.1080/14786441108637169](https://doi.org/10.1080/14786441108637169)

**To link to this article:** <http://dx.doi.org/10.1080/14786441108637169>



Published online: 20 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)

With the current 5.1 amperes the greatest sparking-distance between the two spheres was found to be 11.2 centimetres.

To sum up, the results given above show that the expression (1) represents in its main features the wave of potential at the terminals of the secondary coil when a current is interrupted in the primary, and that it also gives the order of magnitude of the maximum secondary potential. In each of the cases described above some uncertainty with regard to the maximum potential arises from the fact that the amplitude of the oscillograph curve is not always the same with the same primary current; and although each curve was photographed a number of times and the curve of greatest amplitude selected for measurement, we could never be quite certain that the greatest possible amplitude was actually obtained.

Similar differences are observed with other kinds of interrupter. In Plate XIII. fig. 15, are shown the curves of secondary potential at two successive interruptions of the primary current produced by a motor mercury-interrupter of the centrifugal type. The coils and condenser in action at the time were the same as in Case VII.

Bangor, July 1911.

---

LXIX. *On the Spectra of the Electrodeless Ring Discharge in certain Gases.* By H. DONALDSON, B.A. (Camb.), B.Sc. (Lond.), Scholar of Sidney Sussex College, Cambridge\*.

IN an ordinary discharge tube with electrodes, the interpretation of the differences in the spectra of a gas in different parts of the tube is rendered difficult by the separation which takes place between the positive and negative ions.

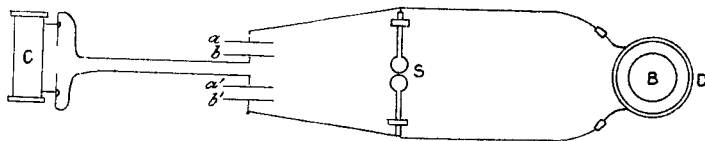
It was thought, therefore, that a study of the spectra of gases in the oscillatory ring discharge, in which a permanent separation between the ions would be unlikely, might afford useful information concerning the dependence of the spectra upon the strength of the ionizing field.

#### *Apparatus.*

The bulbs in which the discharge was obtained were usually about 8 cm. in diameter and were surrounded by a coil of half a dozen turns of well insulated wire wound closely so that the depth of the coil was about 2 cm. The plane through the centre of the coil parallel to the windings was also a

\* Communicated by Professor Sir J. J. Thomson.

diametral plane of the bulb and was vertical. The method of getting the oscillatory discharge in this coil is shown in the diagram.



$a, b, a', b'$ , are the terminals of two leyden-jars,  $a', b$  being connected to the secondary of a Cox induction-coil, and  $a, b'$ , to an adjustable spark-gap  $S$ . To this spark-gap were connected also the terminals of the coil  $D$ , which was placed round the discharge-bulb  $B$  in the manner described. Variations in the intensity of the discharge through  $D$  were obtained by altering the frequency of the hammer-break of the induction-coil, the length of the spark-gap, and the size of the leyden-jars. In the experiments the spark-gap varied between 2 and 15 mm., and the leyden-jars were usually two gallon jars.

The exhaustion of the bulb and the apparatus was carried out by a Toepler mercury pump, and then by charcoal and liquid air, exhaustion to a pressure below that at which any discharge would pass being obtained in each case before the admission of the gas to be examined.

The observing spectroscope was a Hilger constant-deviation instrument in which the wave-lengths of the lines observed could be read directly from a graduated revolving drum. In all cases the gases admitted to  $B$  had been dried by passing through, and being left for some time in contact with, one tube of calcium chloride and two tubes of phosphorus pentoxide, each about 50 cm. long.

### *Method of Experiment*

When the discharge-bulb had been exhausted as above some of the gas to be examined was admitted to the apparatus, which was then gradually exhausted by liquid air and charcoal until the highest pressure at which the true ring discharge would pass was reached. If the spectrum of the discharge gave no indication of the presence of elements other than those composing the gas under observation, the pressure of the gas in the bulb was lowered gradually until no discharge could be obtained, and the spectrum observed at the different stages of this exhaustion. This process was then

repeated, and the effect of variation in the length of the spark-gap and the frequency of sparking was studied.

In all cases, at pressures considerably above the highest at which the ring discharge took place, a feeble electrostatic discharge was seen in the bulb, due to the windings of the surrounding coil not being all in one plane, but this was never used in observations of the spectra.

### *Results.*

*Residual Air* :—The apparatus was washed out several times with air before exhaustion. The spectrum of the discharge was chiefly the positive band spectrum of nitrogen at the highest pressures at which the true ring discharge was obtained, and the colour of the ring was red. At lower pressures many of the nitrogen lines appeared and became very bright as the lower limit of pressure was reached. The negative band spectrum never came out distinctly, even if it were present at all.

Air in which phosphorus had been burned to remove oxygen was then tried and gave the same spectra, a spiral immersed in liquid air being inserted between the inlet apparatus and the bulb to remove the phosphorus and mercury vapours.

Both with residual air and with this deoxygenized air there was an orange after-glow, which persisted brightly for about half a minute after the electric field was removed, and faintly for a much longer time. This afterglow was observed down a tube about a metre long in line with the collimator of the spectroscope. While the discharge was still running the same orange colour could be seen in the centre of the bulb, and its spectrum was continuous throughout the yellow-blue region, but had two places of maximum intensity. As soon as the discharge was cut off, the continuous part of the spectrum died out, but the regions of maximum intensity remained as the spectrum of the true after-glow, in the form of two bands, diffuse on either side and having their centres approximately at wave-lengths 5760 and 5378 tenth-metres, and having a breadth of about 10 such units.

As the first occasion on which this afterglow was observed was one on which there was a possibility of the presence of phosphorus vapour, an entirely new apparatus was set up, but the spectrum remained unchanged.

*Hydrogen* :—The gas was prepared by the action of pure dilute sulphuric acid, to which a trace of copper sulphate solution had been added, upon pure metallic zinc. In the outer of the two rings which constituted the discharge, all

four hydrogen lines appeared at every electric intensity that could be used, though at the highest pressures for the discharge the secondary spectrum was also quite bright. In the inner ring at the pressure for the best discharge, using a short spark, only  $H_{\beta}$  and  $H_{\gamma}$  were present. On increasing the spark length  $H_{\alpha}$  and  $H_{\delta}$  appeared and became brighter as the spark was still further increased. This association of  $H_{\alpha}$  with  $H_{\delta}$  and  $H_{\beta}$  with  $H_{\gamma}$  had been observed previously on several occasions with preliminary residual air-bulbs, but in those cases it was always  $H_{\alpha}$  and  $H_{\delta}$  which appeared with the shorter spark gap.

*Carbon dioxide*:—The gas was prepared by the action between a solution of pure sodium carbonate and pure dilute sulphuric acid. As in almost every gas, the discharge at the highest pressures was always reddish in colour, probably owing to the presence of a trace of water vapour, but the true colour of the carbon dioxide discharge was dark blue, changing to whitish blue as the pressure decreased, or as the spark-gap and frequency of sparking increased.

The spectrum observed was, in every case, the carbon band spectrum although all possible variations of electric intensity, by varying spark-length, spark frequency, and size of leyden-jars were tried.

*Carbon monoxide*:—The gas was prepared by the action between pure strong formic and sulphuric acids, and on its way to the discharge bulb passed through a spiral tube immersed in liquid air, to remove such impurities as mercury vapour.

Until the apparatus had been washed out some few times with carbon monoxide, the spectrum observed was always the carbon band spectrum. When the carbon monoxide was more pure, the spectrum of the discharge, when a small spark-gap and small leyden-jars were used, was still the carbon band spectrum, but as the spark-length was increased to about 4 mm. the Swan spectrum began to appear and grew in brightness relative to the carbon band spectrum as the spark was still further lengthened. The appearance or disappearance of the Swan bands could be obtained by altering the spark-gap about 1 mm. at the critical length.

At lower pressures, the Swan bands were obtained without so great a lengthening of the spark-gap. The spectrum was the same when large jars were used, but in this case the spark-length could not be made so great and the Swan bands were never quite so bright as with the smaller jars.

*Oxygen*.—The gas was prepared by heating pure potassium

permanganate, and was left in contact with solid potash for some time before it was admitted to the apparatus. The bulb in which the discharge was secured was first exhausted and then washed out six times with oxygen, exhaustion to a pressure below that at which any discharge would pass being carried out after each washing. When the pressure of the gas in the bulb was just low enough for the true ring discharge to pass, the colour of the ring was brick-red, especially on the inner edge, and the spectrum seen was the compound line spectrum. On reducing the pressure, a fairly bright continuous spectrum appeared in the blue, superposed on the compound line spectrum, and this further developed into bright oxygen bands, those having their centres at wave-lengths 5590 and 5245 being especially distinct.

At a still lower pressure, the bright lines of the elementary line spectrum began to flash out brightly at certain instants when the discharge was running well, and ultimately they became steadily bright while the intensity of the bands decreased. The violet lines of the elementary line spectrum were especially bright. The only line which persisted throughout the whole range of pressures was the red (6157).

An attempt was made to produce the changes in the spectra at a medium pressure merely by varying the spark-gap and the frequency of sparking. By increasing these, it was found that the elementary line spectrum appeared at a higher pressure than that at which it appeared with smaller spark-gap and frequency. The band spectrum remained in this case with the larger spark-gap, but rather more faintly.

*Argon* :—Certain colour changes occurring in the ring discharge in argon have already been obtained and described \* and an attempt was made to repeat those observations and to examine the colour changes spectroscopically. The argon first used contained a small percentage of nitrogen which appeared in the spectrum of the light from the inner part of the bulb during the discharge.

At no pressure could any trace of the red argon spectrum be seen, but the blue spectrum was very bright, about 30 lines being measured. A portion of the argon, mixed with pure oxygen, was then sparked for three hours over potash. The excess of oxygen was removed by phosphorus, and the argon remaining was used for the discharge, after the bulb had been washed out several times with it. In this case, at the highest pressures, the ring was red and of the 12 lines measured every one belonged to the red argon spectrum. At an intermediate pressure the number of bright lines

\* Strutt, *Phil. Mag.* xlix. p. 293 (1900).

increased and about 50 were measured, distributed amongst the red and the blue spectra. At the lowest pressures, all the lines belonged to the blue spectrum, but there was practically nothing to be seen in the region between wave-lengths 5879 and 5144. An afterglow having the same orange colour, and giving the same spectrum as the afterglow described in the case of air, was observed in this purified argon at all pressures except the higher and lower limits.

In addition to the above gases were tried hydrochloric and hydrobromic acids, sulphur dioxide, and carbon disulphide. In the case of hydrochloric acid at medium pressures the ring was bluish on the outer edge and reddish on the inner, the difference in colour being due, apparently, to the presence of the hydrogen secondary spectrum in the inner part of the ring. At low pressures the red colour disappeared and the blue extended nearly to the centre of the bulb. The spectrum of the blue part of the ring was the four-line spectrum of hydrogen and the chlorine line spectrum. Hydrobromic acid behaved in a similar manner. The sulphur compounds always gave the sulphur line spectrum and never the band spectrum. In the case of carbon disulphide, the bulb was coated inside with a deposit of sulphur after the discharge had been running. The spectrum of the carbon was the ordinary band spectrum, and not the Swan.

### *Conclusion.*

These experiments clearly indicate a dependence of the spectrum of a gas on the electric field responsible for ionizing the gas. In most cases the results support those obtained previously from observations of the discharge spectra of gases in tubes with metal electrodes\*. In such tubes the intensity of the electric field has been shown to be greater round the cathode than in the positive column, and should also be greater in the intermittent spark discharge with a leyden-jar in circuit than in the continuous discharge. Now in the case of oxygen, the presence of four different emission spectra under different conditions has been shown†; the elementary line spectrum in the leyden-jar discharge, the band spectrum in the negative glow of the continuous discharge, the positive line spectrum in the positive column in a narrow tube, and the continuous spectrum in a wide tube with a weak discharge. In the ring discharge the elementary line spectrum is characteristic of the discharge at

\* Stead, Proc. Roy. Soc. lxxxv. (1911).

† Schuster, Phil. Trans. clxx. p. 37 (1879), and others.

the highest electric intensities used, the band spectrum at intermediate intensities, and the compound line spectrum at the lowest intensities. The only possible difference between the results obtained by the two methods is connected with the continuous spectrum, which in the discharge tube appears at the lowest intensities and in the ring discharge at an intensity between those for the compound line and the band spectra. As considerable doubt has been cast upon the existence of a continuous spectrum in pure oxygen in a discharge tube \*, it is probable that the one observed in the ring discharge is independent of that in the tube discharge. The existence of a band spectrum occupying a position intermediate between two line spectra of the same element is interesting in view of suggestions that have been made to ascribe line spectra to atomic, and band spectra to molecular, systems.

Another case which is interesting from the point of view of the ring discharge is that of the Swan spectrum and the carbon band spectrum. The Swan spectrum only appears in carbon monoxide when it is very nearly pure, and then at a high intensity, and we may have the same bulb showing the carbon band spectrum at a low intensity and the same, mixed with the Swan spectrum, at a higher intensity. As, under the influence of the discharge, carbon dioxide would dissociate into carbon monoxide and oxygen, it would obviously be very difficult in this case to get a sufficient electric intensity in the carbon monoxide itself to cause the appearance of the Swan spectrum. This would also be the case with any impure carbon monoxide, and therefore it would seem possible that the carbon band spectrum and the Swan spectrum may be the low and high intensity spectra of the same substance, though these experiments afford no clue as to whether that substance is carbon monoxide, or carbon in some other form.

In the cases of nitrogen and residual air the ring discharge is peculiar in that it has never shown any clear evidence of the presence of the negative band spectrum, the variation from the positive band spectrum to the line spectrum taking place directly. A bulb containing cyanogen, which was not sufficiently pure to give its own band spectrum, showed a change from the positive to the negative nitrogen band spectrum with increasing electric intensity, but this was never observed in nitrogen itself. The general results agree with those given by discharge tubes in assigning the positive band spectrum in nitrogen to the weakest ionizing fields, and

\* Baly, 'Spectroscopy,' p. 443.



the line spectrum to the strongest, between them being the negative band spectrum.

The ring discharge would appear to be a somewhat powerful method of examining the spectra of slightly impure, or of mixed, gases; as in several cases, particularly those of argon and oxygen, the characteristic spectra of the elements have appeared at stages of purity at which they would have been quite absent in the ordinary vacuum-tube discharge.

In view of the influence of electric intensity on spectra, it would be interesting to study by this method the spectra given by a gas having multiple spectra, when that gas is mixed with traces of different impurities.

In conclusion, I wish most heartily to thank Professor Sir J. J. Thomson for the suggestion at which these experiments were begun, and for his kindly interest and advice throughout their progress.

Cavendish Laboratory, Cambridge.

May 8, 1911.

## LXX. *On the Separation of Spectra in Compound Gases.*

*By G. STEAD, B.A., formerly Scholar of Clare College, Cambridge\*.*

**I**N a previous paper† I have described some experiments in which evidence was obtained that a process somewhat akin to electrolysis can occur in gases at low pressure. Compound gases or vapours through which an electric discharge is passed at a pressure of the order of a millimetre usually show the spectra of certain constituents better developed at the anode, whilst the spectra of other components appear more brightly at the cathode. Moreover elements which show a preference for the anode are such as must be supposed on chemical grounds to carry a negative charge, and *vice versa*. Thus in the case of hydrogen chloride the hydrogen spectrum is seen chiefly at the cathode and chlorine lines mainly at the anode. This is partly analogous to what occurs in the electrolysis of a solution of concentrated hydrochloric acid. The present paper gives an account of further work on the same subject, and for a description of the apparatus and method of manipulation the former paper must be consulted.

(i.) *Ethane*.—The gas was prepared pure by the action of distilled water on zinc ethyl.

\* Communicated by the Author.

† Proc. Roy. Soc., August 1911.