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THE RECOMBINATION OF ARGON IONS AND ELECTRONS

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ABSTRACT

Afterglow spectrum in argon due to recombination.—The arc spectrum of argon is found to persist approximately 0.001 sec. after an arc of 0.4 amp. in pure argon at 0.5 mm pressure is cut off. Lines involving jumps from high energy levels are relatively much stronger in the afterglow than in the arc. When sodium vapor is present the D lines are strong in the arc but absent in the afterglow showing that the electron speeds in the afterglow are too low to excite the spectrum of argon by direct electron impact. The highly excited argon atoms must therefore be produced by the recombination of ions and electrons. The presence of 0.001 mm of hydrogen does not affect the intensity of the afterglow so that the persistence of metastable atoms is not involved in the production of the afterglow.

Effect of applied potentials on the afterglow.—Accelerating voltages of 3 to 10 volts quench the afterglow during the period of application of 0.001 sec. Retarding after-voltages up to 90 volts have practically no effect. Measurements with an intermittently connected exploring electrode show that the velocities of the electrons are increased by the applied accelerating voltage but unaffected by the retarding voltage. The quenching is apparently the result of the decreased probability of recombination because of the higher velocities of the electrons. When low accelerating voltages have been applied for 0.001 sec. the intensity of the afterglow and the conductivity of the arc space in the period immediately following this application are both greater than they would be had the voltage not been applied. The intensity of the afterglow is thus directly related to the concentration of positive ions and the quenching of the afterglow shown to be connected with a saving up of ions as it should be if the effect of the after-voltages is to prevent recombination.

Ordinary arc spectra are obtained under conditions which are here most unfavorable to the occurrence of recombination. They are presumaly primarily excitation spectra. The use of intermittent discharges for obtaining recombination spectra and strong high series members is suggested.

The measurements show positive ion concentrations in the afterglow of the order of 10^{12} per cc. The mean energy of the electrons is 0.4 volt. From the measured rate of change of the concentration of ions, there results a value of 2×10^{-10} for the coefficient of recombination. This value may be in error by a factor of 5 because of several unavoidable errors.

WHILE experimenting with a rapidly interrupted low voltage arc in argon and using a synchronously rotating sectored disc and a spectroscope, the writer noticed a striking afterglow. This afterglow persisted several thousandths of a second after the arc was cut off, as was shown by varying the time between the cut-off of the arc and the exposure of the slit of the spectroscope.

The argon at a pressure of 0.5 mm was purified and kept pure by circulating it over a misch-metal arc. The mercury diffusion pump used for circulating the gas was placed between two liquid-air traps so that no mercury vapor reached the experimental tube. The arc took place in a bulb 8 cm in diameter, between a hot oxide-coated platinum filament and a plane tungsten anode, about 1 cm square, mounted 0.5 cm away. The arc current was about 0.4 amp. and the arc voltage 15.5, nearly the ionizing potential of argon.

The afterglow became brighter with the purification of the argon and was found to consist of a large number of bright lines distributed throughout the visible spectrum, and of especial brilliancy in the green. Detailed spectroscopic examination showed that all these lines were arc lines of argon, but with an intensity distribution markedly different from the distribution obtained in the ordinary arc spectrum, the high series members being relatively enhanced in the afterglow.

Spectroscopic Study of Afterglow

The afterglow was photographed with a Hilger glass, constant deviation, spectrograph and with a small Hilger quartz spectrograph. The bulb containing the arc was provided with a quartz window, and the arc space was focussed, by means of a quartz lens, on the slit of the spectrograph. The sectored disc of 10 cm radius revolved a few millimeters in front of this slit, and was so adjusted on the commutator shaft that at the point of cut-off of the arc, the distance yet to be traversed by the edge of the sector before exposure of the slit was about 4 mm. There was thus no possibility of light from the arc itself getting into the spectrograph. The commutator and sectored disc were run at about 1800 r.p.m. and there were two interruptions of current per revolution. The distance of 4 mm thus corresponded to about 0.0002 sec. which was therefore the time between the arc cut-off and the exposure of the slit. Exposures of from 1 to 44 hours were made, some very good photographs being obtained at 12 hours. Eastman Astronomical Green Sensitive plates were used for the green, Cramer Contrast plates for the violet and ultra-violet, Ilford Panchromatic plates for the red and Eastman Extreme Red Sensitive plates for the extreme red. In all about 160 lines were measured on photographs of the afterglow and identified with argon arc lines listed in Meissner's[1] classification of the arc spectrum of argon. Comparison photographs of the afterglow and of the arc showed that, in the afterglow, lines involving jumps from high s and d states to the $2p$ states were very much stronger with respect to $1s-3p$ and $1s-2p$ lines than in the arc. This difference was very striking, and made the two spectra look entirely different at first sight. On arranging the $2p-md$ and $2p-ms$ lines in their respective series and comparing the intensities in the afterglow and in the arc it was found that within each individual series, the high series members were relatively enhanced in the afterglow. Table I shows two such comparisons which are typical of all. This relative enhancement of high series members and the fact that the $2p-md$ lines are relatively so much stronger than the $1s-3p$ lines, indicates that the excited gas producing the afterglow is relatively much richer in atoms in the high excited states than the excited gas in the ordinary arc.

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[1] Meissner, Zeits. f. Physik, **37**, 238 (1926); **39**, 172 (1926); **40**, 839 (1926–27).

TABLE I. *Illustrations of relative enhancement of high series members in afterglow. Comparison of direct arc and afterglow intensity of* $2p_{10}-md$. *Arc exposure = 5 sec; afterglow exposure = 12 hours.*

m	Afterglow Intensity	Direct Arc Intensity	m	Afterglow Intensity	Direct Arc Intensity
5	6	10	5	15	20
6	4	2	6	14	8
7	2	0	7	10	1
8	3	—	8	8	0
9	1	—	9	2	—
10	3	—	10	3	—

Two simple explanations of the production of this afterglow can be offered. (1) The atoms are excited by electrons of high velocity present after the applied voltage is cut off because of a persistence of space charge effects. The different distribution of intensities would indicate a different distribution of velocities from that of the arc. (2) The excited atoms result from the recombination of positive ions and electrons. That (1) is incorrect and (2) is the true explanation is strongly suggested by the observed facts concerning the emission of the *D* lines of Na.

BEHAVIOR OF THE *D* LINES OF SODIUM

Quite accidentally, sodium had been introduced along with the oxides used in coating the filament. This sodium was dislodged from the filament fast enough to give a small trace of sodium vapor in the arc space, so that in the arc itself the *D* lines were the brightest lines in the field of view. In the afterglow the *D* lines were entirely absent. They could be induced in the afterglow however by the application of arc accelerating voltage of 4–11 volts in the after period. An experiment with an auxiliary arc, having a clean hot tungsten wire for a cathode, and placed about 2 cm away from the main arc, showed that the *D* lines were emitted strongly in the auxiliary arc provided only that the main oxide filament was lighted. Sodium vapor must therefore have always been present in the arc space.

The argon lines emitted in the afterglow showed the presence of argon atoms in excited states which were only 0.084 volt below ionization, the spectroscopic term values for which were as low as 684 wave-number units ($13\ d_4 = 684$ cm^{-1}). Therefore argon atoms were present in the afterglow having energy of excitation of 15.6 volts with respect to the normal argon atoms and of 3.9 volts with respect to the metastable $1s_3$ state of argon, but the absence of the *D* lines showed that there was no appreciable number of electrons present having energies as great as 2 volts. These excited argon atoms could not therefore have been produced by direct electron impact. The excitation of the *D* lines by the application of small accelerating voltages is in agreement with this point of view.

The argument is greatly strengthened by the results of the following experiment which was suggested by Professor J. Franck. Hydrogen at a pressure of several thousandths of a millimeter was admitted with no appreciable diminution of the afterglow. This would presumably have precluded the possibility of metastable argon atoms persisting so long. The afterglow is therefore definitely not connected with the presence of metastable atoms. The excited atoms which emit the observed lines could not be produced, therefore, by the excitation of mestastable excited atoms by impact with 3.9 volt electrons but would necessitate the presence of 15.6 volt electrons for their production by single impact. The production of the excited argon atoms by recombination of positive ions and electrons would, however, lead to the emission of the argon arc spectrum, without the emission of the *D* lines, provided the concentration of sodium ions was of a smaller order of magnitude than that of the argon ions.

Discussion of Spectroscopic Results

Miss Hayner[2], using an interrupted arc in mercury vapor, found just such an afterglow as occurs in the present experiment, the high series lines being relatively enhanced in the same way. She also ascribed this afterglow to emission by excited atoms resulting from recombination. Her conclusion that the electron speeds in the afterglow were too low to cause direct excitation was based mainly on the relative weakness of the 2537 line. The argument is somewhat similar to that presented here with respect to the behavior of the *D* lines. It seems to be somewhat more certain in the present case because of the much greater disparity of the voltages concerned.

Mohler[3] has obtained spectra of Cs and K under conditions favorable to the recombination of ions and electrons which he ascribes to recombination. In these spectra there is just such a relative enhancement of the high series lines as is found in the present experiment, and the *F* and *D* series are enhanced relatively to the *S* and *P* series. Mohler also finds continuous spectra in these cases extending beyond the series limits, and a broadening of the lines near the limits. The fact that continuous spectra have not been detected in the present experiment may be connected with the much greater complexity of the argon term system, each continuous region of Mohler's spectra being analogous to a set of ten or a dozen continuous regions in argon spread over a considerable range of wave-lengths. These many overlapping continuous regions would be much harder to detect. Other observers have also found spectra which they ascribed to recombination.[4]

Stroboscopic Study of the Effects of After-voltages

In order to be able to view the afterglow at any point in the cycle, and to study the effects of after-voltages, a stroboscopic device was arranged. This consisted simply of a disc with sectors 2 mm wide cut out to

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[2] Hayner, Zeits f. Physik, **35,** 365 (1925).

[3] Mohler, Phys. Rev., **31,** 187 (1928).

[4] Rayleigh, Proc. Roy. Soc., **A108,** 262 (1925) and **A112,** 14 (1926); Paschen, Sitzungsber. d. Pr. Akad., p. 135, 1926; Stark, Ann. d. Physik **52,** 255 (1917); Belasse, Comptes Rendus, **184,** 1002 (1927).

correspond with the commutator segments, mounted on the same shaft as the commutator, and placed about 15 cm in front of the arc. By placing the eye close to the disc and following it around slowly in the direction of its motion, all the different stages of the arc and of the afterglow could be viewed in succession. First the arc itself was a relatively small red ball of light about 1 cm in diameter surrounding the cathode. After the cut-off of the arc, the afterglow could be seen as an intense yellowish green ball of light starting from a diameter of a centimeter or so and very rapidly expanding to fill uniformly a space several centimeters in diameter, and then gradually diminishing in intensity until just before the next cycle it had practically disappeared.

If the disc were viewed from the distance of several feet, the appearance was somewhat as shown in Fig. 1. The area *A* appears reddish in color and is the area from which light from the arc comes to the eye. Thus *A* corresponds to the "on" period of the arc. *A′* is a narrow dark transition region to be mentioned later. The area represented by *B* and *C* together is yellowish green, being illuminated by the afterglow, and is bright at the left side of *B*, gradually becoming fainter until at the right side of *C* it is dark. The arrow indicates the direction of motion of the disc. The distance represented by the width of area *A* corresponds to a time of about 0.001 sec., which is therefore the time of duration of the arc.

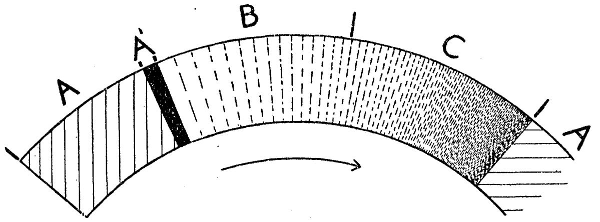

Fig. 1. Appearance of sectored disc rotating synchronously in front of interrupted arc; eye several feet from disc. Period *A* (0.001 sec) represents direct arc and is red in color. Period *A′* (0.00025 sec) is a dark transition region. Periods *B* and *C* represent the afterglow and are yellow-green in color.

The commutator had extra segments which made it possible to apply any desired voltage in period *B*. With positive voltages, the afterglow was quenched in period *B*. This effect, beginning at about +2 volts was quite marked at +4 volts and amounted to a complete extinction at +8 volts. With positive voltages greater than 11, the "abnormal" low voltage arc in argon began to appear, so that *B* was illuminated with reddish light. Negative voltages up to 90 volts, applied in period *B* had no effect on the afterglow except a very slight weakening in the neighborhood of the cold electrode. This latter result agrees with the results of Miss Hayner.[2]

When the arc space was observed in period *C*, with the eye close to the disc, it could be seen that the luminosity in this period was increased by applying positive potentials of 3 or 4 volts in period *B*, but was quenched by applying positive potentials as large as 8 or 9 volts in period *B*.

Reverse potentials up to 90 volts during *B* had no effect on the luminosity in *C*. An auxiliary commutator was now arranged so that a third arbitrary voltage could be applied during period *C*. The currents which could be passed during *C*, with either a small accelerating voltage (3 or 4 volts), or a large negative voltage, were found to increase by as much as 20% when accelerating potentials of 3 or 4 volts were applied in period *B*. On the other hand these currents would decrease from the normal value by about this percentage if a positive voltage of 8 or 9 volts were applied during *B*. Reverse voltages in period *B* up to 90 volts had no effect on the current in *C*.[5] The current which can be passed in period *C* is presumably proportional to the average concentration of ions in the space during that period, so that luminosity and ion concentration are found to go hand in hand, being increased and decreased by the same agency. This is rather striking evidence that the afterglow is connected with recombination, probably more striking, for instance, than if the ion concentration and luminosity were found merely to decay in a way roughly compatible with recombination, in which case the agreement might be fortuitous since obviously both must be falling off with the time.

The afterglow described by Miss Hayner[2] did not appear immediately upon the cut-off of the arc, but appeared only after an intermediate period of about 0.00024 sec., during which time the line 2537, the only line present, fell away in intensity. This intermediate period she explained as a time during which the electron speeds were decreasing, at the end of which they became low enough for recombination to set in. Then followed the afterglow with the high series lines strongly developed. That the same intermediate period exists in the present experiment is evidenced by the narrow dark transition area *A′* between *A* and *B* of Fig. 1. It was found possible to increase the intermediate period to several times its ordinary value by connecting a condenser of 8 mf capacity across the arc. This is, however, nothing more than a method for applying a temporary, changing, positive after-voltage which produces a quenching effect as the steady after-voltages do.

The experiments described below indicate that the positive after-voltages do raise the average velocity of the electrons so that Miss Hayner's explanation of the effect seems to be correct. The width of the normal transition dark space in the present experiment, indicates that certainly within a few ten thousandths of a second after the arc cut-off the electron speeds have fallen to a value low enough to permit recombination. Miss Hayner[2] does not specifically mention any effect of accelerating voltages on the afterglow but does explain the lack of effect[6] of reverse voltages as resulting from a shielding by space charge sheaths.

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[5] Eckart, Phys. Rev. **26**, 454 (1925).

[6] See also Compton and Eckart, Phys. Rev., **25**, 139 (1925).

PROBE WIRE MEASUREMENTS

Since the probability of recombination presumably decreases with increase of the speed of the combining electrons,[7] the quenching effect of the accelerating voltages applied in the after period can be ascribed to a decrease of the probability of recombination resulting from the speeding up of electrons. The ineffectiveness of large retarding voltages would have to be ascribed to the formation of a space-charge sheath around the negative electrode, outside of which the conditions would be unchanged.

Professor K. T. Compton suggested the use of Langmuir's exploring electrode method to get direct experimental evidence as to the velocities of the electrons. Accordingly a 5 mil probe wire about 3 mm long was placed 1.5 cm from the oxide cathode. Connection to this probe was made through an auxiliary commutator, the brushes of which could be rotated around the shaft as axis to any desired position. The width of the segments and brushes were such that the probe remained in circuit for a time corresponding to a rotation of the shaft of 15.5°. The total angle corresponding to the after-period of the arc was about 60°, so that within the limits defined by a rotation of about 45°, the probe could be put in circuit at any desired time after the arc had been cut off. Probe potentials were measured with respect to the arc electrodes which except in special cases were short circuited during the after period.

Langmuir and Mott-Smith[8] showed that where a single group of electrons is present having a Maxwellian distribution of velocities, and in the case of steady currents, the logarithm of the electron current if plotted against the applied voltage should give a straight line over the range of voltages at which the probe is negative with respect to the space around it. The slope of this straight line gives a measure of the mean speed of the electrons. The method is believed to give reliable measurements of electron speeds also in the present case, where the probe is used intermittently, because experiments with steady arcs using the probe first continuously and then intermittently gave the same type of curves and the same values of electron speeds in each case.

Fig. 2 shows a typical example of a large number of curves obtained with this intermittent use of the probe in the afterglow. In this case the probe was in circuit from 0.00064 sec. to 0.0026 sec. after the arc was shut off. The pressure was 1.6 mm and the arc current 0.4 amp. The curve, although not a straight line, can be compounded fairly well of two straight lines, each one representing a group of electrons having a Maxwellian distribution of velocities. Straight line *I* was drawn first, and from this and the experimental curve, straight line *II* was obtained by subtracting the currents represented by corresponding ordinates. The mean energies of the two groups of electrons as calculated from the slopes of the two straight

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[7] Milne, Phil. Mag., **47**, 209 (1924), Mohler.[3]

[8] Langmuir and Mott-Smith, Gen. Elec. Rev., **27**, pp. 449, 538 (1924). A short summary of the method is given by Compton and Eckart,[6] Phys. Rev., **25**, 139 (1925).

lines were 0.9 volt for the high speed and 0.40 volt for the low speed group. It is evident that the choice of straight line *I*, and hence the determination of the mean speed of the fast group is somewhat uncertain. A relatively large change in the slope of this line, however, is necessary to cause an appreciable change in the slope of line *II*, so that the mean speed of the low speed group is probably determined within 10%. The space potential, chosen at 3.6 volts is subject to a probable error of several tenths of a volt.

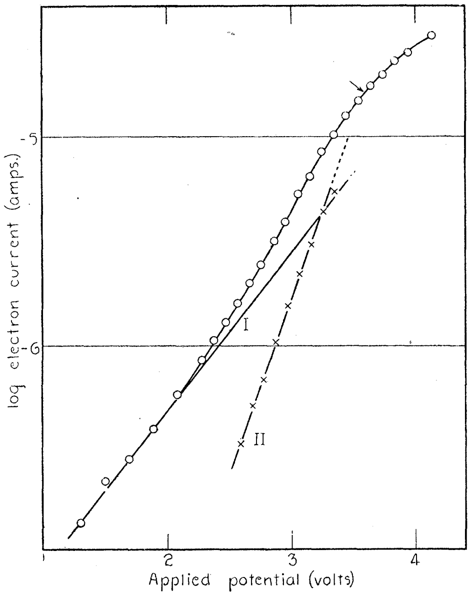

Fig. 2. Current-voltage characteristic of probe, used intermittently in afterglow.

Similar curves taken at various times after the cut-off of the arc, showed that the mean electron speed and the space potential, both being presumably kept up by a positive ion space charge, remained sensibly constant for several thousandths of a second after comparative equilibrium had been reached a few ten-thousandths of a second after the arc cut-off. After this time the currents to the probe became too small for convenient measurement. Currents could usually be measured with a microammeter, a galvanometer being used for currents as small as 10^{-7} amp. More sensitive instruments were not employed, to follow the decay of ionization further, on account of a small transient current, of about 1×10^{-7} amp., which seemed to be caused by capacity or inductance effects accompanying the interruption of the main arc.

EFFECT OF AFTER VOLTAGES ON ELECTRON SPEEDS

With the arrangement of commutators it was possible to take probe measurements in the afterglow superposing any desired after-voltage on the arc electrodes. These after-voltages were applied during period *B* (see Fig. 1) which lasted from 0 to 0.003 sec. after the arc was shut off. Connection was made with the probe wire between 0.0006 and 0.0024 sec. after the arc cut-off. Pure argon at 1.6 mm was used in these experiments. The arc current during period *A* was 400 ma. The results are summarized in Fig. 3. Curve *I* shows the mean speed of the slow group of electrons plotted against the after-voltage. The slow speed group is presumably the group taking part in the recombination. It is seen from the curve that positive after-voltages above 2 volts increase the electron speeds, while reverse voltages up to 90 volts have no appreciable effect. That the increase in electron speeds sets in only at +2 volts is believed to be due to contact difference of potential between the tungsten anode and oxide coated filament. As the positive after-voltage is increased from 2 to 7.5 volts, the mean speed of the slow group of electrons increases by a factor of 5. The mean speed of the fast group was also found to increase from 1 to 6 volts approximately over this range. The quenching of the afterglow by positive after-voltages is now perfectly explained on the theory of recombination since it is certain that the probability of recombination decreases rapidly as the electron speeds increase.[7] The failure of even large reverse voltages to affect the afterglow is thus also perfectly explained, inasmuch as the velocities of the slow electrons and the space potential in the region of the probe are unchanged.

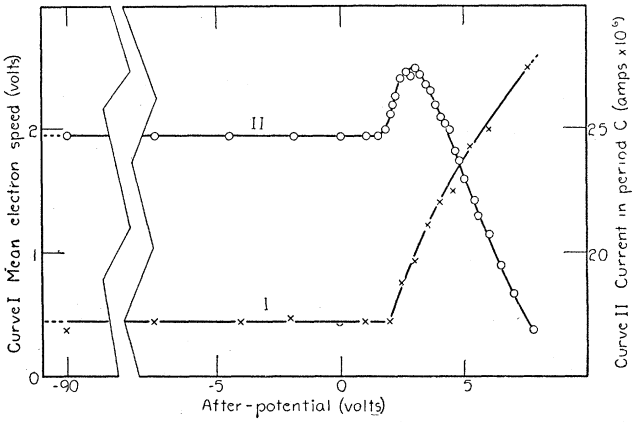

Fig. 3. Effect of after-voltages on electron speeds and subsequent conductivity. I. Variation of mean speed of electrons in afterglow with applied voltage. II. Variation of current in period C with voltage applied in period *B*. Current is between arc electrodes with accelerating potential of 4 volts.

If the ions have been prevented from recombining during period *B*, there should be more of them left over in period *C*, provided that they have not been swept out of the space by the same field which speeded up the electrons and provided that the rate of disappearance of ions from the space by recombination is not normally negligible compared with the rate of disappearance by diffusion to the walls. Curve *II* (Fig. 3) shows the current which could be passed between the arc electrode in Period *C*, with a positive voltage of 4 volts, plotted against after-voltages in period *B*. Large negative voltages were also used in period *C* and quite similar curves were obtained. Such currents are presumably proportional to the average ion concentration in period *C*. It is seen from the curve that negative voltages during period *B* have no effect on the current during period *C*. This agrees with the results of Eckart[5] in a similar experiment with helium. On the other hand, with positive voltages during *B* the currents during *C* are first increased and then decreased, as the voltage is made higher. Moreover, the intensity of the light in period *C* first increased and then decreased in exactly this way. Both phenomena, which are undoubtedly a manifestation of the same thing, are in accord with expectations, the increase in current and light intensity in period *C* being ascribed to a saving-up of the ions during period *B* because of the decreased rate of recombination, the decrease with higher voltages resulting from a sweeping out of the ions by the larger fields. The first of these effects must eventually be outweighed by the second since there are only a limited number of electrons present in the first place. The saving-up effect would be expected to appear before the sweeping-out effect because the rate of recombination decreases rapidly, probably with the fourth power[3] of the electron speeds, or square of the electron energies. The electron energies, however, have been found to increase roughly in proportion to the applied after-voltage over the small range of voltage here considered, so that the rate of recombination should decrease as the square of the after-voltage. On the other hand the rate at which ions are swept out by the field probably increases only in proportion to the applied after-voltage.

The increase of current in period *C* occurs with the application of positive voltages in period *B* which are between 2 and 4 volts. In view of the contact difference of potential, these applied voltages probably correspond to an actual potential drop across the arc space of between 0 and 2 volts. These voltages are too low for the ionization of impurities, or of metastable argon even if present. The increase of current in period *C* must therefore be due to a saving up of ions in period *B* and not to the formation of new ions.

The space potential with regard to the oxide coated electrode was not affected by the application of negative potentials up to 90 volts, but remained at about 3.6 volts above it. A positive ion space charge sheath must in these cases exist around the cold electrode in such a way as practically completely to shield the space from it. The whole applied potential drop must exist between this sheath and the cold electrode. On the other hand when accelerating after-voltages were applied, the space potential did not change with respect to the anode remaining about 3.6 volts above it. Thus in this case there is a shielding space charge of positive ions around the hot cathode. But in this case, however, a large current (10^{-2} amp.) of relatively fast electrons is being shot into the arc space, and since presumably both fast and slow electrons are leaving the arc space the mean speed of the electrons is raised. With reverse potentials applied in period *B*, the currents obtained were less than 10^{-4} amp.

In connection with the quenching of the afterglow by positive after-voltages it is interesting to note that Miss Hayner[2] apparently did not make spectroscopic observations with positive after-voltages, and that Eckart,[5] in his account of an experiment with an interrupted arc in helium mentions only one case where he looked for an afterglow and that was with a positive voltage superposed. That he failed to observe a recombination spectrum of helium, similar to the present one in argon, is thus sufficiently in accord with our observations.

The present experiment explains in general why recombination spectra have so seldom been observed. The reason is, evidently, that in most gaseous discharges just such accelerating potentials exist as are found in this experiment greatly to reduce recombination. For instance, in the present experiment, the arc, when run continuously, appeared as a small bright ball of light around the cathode. This ball of light was reddish in color because of the relatively great intensity of the low series members. The space around this ball was nearly dark. Probe wire measurements showed, however, that there was a sufficient concentration of electrons and positive ions in this dark outer space to have made it brilliantly luminous with the light resulting from recombination had the mean speed of the electrons been 0.4 volts instead of 2.5, as measured. This light would moreover have been yellowish green in color because of the relative enhancement of the high series members. The spectrum of the arc itself is emitted from a region where the average velocity of the electrons is high, and where therefore the rate of recombination will be low. The spectrum of the arc must, therefore, be primarily an excitation spectrum, and it is thus easy to understand why, in it, lines corresponding to transitions between low levels are relatively so extremely intense.

The present intermittent method of obtaining spectra resulting from recombination is of advantage because in such experiments these are emitted under circumstances in which the electron speeds are far too low to cause any direct excitation by collision. The resulting spectra must therefore be characteristic only of the recombination process.

THE COEFFICIENT OF RECOMBINATION

The saving-up effect, above mentioned, which is caused by small accelerating after-voltages, shows that the rate of disappearance of ions by recombination is at least of the same order of magnitude as the rate of disappearance by diffusion. It should therefore be possible to obtain an estimate of the coefficient of recombination, α, from measurements of the ion concentration at various times after the arc is cut off. The rate at which ions recombine[9] is given by $dn/dt = -\alpha n^2$, assuming that the concentrations of positive ions and electrons are equal. Integration gives $1/n = \alpha t + 1/n_0$

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[9] Townsend, "Electricity in Gases," pp. 188–220.

where n_0 is the concentration at zero time. If $1/n$ is plotted against time a straight line should therefore result, the slope of which will be equal to the coefficient of recombination. A set of measurements of electron concentration was accordingly made by the probe method using Langmuir's expression relating the electron current to the probe at space potential and the electron concentration. The positive ion concentration must have been very closely equal to the electron concentration in these experiments because otherwise a large resultant space charge would have been present which would have been detected by its effect on the space potential. The pressure in this case was 0.8 mm and the arc current was 0.4 amp. The electron concentration decreased from 7×10^{12}/cc to 2×10^{12}/cc in the interval from 0.00025 to 0.0025 sec. after the arc was shut off. The mean electon speed of the slow group of electrons, which was the most important group, remained sensibly constant over this interval, at 0.4 volts. Plotting $1/n$ against t, an approximately straight line was obtained, from the slope of which, α, for electrons of this mean speed, was calculated to be 2×10^{-10}/sec. This value, which, since diffusion has been neglected, represents the upper limit for the coefficient of recombination, may be in error by a factor of 2 because of the uncertainty already mentioned in connection with Fig. 1 in locating the space potential. It may be in error by another factor of 2 because of an uncertainty inherent in the intermittent use of the probe, which although not affecting the measurements of the electron speeds, would affect the measurements of the ion concentration. This uncertainty is evidenced by the fact that currents obtained with the probe used intermittently in a steady arc were about twice as large as those obtained with the probe used continuously in the same arc, considering the ratio of the times during which the probe was connected. The measurements as made however should be consistent among themselves. It is hoped that the present method can be refined so as to give a more accurate determination of the coefficient of recombination, and also by applying suitable after-voltages, to yield quantitative information on the variation of this coefficient with electron speeds.

My best thanks are due to Professor L. A. Turner for his very inspiring guidance throughout the course of this work.

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