LOW VOLTAGE ARCS IN IODINE

By H. F. Fruth

Abstract

Ionizing and radiating potentials in molecular and atomic iodine vapor.—Low voltage arcs in monatomic and molecular iodine vapor were investigated together with their spectra. From a study of the current-voltage curves it was concluded that 6.5 volts is the minimum radiating potential of the atom, 8.0 the ionizing potential of the atom, and 9.5 the ionizing potential of the molecule. Non-oscillating abnormal low voltage arcs were maintained down to 4.9 volts and oscillations were observed around 12 volts. With arc currents of about 2 amperes the filament current could be cut off and the arc sustained indefinitely at 30 volts or above.

Variation with potential of spectra of molecular and atomic iodine.—At 4.9 volts the spectrum contained only three lines, ($\lambda\lambda$2062, 2535, 3135), the continuous band 3460, and several groups of bands. At slightly higher voltages arc lines appear and at 8 volts the strongest spark lines begin. These lines are succeeded by new ones at higher voltages, making it probable that the stripping of the atom is in progress. Peculiar behavior of the lines 2535 and 3135A was observed. Three continuous bands (at 4080, 4300 and 4800A) are present in molecular but disappear in atomic iodine. A band system lying between 2224 and 2050A was observed and two groups of four bands each were found at 2880, 2833, 2776, 2716A and 2480, 2379, 2290 and 2243A.

Introduction

THE connection between the critical potentials of an atom or a molecule and the terms of its spectrum makes the knowledge of the critical potentials of great value in the analysis of the spectrum or as a test of the correctness of such an analysis. One of the difficulties in the identification of the critical potentials of a substance is that of distinguishing between ionizing and radiating potentials. And in case the substance may exist as a vapor in various types of molecules, monatomic, diatomic, etc., it is of great importance to identify the critical potentials with the proper molecule. It is the purpose of this investigation to determine the critical potentials of iodine and to distinguish those of the diatomic molecule from those of the atom. Very little progress has been made in the analysis of the spectrum of the iodine atom and only one of the band systems of the iodine molecule has been extensively investigated. The determination and identification of the critical potentials of iodine will then be invaluable in the problems of the analyses of its line and band spectra.

The critical potentials of iodine that have been reported hitherto are given in Table I.

The agreement between the values reported by different observers is not good, and there is little certainty of the correctness of the interpretations of the critical potentials found. There is no spectroscopic confirmation of any of the critical potentials reported in the table.

TABLE I

Critical potentials of nitrogen. M refers to the molecule, A to the atom. R indicates radiating potential.

Volts	Method	Observers
9.89	Glow Discharge	A. Noyes[1]
10.1 ±.5M	Modified Lenard	Foote and Mohler[2]
2.34±.2MR	" "	" " "
8.0 A	" "	Smyth and Compton[3]
9.4 M	" "	" " "
6.8*	" "	" " "
8.5	Total Current	Found[4]
10.5	Photographic	Foote and Mohler[5]
10.25	Low Voltage Arc	Duffendack[6]
10.0 M	Lenard	Mackay[7]

* Ionizing potential of the fluorescing molecule.

A number of observers have attempted to obtain the line absorption spectrum of iodine in order to locate the first several members of the absorption series. E. J. Evans[8] as early as 1910 found that dissociated iodine vapor has no absorption in the visible spectrum. Angerer and Joos[9] observed no absorption lines in the region 6700 to 2400A though they heated the vapor to 1050°C. Zumstein and the writer, using the former's well-known method,[10] failed to obtain a single line in the region 5800 to 2200A. Fuchtbauer, Weibel, and Holm[11] have, however, recently reported several absorption lines, among them 2062A and 1877A which they suggest as possible first members of the absorption series. Compton and Turner[12] are of the opinion that 2062 is not a resonance line but that it has a final state (in emission) approximately 0.55 volt above the normal state. Turner[13] has recently obtained the spectrum of iodine in the Schuman region and reports some 66 lines. He gives reasons for believing that λ1782.9, having a radiating potential of 6.9 volts is the first resonance line. Among the 66 lines he finds 11 that have a wave number difference of approximately 7600 cm^{-1}. This corresponds to an energy difference of 0.94 volt, and he suggests that this is the separation of the two levels of the spectral term the lowest of which is the normal state. This separation is in fair agreement with the value of 0.9

[1] A. Noyes, Am. Chem. Soc. **45,** 337 (1923).
[2] Foote and Mohler, Phys. Rev. **15,** 321 (1920).
[3] Smyth and Compton, Phys. Rev. **16,** 501 (1920).
[4] Found, Phys. Rev. **16,** 41 (1920).
[5] Foote and Mohler, Phys. Rev. **21,** 382 (1923).
[6] Duffendack, Phys. Rev. **20,** 665 (1922).
[7] Mackay, Phys. Rev. **24,** 319 (1924).
[8] Evans, Astrophys. J. **32,** 1 (1910).
[9] Angerer and Joos, Ann. d. Physik **74,** 754 (1924).
[10] Zumstein, Phys. Rev. **25,** 523 (1925).
[11] Fuchtbauer, Weibel and Holm, Zeits. f. Physik **31,** 523 (1925).
[12] Compton and Turner, Phys. Rev. **25,** 791 (1925).
[13] Turner, Phys. Rev. **27,** 397 (1926).

volt calculated by Franck[14] by extrapolation from the frequency separation of the lowest term in neon.

Method

The method employed in the present investigation is a combination of those of the total current and of the low-voltage arc. The total current passing between an incandescent tungsten cathode and an appropriate anode was measured for increasing values of the difference of potential applied to the electrodes. It has been shown[15] that space-charge-limited currents through neutral gases with elastic impacts are proportional to the three-halves power of the applied potential difference. This condition may be expected to obtain in iodine vapor at voltages below the voltage at which ionization begins. Hence the voltage at which a deviation from this relationship between current and voltage was first observed was taken as a critical potential of iodine. The first marked deviation may ordinarily be expected when the applied potential difference reaches the ionizing potential of the gas. In monatomic gases, however, cumulative ionization becomes an important factor, and in such cases the deviation from the three-halves power law may be expected to occur at the minimum radiating potential.

The increase in current that is obtained after ionization occurs depends largely on the thermionic emission from the filament. When the filament is sufficiently hot, the increase in current becomes large enough so that an arc is said to strike. An arc can easily be made to strike and be maintained at the ionizing potential of a gas and under favorable conditions at the minimum radiating potential.[16] By this means the critical potentials determined by the total current method were checked and interpreted. Spectrograms of the low voltage arcs were also taken in order to get additional information of aid in the interpretation.

The critical potentials of the atom were separated from those of the molecule by operating on vapor in a heated chamber so as to effect a high degree of dissociation of the iodine into monatomic vapor in one case and on vapor in which the degree of dissociation was reduced to a minimum in the other case. It was found possible to maintain a sufficiently high degree of dissociation to cause the critical potentials of the diatomic molecule to be completely absent.

Apparatus

The experimental tube employed is shown schematically in the diagram Fig. 1. The tubes were of Pyrex or Corning G702P glass. There were two removable ground stoppers of Corning G702P glass, one containing four and the other three 100-mil tungsten lead-in-wires. The filaments, anodes and grids were fastened upon these leads by means of platinum clamps furnished

[14] Franck, Trans. Farad. Soc. **21,** 438 (1926). Dymond, Zeits. f. Physik **34,** 553 (1925). Langmuir, Phys. Rev. **2,** 450 (1913).

[15] Richardson & Bozzoni, Phil. Mag. **32,** 426 (1916).

[16] Compton and Mohler, Critical Potentials, Bull. Nat. Res. Council.

with platinum-iridium set screws. With these seven large leads available, various combinations could be made. Usually single or double 12-mil tungsten filaments were mounted at F_1. A tungsten or molybdenum box, A, about 1 cm on each edge was used as an anode. The box had a small slit in each side for spectroscopic observation. Immediately in front of the filaments, F_1, and fastened to the box was a sheet tungsten frame holding a platinum gauze, G. Inside the box and about 3 mm from the end were two pairs of 15-mil or 20-mil tungsten filaments, F_2. At times the gauze was omitted and the tube was used as a simple two electrode tube using the end of the box as an anode. On one side of the bulb was mounted a clear fused quartz window. The ground glass stoppers as well as the quartz windows were sealed with hard De Khotinsky cement which was kept cool by means of complete rings made of lead and brass tubing through which water flowed.

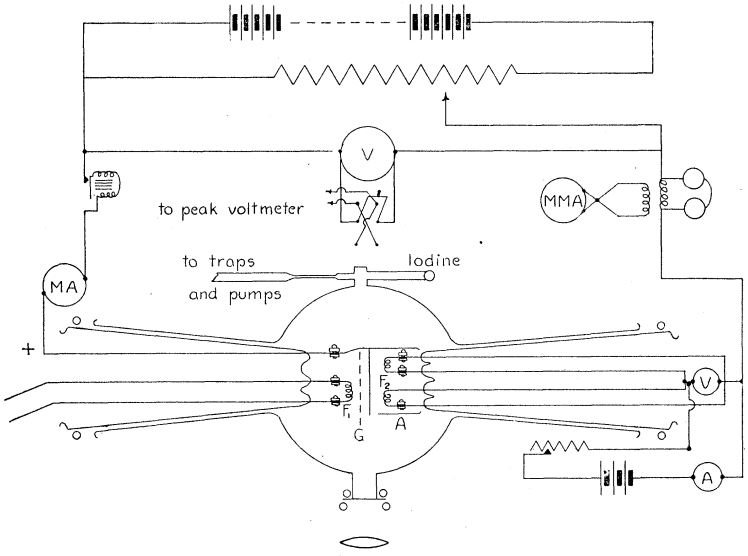

Fig. 1. Diagram of apparatus and electrical connections.

This arrangement allowed rather complete baking and outgassing of the tube and metallic parts. The usual baking was accomplished by means of an electrically heated oven. The filaments were glowed simultaneously, the outside filaments heating the gauze and the inside filaments heating the box to a yellow heat. After a vacuum of 10^{-4} mm or better was obtained, an arc was struck either in nitrogen or iodine or both to the inside and the outside of the box to heat and further outgas the metals.

In the early experiments iodine was introduced into the tube by means of a glass capsule that had previously been evacuated and filled with iodine. After the baking and the outgassing was completed these capsules were cracked open by electrically heating a tungsten wire by means of which the capsules were suspended from the leads. This method, at first suc-

cessful, finally proved a failure. In the flowing process these capsules would sometimes explode and break the entire experimental tube. A side tube containing a large quantity of iodine was later attached. An ice bath was kept on this tube during the baking and glowing process, after which the iodine could be driven into the experimental tube by applying heat. The iodine tube was then heated to drive off absorbed gases. A bath of the desired temperature was then placed on the iodine tube and the iodine was driven back by the baking oven. Two large liquid air traps were placed between the tube and the pumps. A capillary at *C* prevented a too rapid diffusion of iodine into the liquid air traps and gave the desired vapor pressure of iodine in the experimental tube, all parts of which together with connecting tube and windows were kept hotter than the bath on the iodine. Vapor pressures were determined from the curve of Baxter and Grose.[17]

The arrangement was adaptable to both molecular and atomic investigations. When molecular data were desired the outside filaments were used either alone or in connection with a gauze. The gauze as well as the large area of the box anode served to radiate and conduct away much of the heat, thus keeping down the degree of dissociation in the impact region. The gauze also prevented dissociated iodine near the filament from diffusing into the force field between the gauze and the plate.

When investigating atomic iodine the inner filaments were employed. The outer filaments were also glowed to give additional heat and to make up heat losses on that side of the box. With this arrangement no difficulty was experienced in maintaining a high degree of dissociation inside of the box as will be seen later from the results obtained.

The apparatus described above was the final equipment used in obtaining all the results reported in this paper. Preliminary runs were taken with other tubes containing metals other than tungsten, molybdenum and platinum. Very pure and well cleaned iron, copper and nickel were tried and anomalous results were obtained. Iodine attacks these metals forming polarizing, insulating or conducting layers. Some of these layers vaporize readily. At one instance a layer of a dark rubber-like compound covered a nickel anode so completely that only a small plate current could be drawn. After long heating of the filaments, the layer pealed off and touched the filaments. Its resistance was measured and found very high. Some of the discrepancies among the critical potential values obtained by former experimenters can possibly be accounted for by impurities in the tubes caused by the use of metals attacked by iodine. In the final tube only tungsten and platinum, and at times, molybdenum were used. If great care was taken as to cleanliness of the inside of the tube, these metals were left quite unaffected by the action of the arc. In the region near the arc the tungsten came out clean and white, though molybdenum and platinum suffered a slight discoloration. Molybdenum caused a slight brown discoloration of the inside of the tube after continuous runs aggregating up to 90 hours for one "loading" of the tube.

[17] Baxter and Grose, J. Amer. Chem. Soc. **37**, 1061 (1915).

The electrical connections are schematically given in Fig. 1. The potential difference applied to the electrodes was obtained from high capacity storage batteries and was applied to the box and the negative end of the filaments. Its value could be varied by controlling rheostats. This potential difference was corrected to that which obtained between the middle of the filament and the plate by subtracting from the reading of the voltmeter half of the potential drop across the filament. This has been found to be an adequate total correction to reduce voltages read on the voltmeter to the true average accelerating potential of the electrons in low voltage arcs.[18] The plate current was read by means of a Cambridge and Paul unipivotal instrument. A low resistance radio-frequency transformer was also placed in the plate circuit. The secondary was connected to a sensitive thermocross which in turn was connected to a micrometer. This device was a very sensitive detector of oscillations. When oscillations were observed, their peak and minimum voltages were measured by means of a peak voltmeter.

RESULTS

Determination of ionizing potential of molecular iodine. After the tube had been thoroughly baked out and the metallic parts outgassed, iodine was allowed to enter the tube to any desired vapor pressure. The pumps were kept going to sweep out impurities that might accumulate during a discharge. The anode voltage was varied through a series of steps and the corresponding plate currents recorded. A large numbers of such runs were taken using various numbers and sizes of filaments and various distances and arrangements of filaments, gauze and plate. Some resulting current-voltage curves are given in Fig. 2. These curves are typical of a large number taken under conditions of low dissociation. The filament temperature was kept as low as possible and in several instances iodine vapor was made to flow through the discharge region. While these curves show no sharp arcs, they indicate an ionizing potential of the molecule between 9 and 10 volts. The location of the breaks in the curves was fairly independent of pressure over the range from 0.1 to 1.5 mm, though the breaks seem to be sharper at the lower pressures. The average potential of the breaks in the curves, corrected for fall of potential along the filament and initial velocity of emission of the electrons, was 9.25 ± 0.2 volts. The curves with decreasing voltage always repeated the increasing voltage curves within the experimental error except when an arc was made to strike at voltages above the ionizing potential of the molecule, in which case the arc broke at about 8 volts. In such cases the discharge caused an appreciable amount of dissociation so that the arc could be maintained as low as the ionizing potential of the atom. Most of the curves show a slight amount of ionization near 8 volts even when the current is quite small. Long and careful exposure by means of a small Hilger spectrograph either showed no lines at all or only faint traces of lines and a few bands at about 8 volts, but slightly above 9 volts more band spectra were photographed.

[18] Duffendack and Fox, Astrophys. Jour., **65**, 214 (1927).

Arcs in atomic iodine. In studying the critical potentials of the iodine atom, the filaments inside of the box were used as a source of heat to dissociate the iodine as well as a source of electrons. Four 15-mil or 20-mil tungsten filaments carrying total currents from 40 to 75 amperes were used in most of the runs. The box was heated to yellow heat estimated at about 750°C.

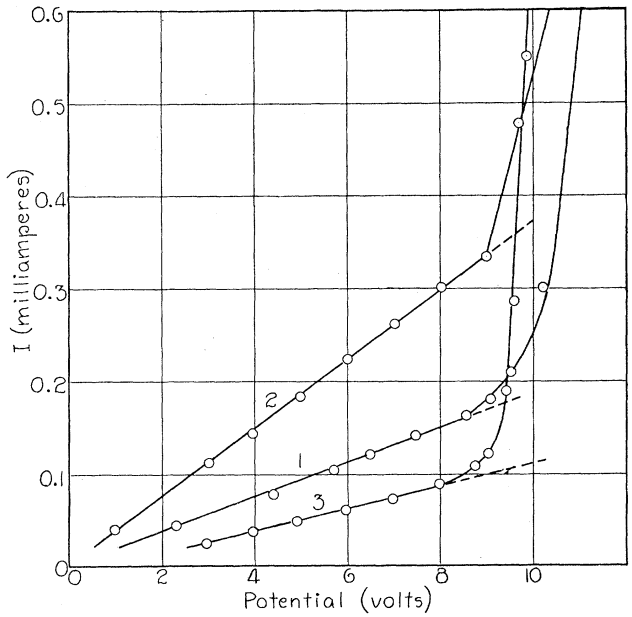

Fig. 2. Current-potential curves in iodine vapor in which there is little dissociation. Curve 1, pressure 0.5mm, I scale×1; curve 2, pressure 0.15 mm, I scale×1; curve 3, pressure 1.5 mm, I scale×2, vapor flowing.

Calculations upon the basis of the work of Stark and Bodenstein[19] on the thermal dissociation of iodine vapor show that iodine is completely dissociated at a temperature of 1200°C at pressures up to 5 mm. The percent of dissociation at 727°C at various pressures covering the range employed in this work are given in Table II.

TABLE II

Dissociation at various pressures of iodine vapor at 727° C.

Pressure	Percent	Pressure	Percent	Pressure	Percent
0.113 mm.	95.	0.699 mm.	81.	2.15 mm.	63.5
.305 mm.	89.5	1.02 mm.	75.5	3.08 mm.	57.
.469 mm.	85.	1.49 mm.	69.		

Thus the dissociation of the iodine vapor near the filaments was always complete and that near the inner surface of the box anode large.

[19] Stark and Bodenstein, Zeits. f. Electrochemie, **16**, 966 (1910).

By setting the applied potential or the filament resistance very critically, an oscillating arc could often be obtained. At one time the arc potentials varied between 17 and 26 volts while the plate current varied from 0.7 to 0.86 ampere respectively. At another time the arc oscillated at a frequency of about 900 cycles, as estimated from the pitch heard in the phones placed across the primary of the radio frequency transformer as shown in the diagram Fig. 1. At the same time the micrometer placed across the thermocross read 60 microamperes. The direct arc current was 0.5 amperes and the voltmeter connected across the arc read 11.8 volts. The peak voltmeter showed a difference of about 4 volts between the peak and the minimum. A third example might be of interest. Using the filaments outside of the box and a vapor pressure of 1.60 mm, the arc oscillated at a frequency of about 200 cycles, 2.5 volts above and below the D.C. voltmeter reading of 12.5 volts. The plate current, as read on a D.C. ammeter, was 0.6 ampere.

The above cases of oscillations are typical of many other instances. In no case were radio-frequency oscillations detected and in no case was there any evidence of oscillations when the arc was maintained below 11.8 volts. In a number of instances when oscillations were detected the attempt was made to lower the voltage so as to obtain the so-called oscillating abnormal low voltage arc. It was thought that by obtaining such an arc at lower and lower voltages and measuring its peak at the lowest voltage obtainable one could get an indication of the minimum radiating potential, for it has hitherto been thought that the upper peak is always at or above this potential. Any attempt to lower the voltage by decreasing the applied voltage or increasing the plate current in such oscillating arcs failed. The arc would either break or stop oscillating.

When the oscillations of the arc stopped in the manner described above, the voltage could be brought down considerably so that a non-oscillatory abnormal low voltage similar to those described by Compton and Eckart[20] was obtained. This could also be obtained from an ordinary arc by lowering the applied voltage by decreasing the resistance in series with the arc or by increasing the current through the arc by raising the filament temperature. Such arcs were maintained at voltages ranging from 6.5 volts to 4.9 volts with currents ranging from 0.5 to 2 amperes. In all cases the plate current was large and the conditions such that the dissociation was of a high degree.

Under certain conditions the current would go up enormously when an attempt was made to raise the voltage beyond a certain value. A circuit breaker that would open and close the plate circuit at a given current was inserted in the plate circuit. An arc was then struck and the voltage raised. To prevent too large currents the filament current was reduced. When the potential reached 60 volts, the filament current was zero. Thus the arc became self-sustained. It was possible to hold this self-sustained arc at a potential as low as 30 volts. The filaments were heated by positive ion bombardment, and they together with the arc current heated the box anode to a

[20] Compton and Eckart, Phys. Rev. **25**, 139 (1925).

bright red. The plate current as read on a D.C. ammeter was steady at times and pulsating at other times and ranged from 2 to 4 amperes. This arc could be maintained for long periods permitting its spectra to be photographed with a spectrograph of large dispersion.

Ionizing and radiating potential of the iodine atom. Of the thirty runs that were made with the box anode at 727°C and the vapor more than 57 percent dissociated, twenty-five showed ionization setting in at 6.5 volts and all showed a large increase of current between 8 and 9 volts. Fig. 3 illustrates the manner in which ionization set in. The first change in slope at 6.5 volts points to a minimum radiating potential and the larger and more persistent change between 8 and 8.5 volts to an ionizing potential. The $I-V$ curves

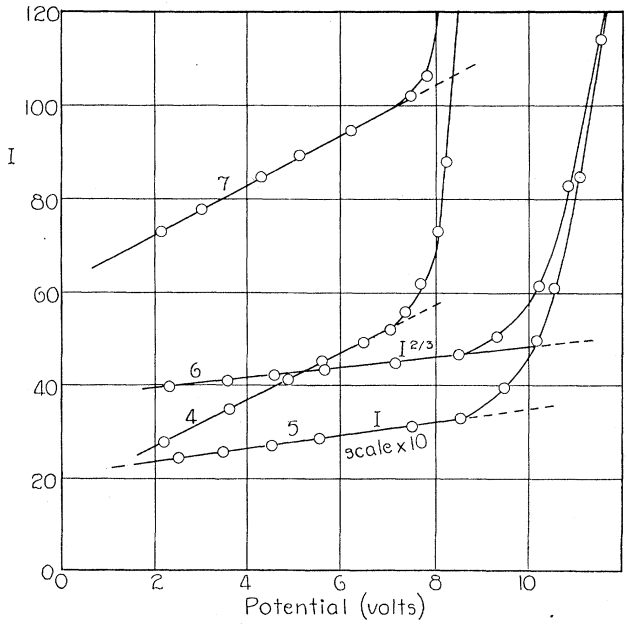

Fig. 3. Current-potential curves for iodine vapor which is more than 57 percent dissociated. Curve 4, pressure 3 mm, I scale×1; curve 5, pressure 2.7 mm, I scale×10; curve 6, pressure 2.7 mm, I scale×1; curve 7 pressure 15 mm, I scale×1.

seem to be linear up to 6.5 volts. This linearity is, however, only apparent, for by plotting them on a more sensitive scale, they have considerable curvatures. In order to test the three-halves power law for space-charge-limited currents through gases when the electrons make elastic impacts, the two-thirds power of the current was plotted against the voltage. Fourteen of these runs covering a wide range of conditions were plotted this way. It was found that a linear relation in these curves existed up to 6.5 volts. The break in the $I^{2/3}-V$ curve occurs between 6.5 and 9.5 volts depending upon condition. Under conditions at which a high degree of dissociation existed, i.e., high temperature or low pressures, the break invariably occurs between 6 and 7 but, not lower, indicating the beginning of inelastic impacts and

ionization by cumulative action. Upon changing conditions so that there is a lesser degree of dissociation, the point where the departure from linearity occurs moves to higher voltages.

A second break occurs at 8.3 volts as seen in Curve 9 Fig. 4. The 8.3 break generally persists in cases where the iodine is largely molecular because dissociation could not be completely prevented. Curve 9 of Figure 4 shows the three effects in one run. The first departure from the straight line occurs

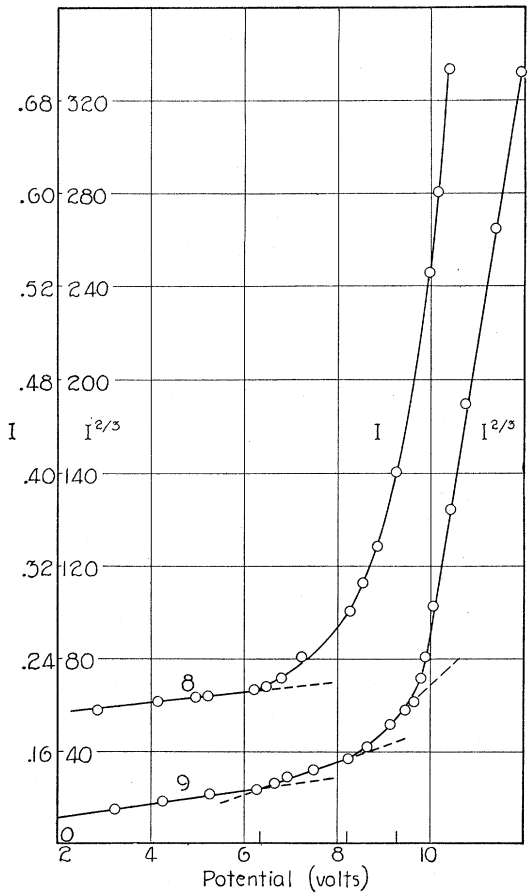

Fig. 4. Current-potential curves for iodine vapor which is largely dissociated, pressure 1.25 mm.

at 6.5 volts, a second break is seen at 8.3 and a third one at 9.5. This, supported by the numerous occurrences of these breaks in many of the other atomic and molecular curves, seems to place the minimum radiating potential of the atom at $6.5 \pm .2$ volts, the ionizing potential of the atom at $8.3 \pm .2$ volts and the ionizing potential of the molecule at $9.4 \pm .2$ volts.

In a recent paper Dymond[21] reports on an investigation of the fluorescence of iodine vapor. He finds that fluorescence can be stimulated by mono-

[21] Dymond, Zeits. f. Physik **34**, 553 (1925).

chromatic light of wave-lengths from λ6438 to λ4995 and that the bands emitted by the fluorescing vapor are of maximum intensity at the wave-length of the stimulating light. The short wave-length limit λ4995 is approximately the long wave-length limit of the continuous absorption band of iodine in this region. Dymond concluded that light of wave-length shorter than λ4995 is absorbed, and, as a consequence, the molecule is dissociated into a neutral and an excited atom: $I_2 \rightarrow I + I_1'$. The heat of dissociation of iodine into neutral atoms, $I_2 \rightarrow I + I$, is 1.4 equivalent volts whereas light of wave-length 4995A corresponds to 2.5 volts. It is suggested that the excited iodine atom absorbs the 1.1. volts excess energy. This would be possible only in case the atom has an energy level 1.1 volt above its normal state, and there is some evidence[13] that this is the case. In view of this, Dymond suggests that the 6.8 volt critical potential reported by Smyth and Compton[3] as the ionizing potential of the fluorescing molecule might be the ionizing potential of an excited atom possessing 1.1 volt potential energy. The sum of these two is 7.9 volts or nearly the ionizing potential reported for the atom.

In the experiments which form the basis of this report, it is certain that a high degree of dissociation of iodine in the region of electron impacts obtained in cases when the box anode was used, and considerable dissociation occurred in all other cases. It would seem more probable that the 6.5 volt potential is a radiating potential of the atom, revealed by ionization by cumulative action and that it depends upon dissociation of a molecule into a neutral and an excited atom and a subsequent ionization of the excited atom. There is at least a strong possibility that the 6.8 volt potential is the same as the 6.5 volt potential determined from these experiments. As yet the analysis of the iodine spectrum has not proceeded far enough to get spectroscopic confirmation of this interpretation, but Turner[13] has expressed the opinion that λ1782.9 is the first resonance line and if so it has a radiating potential of 6.92 volts.

The modern theory of atomic spectra[16] leads one to expect the lowest term in the spectrum of the iodine atom to be a $^2P_{1,2}$ term with the $^2P_2$ as the lowest level and hence the term corresponding to the normal state of the atom. In the light of Turner's[13] investigations the separation of the doublet term is 0.94 equivalent volts. The lines 2062.1 and 1782.9, on this view, originate in a common term, ^2S, and have the excitation potential of 6.92 volts. Since atoms in the $^2P_1$ state may be present in concentration approximating that of atoms in the normal $^2P_2$ state due to the high temperature maintained in the box anode and to the mechanism of ionization, one should expect to find evidences of ionization at 6 volts $(6.92-0.94)$ due to cumulative action on the metastable atoms. As has been mentioned previously, the "break" in the curves at about 6.5 volts was not sharp but occurred between 6 and 7 volts. A critical examination of the curves shows that the break never begins below 6 volts. It is probable, therefore, that cumulative ionization of both normal atoms, $^2P_2$, and metastable atoms, $^2P_1$, is setting in between 6 and 7 volts and that the two "breaks" were not separated. The critical potential thus determined, 6.5 volts, is the mean of the 6.0 and 6.9

voltages necessary to ionize the iodine atoms by cumulative action. The process of ionization suggested by Dymond[21] would lead to a value of the ionizing potential of $6.92+0.94=7.86$ volts which is less than any yet reported. Ionization by this process probably occurs in electric discharges through iodine and according to the results of this investigation should require $8.3-0.9=7.4$ volts. This would still further emphasize the rounded character of the "break" at 6.5 volts. The values of the ionizing potentials of the atom and of the molecule determined by this investigation are in agreement with those of Smyth and Compton.

It was explained in the introduction that very large increases in current might be expected as soon as positive ions are formed. This is in practice seldom realized. The curves instead of having sharp breaks at the critical potentials are rounded. This is due to the distribution of initial velocities of the electrons which has been shown both theoretically and experimentally to be Maxwellian. Another factor entering in here is the distribution of the probabilities of ionization by an electron of sufficient energy. The probability that an electron should ionize an atom or molecule rises from a very small value for an electron with just enough energy to a very large value for an electron of a large excess of energy.[22]

Not even in cases of the striking of an arc are the increases of current as large as might be expected from the theory of space charge neutralization by positive ions. A thousand fold increase at the striking of an arc was hard to obtain even if two to three thousand fold increases are theoretically possible in iodine. This might be explained from a consideration of the conditions in the space between the hot cathode and the anode before the striking of the arc. Immediately surrounding the cathode is a dense electron atmosphere which becomes less dense nearer the anode. Suppose the applied potential difference is above the ionizing potential. Nearly the entire fall of potential is very near the anode. Hence by far the greatest potential gradient is at this place. Only the electrons falling through this potential gradient will have enough energy for ionization. Positive ions are thus formed only near the anode where the electron density is the least. Thus a positive iodine atom will not neutralize its full quota of 1936 electrons and may become neutralized immediately as it passes out of the space of greatest potential gradient and thus pass as a neutral atom into the electron atmosphere where the electron velocity is insufficient for ionization. Since iodine has a very large electron affinity, this atom may even pick up an electron and thus form a negative ion whose size and mobility is the same as that of the positive ion and whose effective space charge is that of 1936 electrons. Moreover, the distance near the anode where the potential gradient is a minimum through which an electron must pass in order to acquire sufficient energy to ionize, might be smaller than the mean free path of the electrons in the iodine vapor at the given pressure, thus making it possible for many electrons to pass through this region without encountering an iodine atom.

[22] K. T. Compton, Phys. Rev. **20**, 283 (1922).

One should thus be able to increase the sharpness of the breaks of the *I-V* curves taken with the same geometric arrangement of filament and plate and the same filament heat by increasing the vapor pressure through a certain range. This was found to be the case for three different sets of filaments and plates and a variety of filament heats. The pressures ranged from 0.15 to 1.5 mm. The maximum sharpness was obtained at about 0.6 mm. The above explanation seems to account for the difficulty of making the arc strike at the minimum radiating potential or even at the ionizing potential. It also accounts for the gradual change of slope of the curves as the applied potential difference is raised through the critical potentials. Gases and vapors in which the electron impacts below the first critical potential are more completely elastic and those which do not have a strong electron affinity yield much sharper breaks in similar *I-V* curves.

Spectroscopic observations. Although it was not the main object of this investigation to obtain and analyze the various spectra of iodine, nevertheless, it seemed advisable to photograph the arcs in iodine under various conditions in order to get additional clues that might help to interpret the critical potentials. A large number of plates were taken and a number of characteristic plates were measured. Since the accuracy of the measurements as taken from dispersion curves was not better than ± 1A, only a few characteristic lines and bands as well as certain general conclusions are reported in this work.

In general a strong line spectrum was obtained whenever conditions were such as to cause a high percentage of dissociation, bands appearing whenever the degree of dissociation was less.

At 4.9 volts, the lowest voltage at which the arc was ever maintained, only three measurable lines and some bands appeared. These lines were 2062A, 2535, 3135 of intensities, 10, 8 and 1 respectively. The arc current in the above low voltage arcs was 1.6 amperes or more and no additional lines appeared when this current or the length of exposure was increased. Upon raising the voltage across the arc, three lines between 3135 and 3200 appeared definitely. The line 2062 remained strong at all voltages but weakened when the voltage was raised above 50 volts. Line 2535 probably 2534.4 discussed by Cario and Oldenberg[23] increased in intensity up to 10 volts and then began to decrease. At 20 volts a companion appeared at 2532. At 23 volts 2532 was by far the stronger of the two lines and at 28 volts, both lines had definitely disappeared.

As the voltage and the current of the arcs were changed, the spectrum of iodine underwent many changes. It was altered from the five line spectrum at 4.9 volts to one of many hundreds of lines at about 40 volts or above. These changes are not only in number of lines, but there are also very marked changes in the relative intensities of the lines. At about 6 volts a few of the "arc" lines and some of the strongest "spark" lines reported and classified by Wood and Kimura[24] were identified. At 7 volts more spark lines showed

[23] Cario and Oldenberg, Zeits. f. Physik **31,** 12, 914 (1925).

[24] Wood and Kimura, Astrophys. **46,** 181 (1917).

up and relatively fewer arc lines. At 8 and 9 volts only some of the strongest spark lines and three of the strongest arc lines were observed. Thus through the successive stages the arc lines disappeared or grew fainter while new spark lines appeared. Some spark lines that showed up at lower voltages either vanished or remained as faint lines at higher voltages. Thus at 40 volts relatively few of the strongest arc lines reported by other observers remained while a large number of new lines not reported in the literature made their appearance. We have thus strong evidence of successive stripping of the atom by electronic bombardment.

A large number of observers have reported line and band spectra of iodine. These spectra contain a large number of lines and differ a great deal amongst each other both in number of lines and in intensity distribution of the lines. The explanation for this variance probably lies in that these spectra were all due to high voltage excitation and probably differed greatly from each other in voltage and other conditions. The spectrograms show qualitatively the development of the iodine spectrum in the region from 5300A to 2050A. They show clearly that the method of low voltage arcs would offer a powerful method in the study of the development of the iodine spectrum.

Unless conditions in the discharge tube were such as to favor a high degree of dissociation, the line spectra were always accompanied by band spectra, both emission and absorption. The bands in the red end of the visible spectrum classified by R. Mecke[25] were observed in absorption and in emission. Bands similar in general appearance were photographed farther into the violet. These will be discussed later.

At voltages somewhat below 20 volts or at higher voltages and currents below 0.5 ampere, four band groups were photographed with a small Hilger spectrograph whose dispersion was not enough to show details of fine structure. Group I consists of three narrow somewhat diffuse bands which cross the faint extension of the so-called electron affinity continuous band whose red end is at about 3460A. Their maxima are at about 3265, 3242, 3215. These bands are equally shaded on both sides. These are probably the same as some of the 44 bands reported by Oldenberg.[26] Group II contains four bands at 2880, 2833, 2776, 2716. These have a fairly sharp red edge at about 25A, 25A, 25A and 50A wide respectively. Group III has four members whose red limits are 2480, 2380, 2290 and 2240 of which 2480 is by far the most distinct and the widest. The other members rapidly become fainter, narrower and more diffuse. Overlapping this region, i.e., from 2567 to 2230 a great deal of fine structure (lines about 3.5A apart) is seen.

The fourth group is by far the largest and most interesting. It consists of twenty narrow equally spaced bands. This group likely extends farther into the ultra-violet as the last band at 2052.5 is very near the violet end of the spectrograph employed. Microphotometer traces show that these bands

[25] Mecke, Zeits. f. Physik **7,** 73 (1921); Ann. d. Physik **71,** 104 (1923).

[26] Oldenberg, Zeitz. f. Physik **25,** 136 (1924).

have a fairly sharp edge towards the red end and that they all have nearly the same structure. They appeared in molecular iodine at low voltages, up to 16 volts, and with plate currents below .5 ampere. Their wave-lengths are as follows: 2052.5, 2062, 2071, 2080.5, 2089.5, 2098, 2107, 2116, 2125, 2133.5, 2142.5, 2151, 2160, 2169.5, 2178, 2188, 2198, 2206, 2215, 2224.

Continuous bands. A number of observers, principally Wood,[27] Steubing,[28] Oldenberg,[26] Gerlach and Groman[29] have reported continuous bands in the spectrum of iodine. Such bands have been observed at λ5100, 4800 and 3460A. The continuous bands might be formed by an electron attaching itself to a neutral atom. Both the atom and the electron may have kinetic energy. The frequency of the long wave length limit of the continuous spectrum corresponds to the difference of the energy between a neutral atom plus an electron and the negative ion, i.e., the electron affinity of the atom. This entrance of the electron with a definite kinetic energy will be accompanied by the emission of energy equal to the electron affinity plus the kinetic energy of the electron, and, since the latter may have all possible values, the spectrum will be continuous. The band at 5100 was found by Oldenberg[25] only in mixtures of hydrogen and iodine. Gerlach[29] and Groman regard the band at λ3460 as due to the electron affinity of the atom and suggest that λ4800 may be due to the electron affinity of the molecule because the former grows stronger while the latter grows weaker as the molecular band spectrum yields to the atomic line spectrum. Oldenberg, however, regards the 3460 continuous band as a recombination spectrum. Thus $I^- + I^+ \rightarrow I_2 + 5.8$ volts. The energy of 5.8 volts is more than sufficient for the emission of the band at 3460 which needs but 3.6 volts. He suggests that the excess energy is used in emitting the diffused bands into which part of this band breaks up when the pressure of another gas, (e.g. nitrogen) is raised. He also suggests that the continuous band at 4800 might arise from a transformation of the excited molecule.

It seems certain from this investigation that the band at λ3460 is due to the atom. There is nothing in its manner of appearance in the arc which is contradictory to the proposal that it is the electron affinity spectrum of the iodine atom. It also seems certain that the other continuous bands observed are connected with the iodine molecule. Further spectroscopic observations on these continuous bands are highly desirable.

In conclusion the writer expresses his sincere gratitude to Professor O. S. Duffendack at whose suggestion and under whose direction this investigation was conducted at the University of Michigan during the years 1924 and 1925. The writer wishes further to acknowledge his indebtedness to Professor H. M. Randall for interest in the work and for obtaining the necessary means for conducting this research.

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UNIVERSITY OF MICHIGAN,
September 23, 1927.

[27] Wood, Researches in Phys. Optics, Part II, p. 51, 1919.
[28] Steubing, Ann. d. Physik **64,** 673 (1921); Zeits. f. Physik **32,** 159 (1925).
[29] Gerlach and Groman, Zeits. f. Physik **18,** 239 (1923).