LOW VOLTAGE ARCS IN DIATOMIC GASES.

I. HYDROGEN, NITROGEN, AND IODINE.

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SYNOPSIS.

Low-voltage Arcs in Hydrogen, Nitrogen, and Iodine Vapor.—After a general review of the previous experimental results and theoretical suggestions, (1) *current-voltage curves* obtained with a simple two-electrode tube are described. Precautions were taken to insure pure gases. The breaking potential was always the ionizing potential of the gas, 16.3, 16.2, and 14.6 volts, respectively, for the three gases. The striking potential was greater than the breaking one by an amount which increased with the pressure and with increasing cathode filament temperature. *In dissociated hydrogen*, maintained at a high temperature within a thin tungsten cylinder heated electrically, an arc was readily maintained at the ionizing potential of the atom, 13.7 volts, and under very favorable conditions, at the radiating potential, 10.0 volts. *In dissociated iodine vapor*, the arc was maintained at 12.1 volts and under certain conditions at the ionizing potential, 10.2 volts. Nitrogen was not appreciably dissociated in the furnace. *The critical potentials* given above agree with the best previous results within $\pm$ 0.2 volt as a rule. Those associated with the atom are experimentally distinguished from those associated with the molecule.

Electric Furnace Spectra of Hydrogen, Nitrogen and Iodine to 2500° C.—In hydrogen, the series lines flashed in when the arc was struck, even as low as 10.6 volts, but the bands did not appear. Evidently the series lines are due to the atom and the bands to the molecule. In nitrogen, a brilliant "flare" was produced at potentials which decreased from 70 to 40 volts as the temperature was increased. This "flare" shows both the positive and negative bands along with the spectrum of tungsten; it is probably due to the formation of "active" nitrogen. At 70 volts the first lines, 5006 and 5003 Å., appeared, and at 90 volts only two more, 5680 and 5667 Å. Reasons are given for assigning the positive bands to the neutral molecule, the negative bands to the ionized molecule and the lines to the atom. In iodine, the arc lines, particularly 4860 Å., flashed in when the arc struck, the enhanced lines coming in at higher voltages. No band spectrum appeared.

New negative bands of nitrogen were found at 5075, 5018 and 4961 Å.

GENERAL THEORY OF LOW VOLTAGE ARCS.

THIS investigation was undertaken to see if additional light could be obtained by this method upon the critical potentials of diatomic gases; to study the effect of the dissociation of a gas upon the potentials at which an arc will strike and break; and to investigate, incidentally, the excitation of the spectra of the substances.

The method of investigating critical potentials by means of low voltage arcs differs from the methods usually employed for determining ionizing and radiating potentials in that very much greater electron

streams are passed through the gas and the gas is usually at a considerably greater pressure. Up to the time this investigation was begun this method had been employed only with monatomic gases and vapors. Some seeming disagreements appeared between the results obtained by means of low voltage arcs and those by the usual methods. When only a moderately dense electron stream was sent through a gas, the arc would strike at the ionizing potential as determined by the usual methods, but when a dense electron stream was employed the arc could be made to strike as low as the radiating potential. The striking of an arc indicates that considerable ionization is taking place, and this is confirmed by the appearance of the spectrum of the substance. As Bohr's theory indicates that the atom is not ionized at the radiating potential, and as the usual methods often indicate the absence of ionization, the striking of the arc at this potential appeared to be in conflict with the previous results.

Various explanations of these anomalous effects with dense electron streams have been proposed. In some cases it was thought that the ionization of impurities present might account for the effect, and McLennan[1] attributed the appearance of "faint arcs" to electrons of abnormally high velocities in the electron stream. These explanations seemed insufficient in most cases and others were proposed. Millikan[2] suggested that the radiation produced by impacts at the radiating potential might act photoelectrically upon the atoms of the filament or of the gas and thus produce additional electrons which would in turn be accelerated by the applied field and make impacts at the radiating potential and so there would be a multiplication of the original current. Richardson and Bazzoni[3] and Van der Bijl[4] put forward the theory of successive impacts, and the former also suggested that a combined action of radiation and of impacts accounts for the ionization. K. T. Compton[5] investigated the adequacy of the theory of successive impacts and concluded that, while it is an important factor, in general, ionization produced in this way is insufficient to account for the observed results. He has recently shown[6] that the cumulative effect of absorbed radiation is far more effective than successive impacts, and it seems that this may account for most of the cases reported.

In order to understand better the results obtained, it will be well for

[1] Proc. London Phys. Soc., 31, 1 (1918).
[2] PHYSICAL REVIEW, 9, 378 (1917).
[3] Nature, 48, 5 (1916).
[4] PHYS. REV., 10, 546 (1917).
[5] PHYS. REV., 15, 130, 476 (1920).
[6] Amer. Phys. Soc. Proc., New York meeting, 1922.

us to recall what is meant by an arc. Richardson has shown that the saturation thermionic current from an incandescent cathode is given by

$$i = aT^2\epsilon^{-\frac{b}{T}}$$

where a and b are constants and T is the absolute temperature of the filament. When this equation is tested, however, it is found that, while it holds quite well at the lower temperatures, the current falls short of the value predicted by the equation for the higher temperatures and reaches a maximum value which is much less than the saturation current. The point of departure from the Richardson relation depends upon the voltage applied and is earlier for the lower voltages. The maximum current obtainable is likewise less the lower the voltage.

The reason for the failure of Richardson's equation was investigated by Langmuir,[1] and it was found to be due to the effect of the space charge of the emitted electrons. If no electrons are emitted by the filament, the potential will vary linearly between the electrodes. When electrons are emitted and, under the influence of the field, pass over to the anode, they form an electric current and build up a space charge. The potential gradient will no longer be uniform between the electrodes but will be less near the filament on account of the concentration of electrons there. These electrons will repel one another and so will impede those just being emitted by the filament. As the speed of an electron is proportional to the potential gradient, there will be a diminution of the average velocities of the electrons near the filament and a resulting increase in concentration. This results in increased impedance until finally the space charge becomes so great that the potential gradient becomes zero or even negative. An equilibrium condition will be reached in which the electrons emitted with velocity components parallel to the electric intensity below a certain amount will be stopped and driven back to the filament. There can then be no further increase in current at the prevailing temperature of filament and potential applied.

Now if ionization takes place, we have a quite different state of affairs. The positive ions will neutralize the space charge of the electrons. The densities of electrons and of ions, and hence the space charges due to them, will vary inversely with their velocities. Their velocities vary directly as their mean free paths and inversely as the square roots of their respective masses. Thus each positive ion neutralizes the space charge of $4\sqrt{2}\sqrt{1846\,M}$ electrons, where M is the molecular weight.[2] Therefore,

[1] PHYS. REV., 2, 543 (1913).

[2] The factor 4 is due to the negligible size of the electron and the factor $\sqrt{2}$ to the fact that its speed is of a higher order than that of the molecules among which it moves. See any treatise on Kinetic Theory.

one positively charged hydrogen atom will neutralize the space charge of 243 electrons, one positively charged hydrogen molecule will neutralize 343 electrons. Now if we have reached the maximum current limited by the space charge, the formation of one positive hydrogen molecule ion will permit the emission of 342 additional electrons. If every electron emitted ionized a molecule, the electron current would increase more than three hundred times. These newly emitted electrons would in their turn be accelerated and would ionize other molecules, and so on, and the current would continue to increase until the saturation current indicated by Richardson's equation is reached. To this current would be added the current carried by the ions and electrons formed in the process of ionization. There would be a further increase in emission due to the heating of the filament as a result of its bombardment by positive ions, and there would be a diminution of current due to the recombination of ions and electrons. The data from hydrogen show ratios of current in the arc to that before the arc of from 2 to 120 depending upon the temperature of the filament. The current through the arc was about that to be expected from Richardson's equation.

Now let us look a little further into the mechanism of the arc. When the space charge immediately surrounding the filament is neutralized or reversed by positive ions, we will have a large increase in electron emission from the filament, and the arc will strike. This is accompanied by a redistribution of the electric intensity in the tube, resulting in a large drop in potential near the cathode. This fall in potential will be a large fraction of the total potential difference between the electrodes, but, obviously, the potential can nowhere be higher than at the anode as this would give a negative gradient and would prevent electrons which had lost their velocities from reaching the anode. The exact distribution of potential cannot be computed for want of knowledge concerning the distribution of space charges. This cathode fall of potential will enable electrons to ionize at their first impact, or, at least, it will greatly increase the ionization near the cathode. This view of the distribution of electric intensity in the arc is supported by the observations that the spectrum is most intense in the region near the filament and that the glow of the arc, if it is small, is confined to the region immediately surrounding the filament.

If we assume the distribution of electric intensity explained in the preceding paragraph, the potentials at which an arc will strike and break can easily be deduced. As the striking of the arc follows the neutralization of the space charge, it will normally occur at or above the ionizing potential of the substance, depending upon the temperature of the

filament and the pressure of the gas. If a considerable fraction of the molecules are in a partially ionized condition, due to the absorption of a quantum of radiation or to an impact with an electron possessing sufficient energy to displace an electron in the molecule but not to remove it, a sufficient number of positive ions may be formed by impacts with these molecules to cause the arc to strike at a potential below the ionizing potential. As it seems improbable from Professor Compton's[1] work that this can be accomplished by successive impacts alone, we need examine only the case of the absorption of radiation. If, as is usually the case, the radiation comes from the substance itself and not from without, electron impacts at the radiating potential will be required to produce the radiation, as radiation corresponding to the first line of the principal series is necessary. Therefore, it is possible to get an arc to strike at a potential equal to the difference between the ionizing and radiating potentials of the substance, provided that this difference is not less than the radiating potential; or at the radiating potential, provided that this is not less than half the ionizing potential. With dense electron streams, the arc has been made to strike in all of the monatomic gases thus far investigated at the radiating potential. It is noteworthy, however, that a distinct time lag in the striking of the arc was noted by nearly all of the observers for voltages between the radiating and ionizing potentials. It was found impossible to get the arc to strike in the diatomic gases investigated at a voltage less than the ionizing potential. This is probably due to the loss of energy by inelastic impacts in the diatomic gases and to the fact that the molecules are unable to absorb and reëmit the resonance radiation, which comes from the atoms.

After the arc has struck, it will continue as long as the space charge surrounding the filament remains positive. With a dense electron stream the arc can be maintained indefinitely at the radiating potential in a monatomic gas, provided that this is not less than half the ionizing potential. Obviously, the arc can be maintained temporarily at a voltage equal to the difference between the ionizing and radiating potentials even when this is less than the radiating potential, but it must eventually break due to the loss of radiation from the tube.

In diatomic gases the arc invariably broke at the ionizing potential, but it is comparatively easy to maintain the arc in monatomic gases at the radiating potential when this is not less than half the ionizing potential. In some cases the arc has been maintained for a considerable time at the radiating potential, or less, even when this is less than half the ionizing potential. This was done in the case of mercury vapor by Hebb,[2]

[1] Loc. cit.

[2] PHYS. REV., 9, 371 (1917); 12, 482 (1918).

Millikan,[1] and Compton and Yao;[2] in sodium vapor by Wood and Okano,[3] and in mixtures of sodium and mercury and potassium and mercury vapors by Hebb. That these are not anomalous cases was shown by Compton and Yao, who worked out a satisfactory explanation of these cases upon the basis of the distribution of velocities of emission of the electrons. The ionizing potential of mercury is 10.4 volts and the radiating potential is 4.9 volts. Compton and Yao maintained the arc in mercury vapor at 1.8 volts. They showed that there are a sufficient number of electrons emitted from a hot filament with initial velocities sufficient to make up the difference between the 1.8 volts observed and the 5.5 volts theoretically required to maintain the arc.

The case of helium is a more striking one. The ionizing potential of helium is 25.5 volts and radiating potentials of 20.4 and 21.2 volts have been found. It should, therefore, be possible to maintain an arc in helium temporarily at 5.1 or 4.3 volts. Kannenstine[4] got evidence that this can be done by taking oscillograph records of the current through a helium arc when an alternating field is applied. These records show a persistence of the arc at about 4 volts when a sixty-cycle circuit was used. This would give a time interval of the order of a hundredth of a second. Compton, Olmstead, and Lilly,[5] maintained an arc for a considerable time at 8 volts, and Miss Davies's [6] work indicates that the arc can be maintained for an indefinite period at 13 volts. These observers do not claim that these voltages are critical potentials; the important point is that in the case of helium it seems possible to maintain an arc indefinitely at a potential far too much below the radiating potential to allow an explanation on the basis of velocity distribution. Miss Davies suggest that helium is converted into a metastable form by electron impacts at 20.4 volts and that this is then ionized by impacts of 5.1 volts or more. When these ions are neutralized the atom remains in the metastable condition and does not return to the normal form. Once this is formed, then, the arc can be maintained at a potential as low as 5.1 volts until the helium is reconverted into the normal form. The process by which the metastable atom is changed into the normal atom is not well understood, although Franck and Knipping[7] suggest that it depends upon the catalytic action of impurities. It should be noted that the arc does not strike in helium at potentials less than 20.4 volts.

[1] PHYS. REV., 9, 378 (1917).
[2] Amer. Phys. Soc. Proc., Washington meeting, 1922.
[3] Phil. Mag., 34, 177 (1917).
[4] Amer. Phys. Soc. Proc., New York and Washington meetings, 1922.
[5] PHYS. REV., 15, 545 (1920).
[6] Roy. Soc. Proc., A, 100, 599 (1922).
[7] Zeit. für Physik, 1, 320 (1920).

APPARATUS.

The apparatus employed in this investigation was of two types. The first was a simple two-element tube, consisting of a tungsten wire filament and a nickel plate anode placed at a distance of about 5 mm. from the filament. A potential difference was applied between the negative end of the filament and the plate and could be varied by control rheostats. The current between the electrodes was read on a sensitive milliammeter placed in series with the arc. The current through the arc was recorded as the voltage was raised by steps from zero. The striking of the arc was indicated by a sudden jump in the current and also usually by the appearance of a glow around the filament and the flashing in of the spectrum of the gas. The potential across the arc was corrected to that which obtained between the middle of the filament and the plate by subtracting from the reading of the voltmeter half the potential drop across the filament. This correction is subject to error when the filament is very hot as there may then be sufficient emission from the negative end of the filament to maintain the arc. The effect of initial velocities of emission from the filament is such as to more or less counterbalance this error.

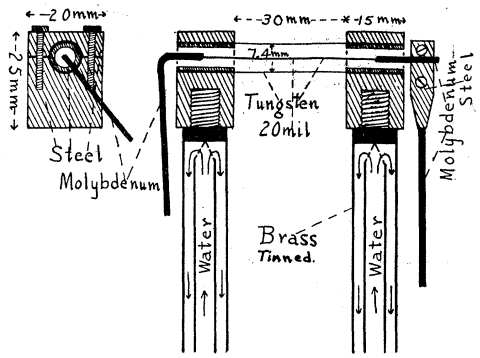

Fig. 1.

It was found impossible in the simple tube to maintain the arc at voltages less than the ionizing potential. The failure to do so was ascribed to there being an insufficient amount of the monatomic gas present in the tube when due only to the dissociating action of the filament and of the arc. Professor Compton suggested that it might be possible to dissociate hydrogen and other gases by means of a tungsten furnace which could also be used as one of the electrodes of the arc. The construction of the furnace developed by the writer is shown in the accompanying diagram. It consists of a cylinder of very thin sheet tungsten mounted on water cooled leads. A tungsten filament ran

axially through the cylinder and was made the cathode. The fall of potential in the furnace and that in the filament were in the same direction. In the earlier experiments with this tube, the potential was applied between the positive end of the furnace and the negative end of the filament. The reading of the voltmeter was corrected to give the potential between the middle of the electrodes by subtracting half the sum of the voltage drops across the furnace and the filament. This correction was checked by a sharp rise in the thermionic current when the voltmeter read this amount. This correction is subject to the same error as in the case of the simple tube for very hot filaments. The parts of the furnace were later modified so that the drops of potential in the furnace and in the filament and also in the furnace leads and filament leads were identical. The potential was then applied between the negative ends of the furnace and filament and the voltmeter read the voltage obtaining between corresponding parts of the furnace and the filament.

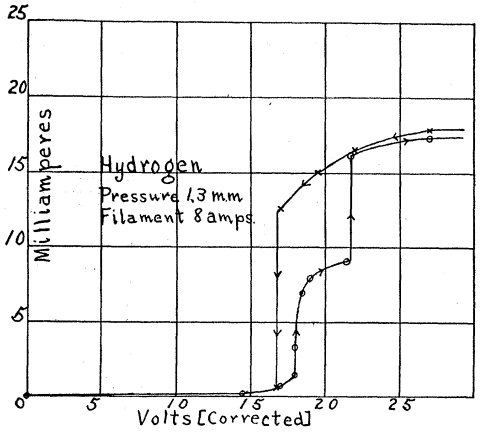

Fig. 2.

This condition was practically equivalent to having two equipotential surfaces as electrodes. The temperature of the furnace was estimated from the resistivity of the tungsten. Calculations of the resistivity showed that temperatures of about 2,500° C. were obtained.

ARCS IN HYDROGEN.

The hydrogen was generated by the electrolysis of dilute sulphuric acid and was purified by passing it over phosphorous pentoxide and through charcoal immersed in liquid air. The pressure of the gas in the tube was read on a McLeod gauge. Before the gas was admitted into the tube, the electrodes were thoroughly glowed out, and when the simple tube was used, it was thoroughly baked.

Figs. 2, 3, and 4 show the effect of the temperature of the filament on the potential at which the arc strikes and breaks. These curves were obtained from three successive runs in hydrogen at a pressure of 1.3 mm. The potential of the break is lower the greater the filament current, becoming slightly less, Fig. 4, than the ionizing potential of hydrogen. This illustrates the error in the zero correction for hot filaments as pointed out in a foregoing paragraph.

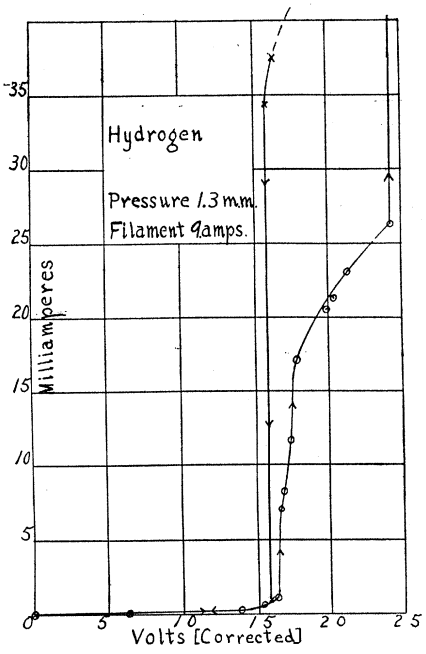

Fig. 3.

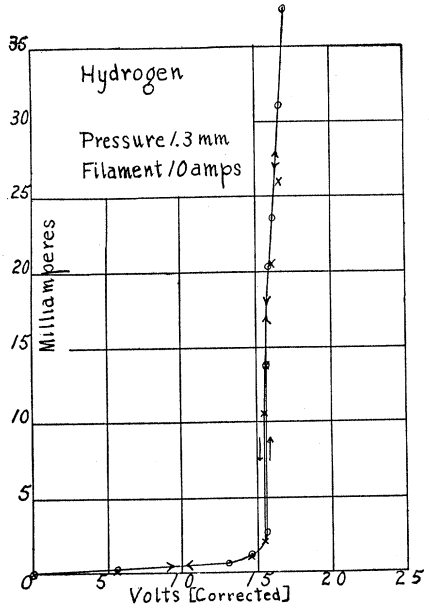

Fig. 4.

Figs. 5, 6, and 7 show the effect of the pressure of the gas upon the potentials at which the arc strikes and breaks. For these curves runs were taken at pressures of 0.4, 2.4 and 5.5 mm. and the filament currents were such as to give practically the same increase in current when the arc struck. The striking potential regularly increases with the pressure as does the difference between the striking and breaking potentials. The curves indicate that there is an optimum pressure at which the arc can be maintained to the ionizing potential of the gas with a moderately hot filament.

At pressures above about 0.5 mm. ionization sets in at the ionizing potential as is indicated in Figs. 2, 3, 6 and 7, but, though there may be a large increase in current, the arc does not strike until the voltage is raised considerably above the ionizing potential, the amount depending

upon the pressure of the gas and the temperature of the filament. If the applied potential is decreased before the arc strikes, the curve is retraced, but after the arc strikes, the current remains at a higher value until the

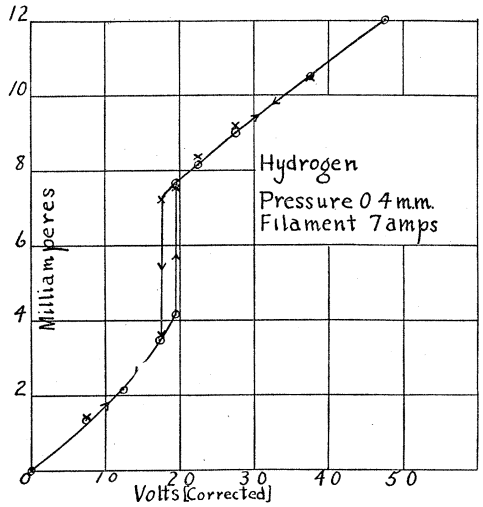

Fig. 5.

arc breaks. Before the arc strikes, the current seems to approach a saturation value as in the case of thermionic currents in high vacua. This is probably due to a gradual shifting of the region of predominately positive space charge toward the filament. A large fraction of the potential difference applied to the electrodes is used up between the filament and the boundary of the region of positive space charge, and so the electrons enter this region at approximately their maximum speeds, the actual speed depending upon the potential and upon energy losses by inelastic impacts. The energy losses by inelastic impacts are greater for the higher pressures due to the increased number of collisions, and so the potential difference required to be applied to cause an electron to enter the region of positive space charge with sufficient energy to ionize upon impact will be greater the greater the pressure of the gas. This accounts for the increase in the striking potential with the pressure. Now, after this region of positive space charge has reached a certain thickness, a further increase in thickness will not greatly increase the probability that an electron entering this region with energy sufficient to ionize a molecule will make an ionizing impact. There will then be very little increase in current until the space charge immediately surrounding the filament becomes positive, and the arc strikes. After the

apparent saturation current has been reached, a slight change in the conditions in the tube or a slight shifting of the space charges will cause the arc to strike, and so the striking of the arc may vary by several volts for the same pressure and filament current.

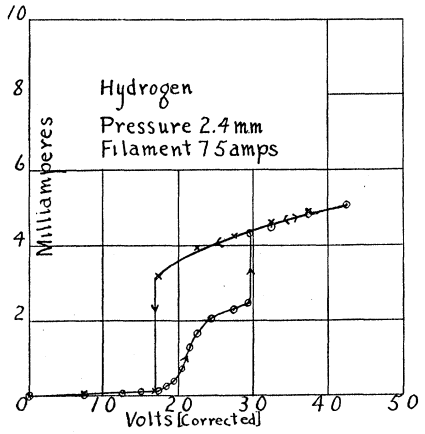

Fig. 6.

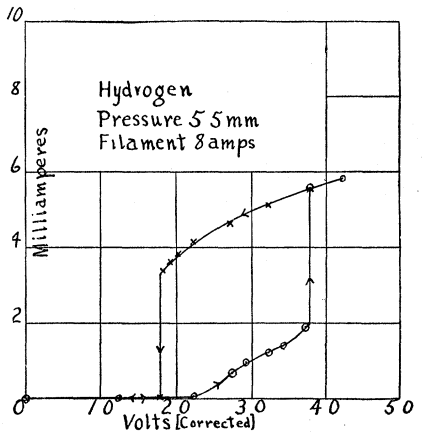

Fig. 7.

In this type of apparatus the potential of the break of the arc was far more constant than that of the strike. For pressures between 0.85 mm. and 3 mm. and with moderately hot filaments the breaks were remarkably constant, having a mean deviation from the average of 0.3 volt. The average of fourteen runs at these pressures gives a breaking potential of 16.35 volts which is within the range of the values of the ionizing potential of hydrogen reported by various observers.

As Bohr's theory puts the ionization potential of the hydrogen atom at 13.52 volts, calculated from the convergence frequency of the Lyman series, and the radiating potential at 10.14 volts, it should be possible to maintain the arc at these potentials if a sufficient amount of monatomic hydrogen could be obtained. The tungsten furnace was designed to dissociate the gas by means of high temperatures. The amount of dissociation to be expected was calculated by means of Nernst's equation of the "reaction-isobar,"

$$\log \frac{x^2}{1-x} P = -\frac{Q_0}{4.571\,T} + 1.75 \log T - \frac{\beta}{4.571} T + \sum \nu C.$$

x = the fraction of the molecules present which are monatomic,
P = the total pressure,
Q_0 = the heat of dissociation at absolute zero,
T = the absolute temperature,
β is a constant depending upon the rate of change of the specific heat with the temperature,

4.571 is the gas constant per gram mol. times the logarithmic modulus,

C is Nernst's chemical constant.

Q_0 can be calculated from Q, the heat of dissociation at ordinary temperatures, by means of the formula: $Q=Q_0+\alpha T+\beta T^2+$ etc., where α = specific heat.

Taking the heat of dissociation, Q, to be 84,000 calories per gram-molecule, β = 0.000225, and the chemical constants for diatomic and monatomic hydrogen to be[1] − 3.4 and − 1.6 respectively, the percentages of monatomic hydrogen in equilibrium with diatomic hydrogen at various temperatures and pressures are indicated in the following table:

Pressure.	1000° K.	1500° K.	2000° K.	2500° K.	3000° K.
0.5 mm.....	.005	2.36	61.5	Complete	
1.0 mm.....	.004	1.69	49.5	98.8	
5.0 mm.....	.002	0.74	26.7	90.4	Dissociation

When the furnace was not heated, the arc struck and broke at the ionizing potential of the molecule, and there was no evidence of ionization below about 16 volts. With the furnace hot, considerable ionization was produced at about 10 volts and 13.5 volts as is indicated by the

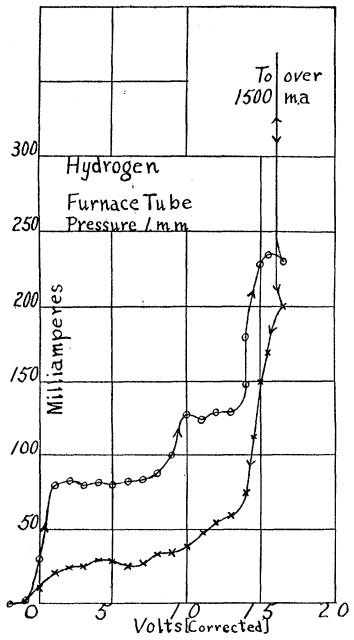

Fig. 8.

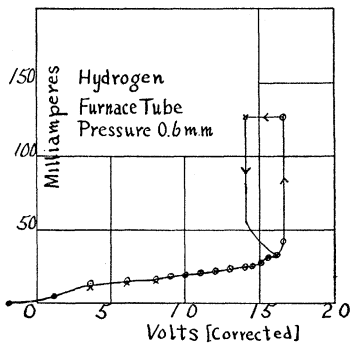

Fig. 9.

[1] Reiche, Ann. d Physik, 58, p. 657, 1919 and Schames, Phys. Zeit., 21, p. 41, 1920.

curve for the thermionic current, Fig. 8. Later a temperature was reached at which the arc struck at the ionizing potential of the molecule and was maintained to the ionizing potential of the atom, Fig. 9, indicating that the increase in dissociation in the arc enabled it to be maintained in monatomic hydrogen. Finally, practically complete dissociation was obtained; the arc struck easily at the ionizing potential of the atom, and the curve shows no indication of a further increase in ionization at the ionizing potential of the molecule, Fig. 10(*b*). With a very hot furnace and a large electron emission the arc was made to strike at 10.6 volts, Fig. 10(*a*) which is very near the radiating potential of the atom, and no further discontinuities were observed at higher voltages. It was quite difficult to do this and it was only done when the furnace had not been maintained at the high temperature for a long time. The curve 10(*a*) was drawn from memory. This striking of the arc was repeated several times and the potential and current noted, but an accident prevented a run being made with the current and voltage recorded by steps. The failure to get the arc to strike at potentials lower than 13.5 volts later was attributed to impurities coming from the walls of the tube and from the clamps and leads when they became warm. As the furnace was mounted on water-cooled leads, the tube had to be put together with Khotinsky cement and so it could not be baked out.

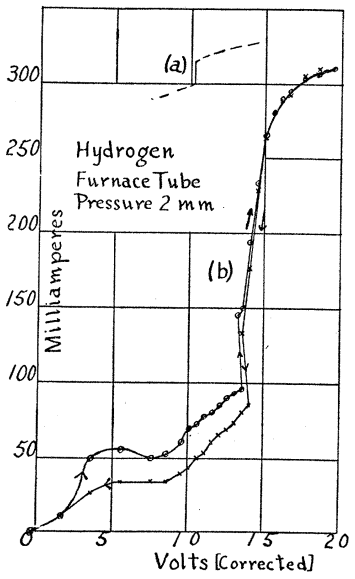

Fig. 10.

This is the first experiment of this kind performed in an atmosphere of atomic hydrogen, and these results constitute, it is believed, the first direct experimental proof of the correctness of the values of the radiating and ionizing potentials predicted by Bohr's theory for the *hydrogen atom* and of the interpretation of the ionizing potential of the molecule as due to its dissociation plus the ionization of one of the atoms.

Table I. gives the critical potentials of hydrogen predicted by Bohr's theory together with the average break points obtained in this investigation and the critical potentials reported by various observers. The heat of dissociation was calculated in each case by subtracting the thirteen-volt break from the sixteen-volt break when ionization was reported in

TABLE I.

Bohr's Theory.	This Investigation.	Franck, Knipping & Kruger.[1]	Davis & Goucher.	Horton & Davies.[3]	Compton & Olmstead.[4]	(Mohler & Foote)[5] Foote, Mohler & Kurth.[6]	Boucher.[7]
29.74 $D+2I$		30.45 $D+2I$					
26.36 $D+I+R$							
22.98 $D+2R$							
						(16.5 I)	
16.22 $D+I$	16.35 $D+I$	17.1 $D+I$	15.8 I	16.9 I	15.9 $D+I$	16.0 I	15.6 I
				14.4 I			
13.52 I	13.7 I	13.6 $D+R$	13.6 R	13.9 R	13.4 I	(13.3 I)	13.6 I
						(12.2 R)	
12.84 $D+R$						11.8 R	
		11.5 I(Mol)				10.5 R	
10.14 R	10. R		11. R, I'	10.5 R	10.8 R, I'	(10.4 R)	10.1 R
						(3.2 D)	
2.7 D	2.55 D	3.5 D		2.5 D	2.5 D	2.7 D	2.0 D

[1] Verhand. d Deutsch. Phys. Ges., 21, 728 (1919).
[2] PHYS. REV., 10, 101 (1917).
[3] Roy. Soc. Proc., A, 97, 23 (1920).
[4] PHYS. REV., 17, 45 (1921).
[5] Jour. Optical Soc. Amer., 4, 49 (1920).
Bureau Standards, 1920, 670.
[6] Amer. Phys. Soc. Proc., Toronto Meeting, Dec., 1921.
[7] PHYS. REV., 19, p. 189, 1922.

both cases. The heat of dissociation was measured by Langmuir[1] who found it to be equivalent to 3.6 volts.

It was not the purpose of this investigation to determine accurately the critical potentials of the gases studied, and no great degree of accuracy is claimed for the potentials reported. The purpose of this investigation was to interpret and not to determine critical potentials.

SPECTROSCOPIC OBSERVATIONS ON HYDROGEN.

A systematic study of the excitation of the spectrum of hydrogen was made during the investigation of the arcing characteristics. A Hilger direct-reading spectroscope was used and visual observations were made.

With the two-element tube, the lines and bands flashed in when the arc struck and disappeared when the arc broke. All of the bands observed belong to Group I. of Fulcher's[2] classification as far as his classification extends and were of those for which Dufour found no Zeeman effect. The observations were made for potentials up to 40 volts which probably accounts for the fact that none of the bands of Group II. were observed, except that one member of each of the two pairs of bands which were placed in both groups was observed. The bands of Group II. are those which increase in intensity with the voltage and include those which Dufour found to show the Zeeman effect.

In the tungsten furnace, the lines flashed in when the arc struck, as low as 10.6 volts, and were strongly reversed in the intense arc of the furnace. The bands did not appear when the furnace was hot and the gas was practically completely dissociated. This is additional evidence that the line spectrum is due to the atom and the band spectrum to the molecule and is in agreement with the conclusions of G. P. Thomson[3] as a result of an investigation of the spectrum emitted by positive rays in hydrogen.

Fulcher's work shows that there are at least two groups of bands in the second spectrum of hydrogen, and Merton[4] suggests that there are three. There are several possible explanations for the different kinds of bands; all of them attributing the radiation to the molecule, as follows: One, or both, of the electrons of a neutral molecule may be set radiating as a result of their disturbance by an electron impact which does not dissociate or ionize the molecule, or by the recombination of an electron with an ionized molecule, or by the recombination of two neutral atoms. It is by the recombination of neutral atoms that Strutt suggests the glow

[1] Langmuir, Irving, Amer. Chem. Soc. Jour., 34, p. 860, 1912, and 37, p. 417, 1915.

[2] Astrophysical Journal, 37, p. 65, 1913.

[3] Phil. Mag., 40, p. 240, 1920.

[4] Royal Society Proc., A, 96, 382, 1919.

of active nitrogen is produced. The remaining electron of an ionized molecule may be set radiating as a result of its disturbance by an electron impact which does not produce dissociation, or by the union of a neutral atom and an ionized atom. There was no means of testing any of these proposed explanations from the data of the investigations reported. I merely wish to point out that there are possible mechanisms for the radiation of several kinds of bands by the hydrogen molecule. The H_3 molecule, which is often present in positive rays in hydrogen, offers additional possibilities for band spectra, and Wendt and Landauer[2] suggest that it may be the source of the bands observed by them.

ARCS IN NITROGEN.

Nitrogen was generated by the reaction of sodium nitrite and ammonium chloride. It was passed through a tube of hot copper turnings and collected over distilled water. Before being admitted into the experimental tube it was passed over phosphorous pentoxide and through a tube immersed in liquid air.

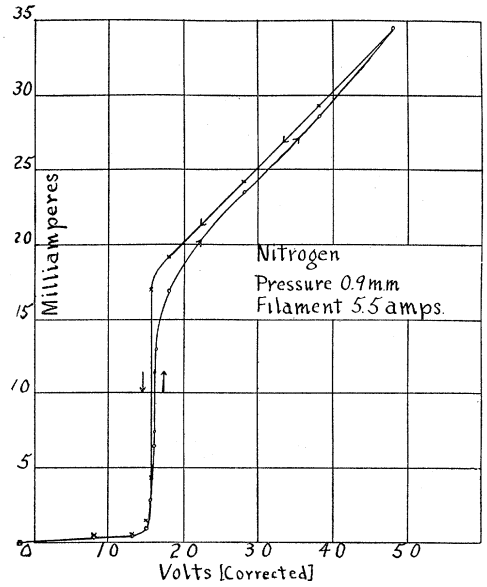

Fig. 11.

The curves obtained for nitrogen, Figs. 11 and 12, are similar in most respects to those for hydrogen when the simple tube was used. The striking potential was higher than the ionizing potential for high gas

[2] Amer. Chem. Soc. Jour., 44, 510, 1922.

pressures, but there was less definite evidence of an apparent saturation current before the arc struck. The difference between the striking and breaking potentials was less in nitrogen than in hydrogen for the same mean free path of electrons. These differences are probably due to the greater elasticity of impact and consequently to the greater space charge

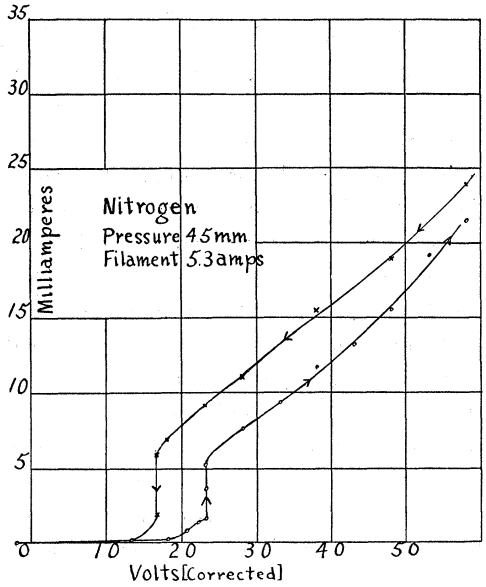

Fig. 12.

in hydrogen than in nitrogen, combined with the greater effectiveness of nitrogen positive ions in neutralizing the space charge of electrons. The current continues to increase quite rapidly with the voltage after

TABLE II.

	Davis & Goucher.[1]	Smyth.[2]	Found.[3]	Mohler & Foote.[4]	Stead & Gosling.[5]	Brandt.[6]	Boucher.[7]
Resonance Potentials....	7.5 9.0	6.29 7.3 8.29		8.18		7, 8.5	8.4
Ionization Potentials.....	18	18	15.8	16.9	17.2	17.75	15.8

[1] PHYS. REV., 13, 1 (1919).
[2] PHYS. REV., 14, p. 409 (1919).
[3] PHYS. REV., 16, p. 41 (1920).
[4] Jour. Optical Soc. of Amer., 4, p. 49 (1920).
[5] Phil. Mag., 40, p. 413 (1920).
[6] Zeit. für Phys., 8, p. 32 (1921).
[7] PHYS. REV., 19, p. 189 (1922).

the arc has set in, while in hydrogen the current did not increase much after the arc had struck. It was impossible to maintain the arc at potentials lower than the ionizing potential, and the average of the break points was 16.15 volts, which is within the range of ionization potentials reported for nitrogen as shown in Table II.

It was impossible to maintain the arc at lower potentials in the tungsten furnace and so it was concluded that the degree of dissociation of nitrogen at the temperature of the furnace was small. This is in agreement with the conclusion reached by Langmuir[1] for the heat of dissociation of nitrogen.

When the filament was quite hot, the conductivity of the arc increased very rapidly for voltages of 70 volts or more, and, with no further change in the control rheostats, the current increased enormously while the voltage decreased and the arc turned into a brilliant "flare." When the rheostat was operated so as to normally increase the potential across the arc, the voltage decreased instead and the current increased. In this manner a current of more than 15 amperes was obtained at a voltage of about 25 volts. There was a rapid wasting of the tungsten filament in the flare and the nickel anode and the leads supporting the filament were usually quickly melted. By using a tungsten anode and five tungsten filaments in parallel, the flare was maintained for a considerable time and its spectrum studied. Besides the spectrum of nitrogen, the spectrum of tungsten showed up strongly. A black deposit accumulated on the walls of the tube which appeared to be tungsten nitride. The wasting of the filament was not sufficiently rapid to justify the conclusion that the arc was now maintained in tungsten vapor, and so a more probable explanation was sought.

As the conditions in the arc are similar to those in a condensed discharge in a vacuum tube, it was concluded that "active" nitrogen was formed. The excitation of the tungsten spectrum was, then, analogous to the excitation of the spectra of hot metals in "active" nitrogen as accomplished by Strutt,[2] and it was explained by him to be due to the burning of the metals in this nitrogen. He found that this glowing nitrogen has a high electric conductivity, comparable to that of salts in a Bunsen flame, and so this accounts for the increased conductivity of the arc in the "flare." This explanation of the production of the "flare" probably also accounts for the anomalous thermionic emission of tungsten filaments in nitrogen for potentials above 75 volts as discovered by Langmuir.[3]

[1] Amer. Chem. Soc. Jour., 34, 860 (1919).

[2] Royal Soc. Proc., A, 85, p. 219 (1911) et seq.

[3] PHYS. REV., 2, p. 450 (1913).

Strutt concluded that "active" nitrogen is simply monatomic nitrogen and results from the dissociation of nitrogen in the electric discharge. It was possible to get the "flare" in a hot tungsten furnace at a somewhat lower voltage than in the simple tube, *i.e.*, as low as 40 volts instead of 70, and this may be accounted for on this assumption, by a slight increase in dissociation due to the temperature of the furnace. This is the only evidence obtained that there was any dissociation of nitrogen by thermal action.

Spectroscopic Observations on Nitrogen.

Nitrogen has a rich line spectrum and a very complicated band spectrum. The band spectrum has been classified by Deslandres[1] into three positive band spectra and a negative band spectrum. The first positive bands came in with the arc and increased slightly in intensity with the voltage. They have been excited in various ways by slow cathode and canal rays. The second positive bands came in with the arc and decreased in intensity with increased voltage as has also been observed by Fulcher.[2] These bands disappear as the potential is increased, but reappear in the "flare" along with the spectrum of tungsten.

This reappearance can be accounted for on the basis of the explanation of the "flare" as given above, for these bands were found by Fowler and Strutt [3] to be invariably present in the spectrum of the nitrogen afterglow. Besides the second positive bands they find also the first positive bands, with certain groups greatly enhanced, and the third positive bands in the afterglow. They concluded that "active" nitrogen was simply monatomic nitrogen and that the glow was produced by the reunion of the atoms. This manner of excitation corresponds in energy to electron impacts at quite low potentials, very probably less than the ionizing potential.

L. and E. Bloch[4] photographed one of the ultraviolet bands of the second group at 12 volts, which is considerably under the ionizing potential of nitrogen. Erich Brandt [5] by using a four-element tube and varying the potential by intervals of 0.05 volt got a series of discontinuities in the galvanometer current for voltages between 7.5 and 8.2 volts. By applying the $h\nu$ relation to these discontinuities he constructed a band which agrees in frequency difference with some of the positive bands. He found this band characteristic of these discontinuities to persist beyond the ionizing potential and concluded that the

[1] Comptes Rendus, 101, p. 1256, 1885 et seq.
[2] Astrophys. Jour., 37, p. 60 (1913).
[3] Roy. Soc. Proc., A, 85, p. 377 (1911).
[4] Comptes Rendus, 170, p. 1380 (1920).
[5] Zeit. für Phys., 8, p. 32 (1921).

nitrogen molecule is ionized without dissociation. A survey of the various ways in which the positive bands are excited indicates that they can all be excited at less than the ionizing potential and so must be due to the neutral molecule.

The negative bands appear a volt or two above the ionizing potential and increase markedly in intensity with the voltage. Three bands not previously reported were observed at 5075, 5018 and 4961 Å. in good agreement with their calculated positions. The negative bands appear intensely only in regions of strong ionization and positive space charge and must, therefore, be due to the ionized molecule.

At about 70 volts the green doublet 5006, 5003 of the line spectrum appeared faintly and increased in intensity with the voltage. At 90 volts it was quite strong and the yellow lines 5680 and 5667 were also seen. None of the other strong lines were observed although the regions in which they lie were thoroughly searched.

It is difficult to account for the non-appearance of the line spectrum even in the "flare" at potentials less than 70 volts. It may be impossible to dissociate the molecule and ionize one of the atoms at a single impact. Sir J. J. Thomson,[1] from a consideration of the Doppler shifts of the lines in positive rays in nitrogen, concluded that some of the lines, the line 5003 being one of them, are due to the double ionization of the atom and are therefore enhanced lines. This accounts for the high potential required for the excitation of some of the lines but does not explain why so few lines appeared. Perhaps a grouping of the lines in series will clear the matter up. A more complete discussion of the excitation of the spectrum of nitrogen will be published in the Astrophysical Journal.

ARCS IN IODINE.

Chemically pure iodine was resublimed into a bulb having a thin wall. The distilling apparatus was kept connected to a diffusion pump through two liquid air traps, and the sublimation was carried on at a very low pressure. After a sufficient amount had been condensed, the tube was sealed off under a vacuum and then sealed into a second bulb which was connected to the experimental tube. After all the parts had been heated to clean up the surfaces, the iodine was liberated by breaking the thin-walled bulb by means of an iron weight lifted by a magnet.

The vapor pressure of the iodine in the experimental tube was controlled by means of a water bath. When the simple tube was employed, the tube containing the iodine was kept at the temperature at which iodine has the vapor pressure desired. The pressure was determined

[1] Rays of Positive Electricity.

from the curve of Baxter and Gose.[1] In the case of the furnace tube, a considerable amount of iodine was driven into the experimental tube, and allowed to condense on metal end pieces which were water-cooled. The iodine vapor passing out of the tube during a run acted as a diffusion pump and carried off gaseous impurities from the tube. These end pieces were of large area and were kept at the temperature desired, while the bulb containing the iodine originally was maintained at a higher temperature. In both cases the experimental tube was kept connected to a diffusion pump through two liquid air traps. A short piece of capillary tubing was inserted between the experimental tube and the first trap to prevent too rapid loss of iodine, and to insure the desired pressure. When two liquid air traps were used, no difficulty was experienced in keeping mercury out of the apparatus; whereas when only one trap was employed, mercuric iodide invariably appeared after a time.

With the simple tube, the arc struck at or above an average of 14.6 volts and broke at this potential. The pressure was varied from 0.5 to 1.5 mm., the deviation of the critical potential from the average given above being 0.3 volt in the four runs made. With the tungsten furnace, the arc struck at from 10.25 to 36.5 volts depending upon the condition of the tube. As this tube could not be baked out on account of its construction, it was impossible to get entirely free from impurities, although the furnace was run for a considerable time and the tube heated from the inside in this way for two hours before iodine was admitted. The presence of a slight amount of impurity seemed to be sufficient to prevent the striking of the arc at 10.25 volts. On two occasions, once with vapor pressure of 0.3 mm. and the other time at a pressure of 1 mm., the arc was maintained to 10.25 volts. In the former of these runs the arc also struck at this potential. In both cases the filament was as hot as it could be used with safety. In a number of runs the arc struck at about 12 volts, and the average of the breaking potential of 16 runs was 12.1 volts, indicating that this is undoubtedly a critical potential for iodine. Several of the runs showed three sharp discontinuities in the current-potential curve, but there was no agreement in the values of the higher potentials. Iodine probably has several critical potentials, and further investigation to determine them is desirable. It is not surprising that this is the case with so complex an atom as the iodine atom is known to be.

There is no doubt that the iodine was dissociated in the tungsten furnace. Ordinarily the furnace was maintained at a bright yellow heat. Higher temperatures were tried, but there were no differences in the

[1] Amer. Chem. Soc. Jour., 37, 1016, 1915.

critical points obtained. In fact, the heat of the filament and the action of the arc were sufficient to produce practically complete dissociation inside the furnace cylinder. Calculations based upon the work of Starck and Bodenstein[1] on the thermal dissociation of iodine indicate that the vapor would be completely dissociated at pressures up to 5 mm. at 1200° C.

Why it was so difficult to maintain the arc below 12 volts is not clear in as much as the ionizing potential of the iodine atom is usually put at 10 volts or less as is seen from Table III. Compton and Smyth made no attempt to distinguish between radiation and ionization, and, as the total

TABLE III.

	Radiating Potential.	Ionizing Potential.
Found[2]	——	8.5
Mohler and Foote[3]	2.34	10.1
Compton and Smyth[4]	——	8.0 atom
		9.4 molecule
		6.8 fluorescing molecule

effect in their experiments was small, the ionization produced at the lower potentials may have been due to cumulative action. They point out in their paper that an inspection of Found's published curves shows that there are two break points, a pronounced one at 9.8 volts and another less sharply defined at about 8.3 volts. It would seem, then, that ionization is first definitely detected at about 10 volts, and the 10.25-volt break obtained in this investigation agrees with this within the limits of experimental error. There is no evidence in a comparison of the results of the simple tube and the furnace tube that the molecule is dissociated and one of the atoms ionized at a single impact as there was in the case of hydrogen. While the critical potential obtained from the simple tube is higher than those of the furnace tube, the differences do not correspond to the heat of dissociation of iodine which is equivalent to approximately 1.5 volts. This was a rather surprising result in view of the evidence obtained on this point by Compton and Smyth.

Iodine vapor acts quite rapidly on hot tungsten, and the life of a filament or a furnace was short. This made frequent renewals necessary, and so the progress of the investigation was slow and difficult.

[1] Zeit. Elektrochemie, 16, 966, 1910.

[2] PHYS. REV., 16, 41, 1920.

[3] PHYS. REV., 15, 321, 1920.

[4] PHYS. REV., 16, 501, 1920.

SPECTROSCOPIC OBSERVATIONS ON IODINE.

The line spectrum only appeared in the iodine arc, no trace of any bands being found. With the simple tube a few faint lines appeared, but most of the strong lines were seen with the furnace tube. A few lines flashed in when the arc struck and remained quite strong until the arc broke. The line 4862 was the strongest and most persistent of these and this together with the others of this group have been identified with the "arc" lines listed by Wood.[1] A number of additional lines appeared at higher voltages and increased more rapidly in intensity than those which appeared first. These lines faded out gradually as the voltage was diminished and vanished before the arc broke. They have been identified with other strong lines listed by Wood, being of those which increased in intensity when a spark gap was connected in parallel with his vacuum tube. This manner of appearance suggests that the first lines to appear are due to the neutral atom while the lines coming in later are due to the ionized atom and are enhanced lines. On the basis of the structure of the iodine atom given by the Lewis-Langmuir theory one would expect successive ionizations to occur rather easily.

In conclusion, the writer wishes to express his appreciation to Professor K. T. Compton, under whose direction this work was done, for his many helpful suggestions and unfailing interest during the course of this investigation.

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[1] Researches in Physical Optics, Part II.