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VOLUME IONIZATION PRODUCED BY LIGHT OF EXTREMELY SHORT WAVE-LENGTH.

By Frederic Palmer, Jr.

Introduction.

In 1900 P. Lenard[1] showed that in addition to the well-known Hallwachs effect, or ionization produced at a charged metallic surface when struck by ultra-violet light, there existed also a volume effect which took place in the gas itself, and could be detected at some distance (50 cm.) from the source of illumination. He employed a spark from an induction coil between terminals of aluminum. Since the light from this spark passed through a quartz window and a layer of air more than one centimeter thick it is very unlikely that it contained any effective rays of wave-length less than λ 1800. It seemed worth while, therefore, to investigate the effect of that part of the spectrum discovered by Schumann[2] which lies on the more refrangible side of λ1800. The present research was accordingly begun in February, 1904.

Lenard[1] showed that the ionization observed by him was closely connected with the absorption of ultra-violet light by the gas under investigation. Therefore, since it is known that wave-lengths in the Schumann region are completely absorbed by a thin layer of air at atmospheric pressure, the object of this research was to find out if possible whether this absorption was accompanied by ionization; and if so, whether this result increased as the wave-length of the effective light diminished.

[1]Ann. Phys., 1, p. 486, 1900; 3, p. 298, 1900.

[2]Smiths. Contrib. No. 1413, 1903; T. Lyman, Astroph. Journ., 23, p. 181, 1906.

E. Bloch[1] has shown that volume ionization produced by the light from an aluminum spark is greatly reduced if the gas under investigation is filtered through a plug of cotton wool; and he therefore has ascribed the effect observed by Lenard to photo-electric particles held in suspension in the gas, and not to ionization of the gas itself. More recently J. Stark[2] from other considerations has stated that the Lenard effect is probably due to photo-electric particles in the gas. He has also shown that volume ionization may be produced by the light from a quartz mercury lamp in certain organic vapors. The effective wave-lengths lay in the region between $\lambda 1850$ and $\lambda 3800$. He obtained currents through the vapors as large as 5×10^{-9} amp. under a pressure of about 50 mm.

J. J. Thomson and W. C. McKaye[3] have found that the light from a Wehnelt hot lime-covered cathode produces ionization in air, carbon dioxide, and ammonia; but the currents obtained by them were excessively small.

In this paper it will be shown that comparatively large currents may be obtained in air at atmospheric pressure when the extremely short wave-lengths which lie in the Schumann region are used as a source of illumination.

Before undertaking the main part of the research, Lenard's experiments were repeated both with the steam-jet and with a cylindrical condenser as the detecting apparatus. A Dolezalek electrometer instead of an electroscope was used to measure the leak between the cylinders. The chief sources of error were : (1) irregularities in the illumination produced by the aluminum spark; (2) the Hallwachs effect, which was eliminated by the proper use of soap solution; (3) photo-electric fatigue,[4] which resulted in the falling off of deflections obtained successively in the electrometer under apparently similar conditions.

GENERAL ARRANGEMENT.

Since it is purposed to employ the very short wave-lengths in the Schumann region, the form of the source of light is of the

[1]Comptes Rendus, 146, 17, p. 892.
[2]Phys. Zeitsch., 10, 18, p. 614.
[3]Proc. Comb. Phil. Soc., 14, p. 417, 1908.
[4]Cf. Hallwachs, Phys. Zeitsch., 21, p. 766, 1906.

utmost importance. It has been shown[1] that, when the secondary of a transformer is connected without additional capacity to the electrodes of a hydrogen-filled discharge tube containing traces of hydrocarbons, the excitation of the tube gives rise to carbon bands extending from the ultra-violet down to λ1700, and to strong hydrogen lines from λ1650 to λ1250. It was therefore determined to use a tube of this type as the source of illumination. While it is recognized that the carbon bands are capable of producing ionization, this investigation is chiefly concerned with the properties of the shorter waves; and therefore in order to get rid, as much as possible, of the effect produced by the carbon bands the tube was always carefully washed out with pure dry hydrogen several times before use.

The apparatus for producing ionization consisted essentially of three parts: (1) the discharge tube, (2) the screen cell, (3) the ionization chamber (see Fig. 1). The discharge tube *A* was a duplicate of the one already described by Lyman.[2] It could be exhausted by a mercury pump and filled with dry hydrogen from a small electrolytic generator. The pressure within could be measured by a McLeod gauge. The tube was excited from the secondary of a small transformer, the primary of which used about 4 amp. from a 110-volt A.–C. lighting circuit. The current through the tube, as measured by Pierce's crystal rectifier,[3] proved to be between .03 and .04 amp.

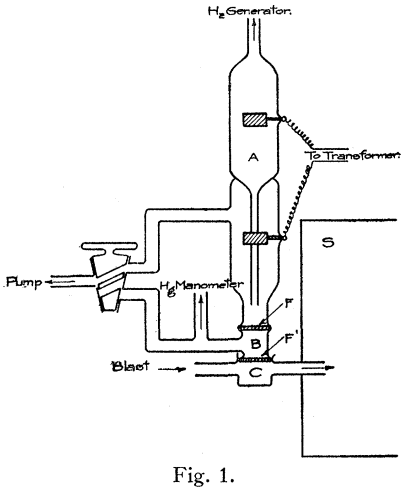

Fig. 1.
Apparatus for producing ionization.

The screen cell *B* was used as a diaphragm to cut off more or less of the effective rays according as the pressure in it was varied.

[1] T. Lyman, Astroph. Journ., 23, p. 181, 1906.
[2] *Loc. cit.*
[3] PHYS. REV., 25, p. 31, 1907.

It was 1 cm. in diameter and 1.0 cm. thick, and was separated from the discharge tube by a window of clear white fluorite F 1 mm. thick cemented with Khotinski cement. Ordinarily oxygen was used in the cell as an absorbing gas because its behavior was found to be more regular, and its absorption was better known than that of other gases. Dry oxygen could be admitted to the cell from a small electrolytic generator, and the pressure could be read either upon a closed mercury manometer or the McLeod gauge. A three-way stop-cock connected either the cell or the discharge tube to the mercury pump.

Another clear fluorite window F' 1 mm. thick separated the screen cell from the ionization chamber C, but the latter was arranged to slip over F' before being cemented in place so that the under surface of F' could be brought to a level with the side tubes of C. A blast of the gas under investigation could be maintained through C so that the ions, which were formed in this chamber, could be speedily swept away into the testing cylinders. The volume of the chamber was 1.4 c.c., and the distance between its center and the test cylinders 3 cm. Early in the investigation an ionization chamber was used which was open at the bottom so that a vessel containing mercury covered with soap solution could be raised from below to close the opening, and thus prevent surface ionization. However the soap solution was found to be the source of many irregularities in readings obtained, and so the form shown in Fig. 1, made of glass, was finally adopted. A comparison of readings obtained with the two chambers showed almost identical results, which may indicate that the ionization produced by light

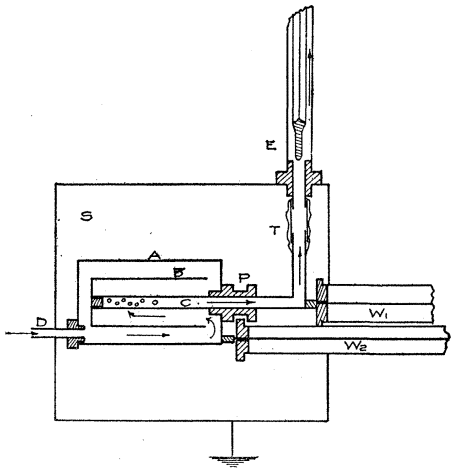

Fig. 2.
Testing apparatus.

of extremely short wave-length is confined to a region very close to the fluorite window F'. The velocity of the gas blast was maintained nearly constant. The value of the velocity was measured by a small open water manometer.

The apparatus for investigating the state of the gas issuing from the ionization chamber consisted of two parts: (1) the test cylinders, (2) the electrometer and its connections (see Fig. 2). The test cylinders of brass consisted of a concentric system of which the outside one A was closed at both ends by brass caps screwed on air-tight. It was 6.0 cm. long and had an inside diameter of 3.5 cm. The inner cylinder B was 5.0 cm. long and 2.0 cm. in diameter outside. The end nearer to the incoming gas was closed with a brass cap. A small brass tube C 0.4 cm. in diameter held B in place. The gas entered the system through the glass tube D which was placed opposite the annular space between A and B. The gas left the cylinders through the holes in the tube C. Thus the gas had to travel down between the cylinders, turn and pass up inside of B, turn again as it entered C, and pass along it for some 15 cm. before finally emerging past a thermometer. It thus seemed probable that even with a small potential gradient between the cylinders and a fairly rapid rate of flow of the gas, it would be possible to catch all of the ions before the gas escaped into the air. This assumption seems to have been justified by the actual performance of the apparatus. The tube C was insulated from A by the vulcanite plug P. A short piece of rubber hose covered with tin foil T connected C to the exit tube E. A stiff wire W_1 connected to C led through a grounded brass tube into the cabinet containing the electrometer and its connections. A similarly screened wire W_2 could be screwed to A, and by means of it A could be charged to any desired potential by a suitable storage battery. The entire cylinder system was enclosed in a large brass cylinder S, 10 cm. in diameter, which could be grounded and thus screen the testing apparatus from all outside influences. The Dolezalek electrometer after being properly adjusted, as described by Rutherford,[1] had a very slight normal leak, and could be made to have a sensitiveness of anything up to 7,500 scale divisions per volt P.D. between

[1]Radioactivity, 2d ed., p. 95.

the quadrants. The electrometer needle was suspended by a fine quartz fibre, and was charged from a water-battery by contact, usually to a potential of 40–100 volts. The electrometer was placed inside a cabinet lined with tin foil, and all contacts with it were made without opening the cabinet by means of levers operated by strings from the observer's seat. Either pair of quadrants could be connected (1) to the ground, (2) to a source of known E.M.F., (3) to the test cylinders. Deflections of the electrometer needle were read with a telescope and scale at a distance of about 2 meters. A standard cadmium cell of potential $V = 1.0177$ volts was used for calibrating the electrometer. On account of the sensitiveness of this instrument it was necessary to tap off a known fraction of the E.M.F., and suitable resistances were used in a simple potentiometer device to give one-eleventh the E.M.F. of the standard cell.

In using the apparatus it was desirable to know the pressure in the discharge tube which would produce the maximum effect in the ionization chamber. A preliminary experiment in which the pressure of air in the screen cell was kept at a low constant value (about .15 mm.), while the pressure of hydrogen in the tube was varied, showed a sharp increase in the effect up to a pressure of 1 mm. and a more gradual diminution from that point up to 10 mm. In all subsequent work, therefore, the pressure in the discharge tube was kept at an approximately constant pressure of 1 mm. This was also the pressure giving a maximum brilliancy when the tube was excited, though it did not correspond, as might have been expected, to the passage of maximum current through the tube, as was shown by measuring this current by means of Pierce's crystal rectifier. The maximum for the current took place at a pressure of 0.3 to 0.4 mm. To obtain constant results it was necessary that the tube should be excited for a constant short interval of time. A long excitation, by heating the tube, might set free occluded gases and thus change the pressure and therefore the tube's effectiveness. To this end a contact-maker was employed which illuminated the tube for one and one-fourth seconds. This instrument was tested for constancy of operation by connecting it to a chronograph. The greatest deviation from the mean of seven readings proved to be 2.25 per cent.

Another factor which it was necessary to make constant was the velocity with which the gas to be tested was blown through the ionization chamber. This was done by choosing arbitrarily a value on the water manometer which gave a deflection in the electrometer of the desired amount and then regulating the blast so that the manometer indicated this same reading each time an observation was made. The mean error of setting the blast repeatedly upon an arbitrarily chosen manometer reading was found to be about 2 per cent.

During an experiment it has been noticed repeatedly that apparently identical conditions gave rise to electrometer deflections which differed from one another by about five per cent. It seems that practically all of this may be accounted for by variations in the blast and length of exposure.

MANIPULATION.

Lyman[1] has found that the absorption of light in the Schumann region by oxygen is in the form of a band; and that, as the pressure increases, the absorption spreads much more rapidly toward the less refrangible side than in the other direction. For a column of gas 1 cm. thick at atmospheric pressure the band extends from λ1268 to λ1770, and for a pressure of .02 atmosphere from λ1350 to λ1500.

If oxygen is admitted to the screen cell at pressures varying from .0001 to 1 atmosphere, more and more of the effective rays from the discharge tube will be absorbed in passing through it. Thus the ionization produced in the chamber should be reduced with each increase of pressure in the screen cell. The wave-lengths which are available for the production of ionization in the chamber are those which get through the screen cell at any given pressure, and these may be determined when the width of the oxygen absorption band for the given pressure has been found.

The method of procedure in getting the relation between the two quantities—light entering the ionization chamber, and resultant ionization— is as follows: The pressure in the screen cell is reduced very low and measured on the McLeod gauge. A gas is allowed to

[1]Astroph. Journal, 27, p. 87, 1908

blow through the ionization chamber and test cylinders at the desired constant velocity as indicated by the water manometer. Before reaching the chamber the gas has to pass through 30 cm. of glass wool and over 25 cm. of calcium chloride and 25 cm. of phosphorus pentoxide. It is therefore assumed to be dust-free and dry. While one pair of quadrants in the electrometer is kept in connection with the earth, the other pair, connected with the inner of the test cylinders, is now insulated. The contact-maker is set in motion and allowed to excite the discharge tube once. Shortly after the illumination ceases the stream of gas is shut off, and the resulting deflection in the electrometer observed. Both pairs of quadrants, together with the inner test cylinder, are then connected to earth, and oxygen from the electrolytic generator carefully dried over phosphorus pentoxide is admitted to the screen cell changing the pressure therein by a desired amount, as indicated by the closed mercury manometer. The tube is again excited, the resulting deflection made, and so on.

Since, as has already been shown, the light of short wave-length entering the ionization chamber depends upon the pressure of oxygen in the screen cell, and since the electrometer deflections are very nearly proportional to the resulting ionization, curves have been obtained showing the relationship existing between these two quantities for different gases. None of the gases used produced measureable deflections when blown unilluminated by the discharge tube through the test cylinders.

OXYGEN.

Oxygen, 92 per cent. pure, made by the potassium chlorate black oxide of manganese process and put up in a cylinder under pressure, was passed through distilled water, then through two large U-tubes each arm of which contained 10 cm. of phosphorus pentoxide held in place by plugs of glass wool. These were supported vertically so that the oxygen was forced slowly through the phosphorus pentoxide, not over it. The gas was collected over mercury and finally blown through the ionization chamber. Glass tubing only was used for all connections. After passing the entrance to the water manometer the oxygen was again dried over phosphorus pen-

toxide before finally entering the chamber. With oxygen thus dried results were obtained which the curve showing pressures of oxygen in the screen cell, in centimeters of mercury, plotted against electrometer deflections is given in Fig. 3, *A*. Since

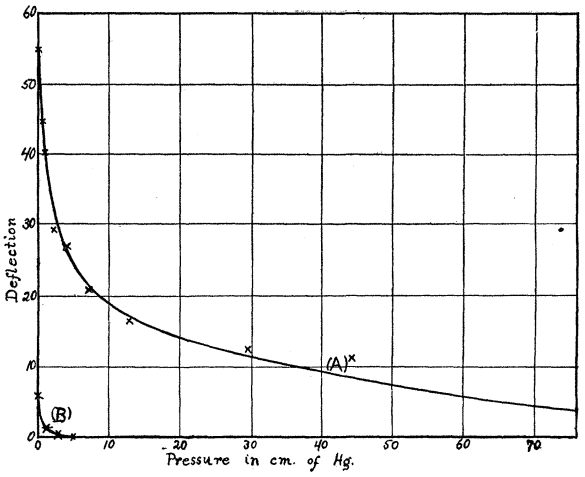

Fig. 3.

(*A*) Negative leak. Oxygen. (*B*) Negative leak. Hydrogen.

the outer of the test cylinders (*A*, Fig. 2) was charged to a potential $V = -20$ volts, this curve represents the negative leak between the two cylinders. A large proportion of the work has been done with the outer test cylinder at a constant potential $V = \pm 20$ volts. The saturation curves (not here shown) which have been obtained, show that for the gas velocities generally used this value of the potential was sufficient. The gas was at a temperature of 24° C., and its velocity through the ionization chamber was 20 cm./sec. The electrometer had a sensitiveness of 165 cm. per volt P.D. between the quadrants, and its capacity, together with that of the test cylinders and connections was 111 cm., or $111/9 \times 10^{-11}$ farads. Taking the maximum deflection in the above curve, it is easy to see that the insulated pair of quadrants has acquired a potential $V = 55/165$ volts, and, since $Q = VC$, $Q = 55/165 \times 111/9/\times/10^{-11}$, or 4.2×10^{-11} coulombs. If it is assumed that the average current may be obtained by dividing this quantity

by the time during which the gas is exposed to ultra-violet light, then

$$i = \frac{4.2 \times 10^{-11}}{1.25},$$

or the average current is 3.3×10^{-11} amperes. Considerably larger currents have been obtained. The normal rate of leak in the electrometer used in these experiments was 0.4 cm. per *minute*, and the maximum leak in the ionized gas was in this case at the average rate of 44 cm. per *second*.

An examination of curve *A* shows it to be made up of two parts: first, a nearly straight portion, rising slowly as the pressure in the screen cell is changed from 76 to about 19 cm. of mercury; second, a curved part, which rises rapidly as the pressure is reduced from this point down to the lowest value reached. An inspection of Lyman's paper[1] shows that, according to the evidence of the photographic plate, as the pressure in the absorbing cell is reduced from 76 to 19 cm., the width of the absorption band in oxygen becomes only slightly less, *i. e.*, changes from λ1770–1268 at 76 cm. to λ1740–1280 at 19 cm.; while from this point on the band rapidly becomes narrower with decreasing pressure, extending from λ1600 to λ1335 at a pressure of 4 cm., and disappearing entirely below a pressure of 1.5 cm. The absorption band is thus unsymmetrical, the change taking place more rapidly on the less refrangible side of the band. It, therefore, seems justifiable to assume in these experiments that, when the pressure of oxygen in the screen cell is about 19 cm. of mercury, two narrow bands of light pass through into the ionization chamber, in addition to all the light which went through at a pressure of 76 cm. These two bands extend from λ1770 to λ1740, and from λ1280 to λ1268. To them may be due the rise of curve *A*, which takes place slowly between the above pressures. Then, as the pressure in the screen cell is reduced to its lowest value, more and more of the wave-lengths in the Schumann region pass through into the ionization chamber. To these wave-lengths is due the rapid rise of curve *A*, which takes place at the lower pressures. It may be mentioned here that there is no reason to believe that the

[1] *Loc. cit.*

smallest amount of energy necessary to produce a chemical effect upon a photographic plate is the same as, or even comparable with the smallest amount necessary to produce ionization detectable by the method employed in this research. It is, therefore, quite probable that the sensitiveness of one method differs considerably from that of the other.

In consideration of these facts the author[1] has already stated that volume ionization is produced by light of wave-length less than λ1800, and that this effect increases with decrease in wave-length, at all events in the region between λ1850 and λ1400.

When the outer test cylinder was charged positively the results were, within experimental error, the same as those given above, showing that in the ionization chamber positive and negative ions are formed in equal numbers.

Hydrogen.

The gas was made electrolytically, passed through phosphorus pentoxide and collected over mercury in the same manner as the oxygen. In order to obtain deflections large enough to measure accurately the velocity of the gas stream was increased to 30 cm./sec., and the sensitiveness of the electrometer to 190 cm./volt. However, for the sake of comparison with the oxygen curve, the leak in hydrogen when the outer test cylinder was charged to a potential $V = -20$ volts has been plotted on Fig. 3 as curve B, and is on the same scale as curve A.

Nitrogen.

This gas was prepared by passing the nitrogen from a cylinder obtained from the Lindé Air Products Co. of New York through distilled water, over red hot copper, and through phosphorus pentoxide. It was collected in the same gasometer over mercury and used as were the other gases. The manner in which the gas in the cylinder is made by the company permits the presence of small quantities of argon and helium as impurities, but precludes the possibility of carbon dioxide or monoxide. A specimen of this gas analyzed for traces of oxygen and oxides of nitrogen showed:

[1]Nature, 77, p. 582, 1908.

"Oxygen 0.4 per cent., oxides of nitrogen 0.02 per cent. This does not include nitrous oxide or nitrous anhydride. The presence of the latter is, however, almost impossible, and of the former very unlikely." The results obtained with this nitrogen are plotted in Fig. 4. This curve represents the negative leak, since the potential of the outer test cylinder was -20 volts. Moreover, the gas velocity through the ionization chamber was only 11.5 cm./sec., and the electrometer had a sensitiveness of 75 cm./volt, which corresponds to a capacity of 70 cm.

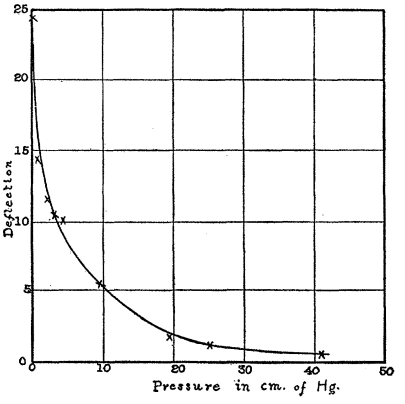

Fig. 4.
Negative leak. Nitrogen.

Nitrogen was also made from potassium nitrite by Gibbs's method. A specimen of this gas which was analyzed gave: "Oxygen none, oxides of nitrogen none." The steep rise of the ionization curve for pressures less than 2 cm. was even greater in this case, which indicates that the sharp rise is not due to the impurity of the gas.

AIR.

Air from the laboratory was passed through distilled water, and then through the same tubes of phosphorus pentoxide, being collected as before in the mercury gasometer. The results obtained for the negative leak are shown by the curve in Fig. 5. The conditions of this experiment were similar to those for the other gases, though it is not possible to compare the magnitudes of the curves given thus far, owing to differences in gas velocity and sensitiveness of the electrometer.

COMPARISON.

It has frequently been shown that absorption and ionization in a gas go hand in hand. Therefore since it is known that air and oxygen absorb light of extremely short wave-length very strongly,

while nitrogen is much more transparent and hydrogen hardly absorbs at all, it was to be expected that ionization would be detected in air and in oxygen, but that in nitrogen and in hydrogen, the amount of ionization, if it could be detected at all,

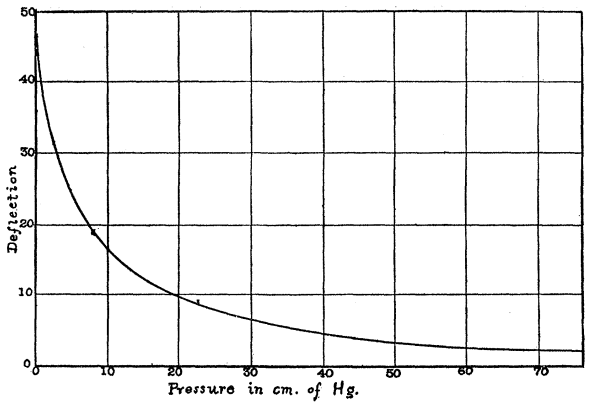

Fig. 5.
Negative leak. Air.

would be extremely small. In Fig. 6 are given the ionization curves obtained all in a single day, and under as nearly the same conditions as possible. The gas velocity was less than that of any of the previous curves and was the same for all. The potential of the outer test cylinder was $V = -16$; and the electrometer had a sensitiveness of 170 cm./volt. Under these conditions the ionization in hydrogen, even when the gas velocity was doubled, was so small as to be unmeasurable.

An inspection of the curves indicates that while air and oxygen show marked ionization, and hydrogen practically none, the ionization which takes place in nitrogen is unexpectedly large, and increases greatly for pressures in the screen cell less than 1 cm. Moreover, since a given thickness of air is more transparent than the same thickness of oxygen, it might be expected that the air curve of ionization would be lower than that for oxygen, but the opposite has always been found to be the case. It may be possible that small amounts of ozone, carbon dioxide, and carbon monoxide, present in the air account for a small portion of the ionization de-

tected, but it seems as if much more of it might be due to nitrogen than had previously been supposed possible.

In all four gases there is unmistakable evidence of a sharp rise in the ionization curve when the pressure of oxygen in the screen cell is reduced below 2 cm. Since it was earlier shown that the shortest

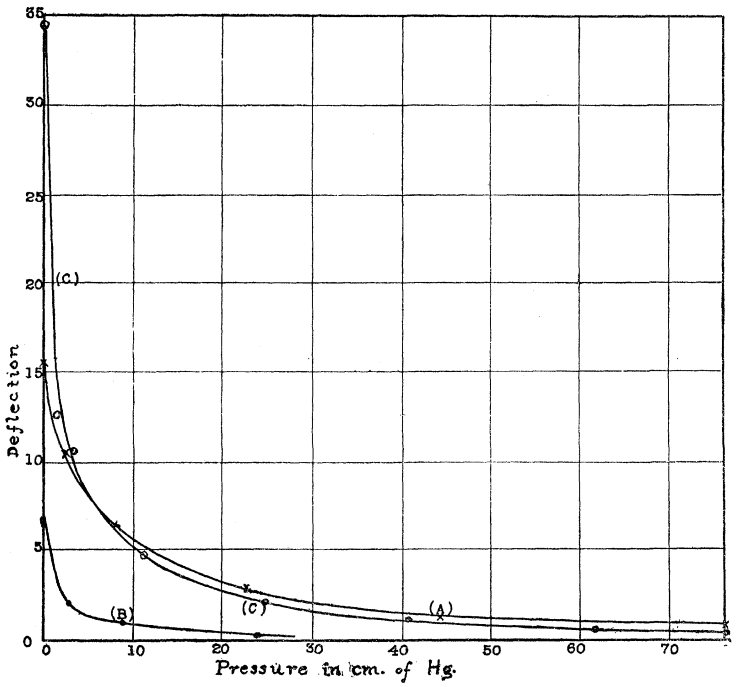

Fig. 6.
Negative leak.

wave-lengths passed through the screen cell only when the pressure in it was as low as 2.5 cm., the above result indicates that ionization increases very greatly as the wave-length decreases, at all events in the region between λ1850 and λ1400.

Although Lyman[1] has found that the absorption of ultra-violet light by nitrogen is small and increases regularly with decreasing wave-length, Schumann[2] states that nitrogen absorbs particular wave-lengths very energetically. It is known that nitrogen absorbs

[1]*Loc. cit.*
[2]*Loc. cit.*

wave-lengths between λ1500 and λ1300, such as pass through the screen cell at the lowest pressures, and if the absorption is particularly energetic in this region it may account for the observed rise in the ionization curve.

Dust.

The work of E. Bloch[1] seems to show that minute particles held in suspension by a gas, when acted upon by ultra-violet light, may produce a photo-electric effect which simulates that of volume ionization. In order to show that the results obtained in these experiments were not due to such a photo-electric effect, a plug of cotton wool 15 cm. long was inserted in the gas blast in addition to the many plugs of glass wool already there. The insertion of the cotton wool produced no detectable effect. It is also to be observed that the ionization in hydrogen is extremely small, yet from the manner of its production, there might be as much dust in hydrogen as in the other gases.

Water Vapor.

If water vapor has any effect, it is of great importance in this work, since it might produce absorption in the oxygen of the screen cell, resulting in a *smaller* electrometer deflection than if the oxygen were dry; or it might produce ionization in the gas being tested, resulting in a *larger* deflection. The following experiments will show that water vapor not only has an effect both in the screen cell and in the ionization chamber, but also that this effect is most pronounced.

Curve *A*, Fig. 7, is the same curve previously shown as *A*, Fig. 3, and represents the negative leak in oxygen when both the oxygen in the screen cell and the oxygen in the ionization chamber are dry. If the oxygen in the screen cell is kept dry, while oxygen which is slightly damp is taken from the previously mentioned oxygen cylinder, and passed through the ionization chamber, the result is curve *B* which falls much less rapidly at low pressure than *A* and does not reach it until the pressure in the screen cell has risen to 54 cm. of mercury. If this same undried oxygen from the cylinder is used in the screen cell as well as in the ionization chamber, the result is curve *C*, which is distinctly lower than *B* even up to atmospheric

[1] *Loc. cit.*

pressure, with the exception of the region below a pressure of 2 cm. of mercury. It was not convenient to saturate the oxygen which was admitted to the screen cell with moisture; so, instead, upon one occasion when the air in the laboratory was exceedingly damp it

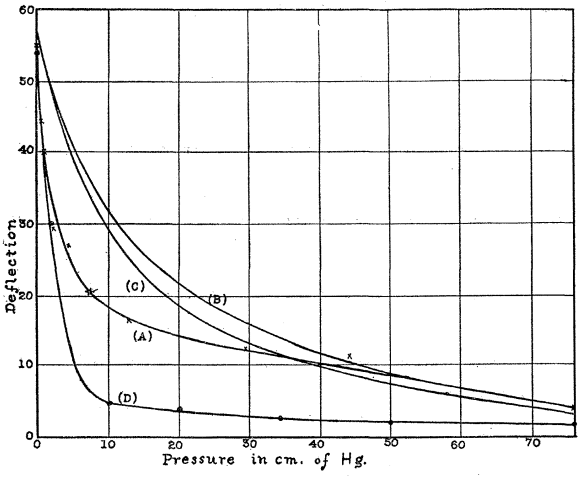

Fig. 7.
Effect of water vapor.

was admitted directly to the cell, while slightly damp oxygen from the cylinder was passed through the ionization chamber. The resulting state of affairs is shown in curve *D* and is conclusive in regard to the possibility of absorption due to water vapor in the screen cell.

MERCURY VAPOR.

W. Steubing[1] has found that mercury vapor is ionized by light in the region of λ1800–2400. It is possible that it may be ionized also by light in the region of λ1250–1800. If so, since all of the gases examined were collected over mercury, and since the screen cell was in continuous connection with a mercury manometer, it might be possible for mercury vapor to play a part in the phenomena here under investigation. However, since the vapor pressure of mercury is so small at atmospheric pressure, it is not likely that such minute quantities of this vapor as could mix with the gas

[1]J. Stark, Phys. Zeitsch., 10, 18, p. 623.

under investigation in the gasometer would affect the amount of ionization observed, even if the vapor were capable of producing any effect at all. No effect ascribable to mercury vapor in the ionized gas has been detected in these experiments.

Since the oxygen admitted to the screen cell is subjected to pressures all the way from atmospheric down to .01 mm. of mercury, it might very well be the case that at the lowest pressures used mercury vapor might constitute nearly one per cent. of the gas in the cell, and might produce a much greater percentage of absorption. Evidence of such an effect has been observed with all the gases examined at very low pressures of oxygen in the screen cell; but this is especially noticeable with nitrogen, since such a large proportion of the observed ionization in this gas is produced with low pressures in the screen cell.

Chemical Changes.

Many investigators have shown that ordinary ultra-violet light changes oxygen into ozone, and Lyman[1] has found that the light of extremely short wave-length used in this work does so to a very marked degree. It is therefore undoubtedly true that some of the oxygen used in the screen cell in these experiments is turned into ozone. However, since it has also been shown[1] that the absorption due to ozone does not differ appreciably from that due to oxygen this fact alone should not be a source of error here; unless, indeed, the method of ionization should prove to be superior to the photographic plate as a detector of absorption. If, on the other hand, the ozone when formed produces or facilitates other chemical changes, it might be possible that the resulting products of such changes would form a very considerable source of error.

Two effects have been observed which might be accounted for on the assumption that the ozone facilitates the formation of a layer of gas very close to the fluorite window, like that described by Hallwachs[2] in his explanation of photo-electric fatigue. One of the observed effects is the falling off of deflections in the electrometer taken successively under apparently the same conditions, when

[1] *Loc. cit.*

[2] Phys. Zeitsch., 21, p. 766, 1906.

the pressure of oxygen in the screen cell is anything from 1 to .0002 atmosphere. This effect is very similar to that ascribed to the presence of mercury vapor, but differs from it in that the deflection can be brought up to its initial maximum value either by waiting for ten minutes between readings, or by admitting fresh oxygen and reëxhausting to the same pressure as before. The first operation might give the ozone time to break up into oxygen, and the gas layer to become dissipated; while the second might be effective through breaking up of the gas layer by the inrush of fresh gas, followed by the loss of some of the ozone by reëxhaustion as well as by the natural process of breaking up into oxygen.

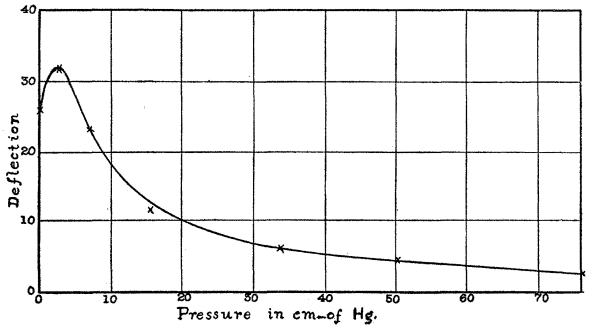

Fig. 8.

Effect of chemical action on fluorite.

The other effect has been observed not infrequently after the apparatus, as shown in Fig. 1, has been in use for some time. It consists of a complete change in the character of both positive and negative ionization curves for pressures less than 2.5 cm. of mercury in the screen cell. Instead of increasing as the pressure in the cell is reduced to its lowest value the curve passes through a maximum at a pressure of about 2 cm., falling off sometimes to only 80 per cent. of its maximum value when the lowest pressures are reached. Fig. 8 represents such a case when $V = -20$ volts and the ionized gas was oxygen. Upon taking apart the apparatus no film was found on the side of the fluorite window F (Fig. 1) next the discharge tube, where one might have been formed from a metallic deposit from the aluminum electrodes; but a film was formed on

the side of the window F next the screen cell. No film has ever been found on the window F' (Fig. 1). The film has always been observed whenever the character of the ionization curve has undergone change, as in Fig. 8. Upon one occasion when the film was carefully examined, it was found to consist of two distinct parts; one was composed of fine, white, microscopic dust, which could be brushed off easily by a touch from some cotton wool; the other, when viewed in reflected light, appeared like a very thin film of whitish metal, which could be removed only after soaking in alcohol, and then rubbing briskly with cotton wool. The layer of dust occupied the exact central portion of the window and was in the form of a disc of diameter very little larger than the end of the capillary in the discharge tube, exactly opposite to which it was situated. The other film was also circular in shape, though its outline was not so clearly defined as that of the disc of dust, and its diameter was about three times as great, the two being concentric. On one side a notch in the circumference of the outer film was noted where no deposit existed. In this instance the fluorite window was 2.5 mm. thick, and a close examination showed a flaw on the side next the discharge tube which proved to be in a straight line from the end of the capillary to the notch noted above, thus indicating that the flaw had cast a shadow, in the line of which no chemical action on the fluorite had taken place. This shows that the action must take place extremely close to the window; that the dust layer must be formed by the more intense light which shines down some length of the capillary; and that the larger film must be produced by the weaker illumination which comes from close to the end of the capillary. Furthermore, since no effect has ever been found on the window F', it shows that the effective rays here are the very shortest. When carefully dried oxygen is used in the screen cell the apparatus may run for weeks without the formation of the film; but if oxygen from the storage cylinder is used, or if air is admitted from the room even if partially dried, the film forms quite quickly, sometimes in a day. The formation of the film, then, seems to be due to the action on the fluorite of ozone in the presence of a small amount of water vapor. This suggests that hydrogen peroxide may be the effective agent.

Since the curves shown represent the ionization produced by the sum total of all the light passing through the screen cell at any given pressure, it is not easy to see how a maximum in such a curve could be produced. It is probable that the dust layer described above plays a double role in this process: (1) absorbing much of the light of shortest wave-length, (2) facilitating the formation of a gas layer on the fluorite by presenting a roughened instead of a smooth surface. If it is assumed that this gas layer forms more readily on the roughened surface at low pressures, or that its absorption is abnormally large for such pressures, and that it absorbs the shorter wave-lengths more easily than pure oxygen, it can be seen how starting with a very low pressure in the cell practically all the absorption taking place would be due to the dust film and to the gas layer; but if a little more oxygen were admitted to the cell the gas layer might be disturbed, while the absorption due to the oxygen itself would increase.

If the increase in absorption due to the introduction of the oxygen was not as great as the gain in transparency due to the breaking up of the gas layer, the curve of ionization would rise. As more oxygen was admitted, the increased absorption due to the oxygen would overbalance the decrease due to the change in the gas layer, and therefore the ionization curve would begin to fall again, and would continue to do so up to atmospheric pressure.

It is possible that the effect here described is the same as that noted by C. T. R. Wilson[1] in his experiments on the formation of clouds by ultra-violet light. He has suggested that the formation of hydrogen peroxide by ultra-violet light would explain the phenomena observed by him. Although his source of illumination (zinc spark in air) gave rise to no such extremely short wave-lengths as those effective here, nevertheless it was a much more intense source than the hydrogen tube of these experiments, and might have produced hydrogen peroxide on that account. Lenard[2] has also found that ultra-violet light produces cloud nuclei which are non-electric in character, though he has not suggested what their real nature might be. It is quite possible that these, too, may be minute

[1]Phil. Trans., 192, p. 403, 1899.
[2]Ann. Phys., 3, p. 298, 1900.

particles of hydrogen peroxide. It may be also that the roughening of a surface under the action of ultra-violet light noted by many investigators is due to the same cause as that which produced the dust layer described above.

Whatever may be the explanation of the phenomenon, it is certain that the maximum in the ionization curve exists only when the film on the fluorite window is present.

Temperature.

The gases examined were all at nearly the same temperature, that is from 15° C. to 25° C. Between these limits there was no detectable temperature effect.

Conclusions.

In conclusion it should be noted that the objection raised by Bloch to Lenard's work (dust) does not apply to the present investigation, since the insertion of a long plug of cotton wool in the gas stream was without effect. Furthermore, since it has been shown that the ionization produced in hydrogen is *extremely* small, this fact proves conclusively that the results obtained were not due to photo-electric action at the inner surface of the ionization chamber. This point meets the objection recently raised by Stark.

Finally, although the hydrogen tube used emitted light of low intensity, it was possible to obtain rather large currents through air, oxygen and nitrogen, owing to the great power of ionization possessed by the very short wave-lengths. Therefore, it seems clear that the reason why J. J. Thomson and McKaye, and others have obtained only extremely small currents in oxygen is because they have not employed a source of illumination emitting light of sufficiently short wave-lengths. The large currents measured by Stark were obtained in vapors having a very complex molecular structure, and not in oxygen. During the course of the present investigation it was found that, if alcohol or ether vapor were mixed with the gas under examination, the electrometer deflection in one second was so large as to be unmeasurable. This shows that for vapors of complex molecular structure the shortest wave-lengths also are capable of producing very large currents.

SUMMARY.

1. Using a discharge tube filled with hydrogen as a source of light and a screen cell filled with oxygen at various pressures, ionization curves have been obtained in air, oxygen, hydrogen and nitrogen.

2. The ionization in air, oxygen and nitrogen is considerable. That in hydrogen is exceedingly small. The currents obtained for all gases are large compared with the values of most other observers.

3. The power of ionization increases greatly with decrease in wave-length of light, at all events in the region below $\lambda 1850$.

I take this opportunity of thanking Professor G. P. Baxter for valuable suggestions as to the production of pure nitrogen and also for superintending the analysis of the specimens of that gas.

The investigation was carried on in the Jefferson Physical Laboratory at Harvard University.

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