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PHYSICAL REVIEW.

IONIZATION AND EXCITATION OF RADIATION BY ELEC-TRON IMPACT IN MERCURY VAPOR AND HYDROGEN.

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MERCURY VAPOR.

Introduction.—It has recently been pointed out by Van der Bijl¹ that the regular Lenard method for the direct determination of the ionizing potentials of different gases and vapors, in particular mercury vapor, is open to an objection which has not been considered by the experimenters hitherto employing this method. The objection is based on the fact that the positive charging up of the collecting electrode may as well be due to a photo-electric emission of electrons from it, under the action of the ultra-violet light emitted by the impacted atoms of the gas or vapor, as to the formation of positive ions by impact. This fact could not be determined from the curve shape since the number of radiating sources (intensity of radiation) and the positive ions produced would both be proportional to the number of impacts.

The possibility that this is the case in mercury vapor at a voltage less than the true ionizing voltage is rendered highly probable, because of the nature of the experimental results obtained by Tate,² Goucher,³ and McLennan and Henderson.⁴ Tate and Goucher have shown that below the region of 10 volts an effect is obtained setting in at 4.9 volts, but that this is small compared to the effect occuring at 10+ volts.

It had previously been shown by Franck and Hertz⁵ that impacts in mercury vapor were elastic up to a certain minimum energy of the im-

¹ PHys. Rev., pp. 173-175, Feb., 1917.

² PHYS. REV., pp. 686–687, June, 1916.

³ PHys. Rev., pp. 561-573, Nov., 1916.

⁴ Proc. Roy. Soc., A, Vol. 91, 1915.

⁵ Verh. d. D. Phys. Ges., Vol. 11, p. 512.

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pacting electrons, viz., 4.9 volts, and that at this voltage the electrons lost their energy and at the same time emitted the radiation of wavelength $\lambda = 2536.7$ Å., the frequency of which was connected with the voltage (4.9) by the quantum relation $Ve = h\nu$. They had assumed that this loss of energy was accompanied by ionization. McLennan and Henderson extended this work and found that in mercury vapor this single line $\lambda = 2536.7$ Å. alone apparently was emitted up to a value of the voltage slightly greater than 10 volts, but that the many lined spectrum of mercury suddenly appeared if the voltage was increased much beyond this value. They also pointed out that this value 10+ volts is near that calculated from the quantum relation, $Ve = h\nu$, when the frequency taken is that of the head or shortest wave-length of the Paschem combination series of the mercury spectrum $\nu = 1.5S - mP$, viz., 10.4 volts; whereas the line $\lambda = 2536.7$ Å. is the first or longest wave-length of the second subordinate group of this same series, viz., $\nu = 2p - mS$. From theoretical considerations then, in light of the Bohr theory, McLennan was led to question whether ionization really took place at 4.9 volts, or only at 10+ volts at which the many lined spectrum was emitted. He was led to conclude however by his own (McLennan and Keys)¹ experiments on the conductivity of flames in which mercury vapor was present in a state of emitting only the line $\lambda = 2536.7$ Å., that ionization really did take place at this voltage and that therefore there seemed to be two types of ionization in mercury vapor. It should be noted however that the flame conduction experiments are open to the same criticism as those employing the direct method of Lenard.

It may be pointed out that there are no theoretical grounds for believing that there should be two tpes of ionization in mercury vapor; nor yet why, if a single line was emitted without ionization at its corresponding voltage, the other lines were not emitted at their corresponding voltages, instead of appearing altogether when ionization had taken place as the experiments of McLennan seemed to indicate. McLennan looked carefully for the other intense line in the series, viz., $\lambda = 1849$ Å., which is the longest wave-length of the principal series, $\nu = 1.5$ S-mP, but was unable to find any trace of it.

All these facts rendered it highly desirable to determine whether or not the effects occuring below 10.4 volts were due to ionization or to the emission of ultra-violet light from the bombarded atoms, and whether or not positive ionization actually took place at 10.4 volts. For the purpose of testing with regard to these possibilities, the following modification of the Lenard method was proposed by one of us (Goucher).

¹ Proc. Roy. Soc., A, Vol. 92, p. 591, 1916.

Apparatus.—The modification consisted essentially in the introduction of a second gauze, C, Fig. I in the apparatus employed in the regular

Lenard method and described in detail by Goucher; where A is the platinum equipotential surface electron source; Bthe platinum gauze through which the electrons from Aare accelerated; D the collecting electrode of aluminum.

The gauze C was of rather large copper wire and coarse mesh, and was supported by the tight-fitting flange of brass in the glass part as shown. The arrangements were otherwise quite the same as those employed in the vessel used by Goucher, with the exception of the palladium tube Psealed in for the purpose of admitting hydrogen into the apparatus when desired.



All joints not of glass were ground and sealed with De Khotinsky cement, the heater leads being also sealed in with this cement.

The vessel was connected through a large $\frac{3}{4}$ in. exhaust tube, a liquid air trap, and a large stop-cock, furnished with a capillary by-path, to a mercury diffusion pump of the Langmuir type, and to a McLeod gauge.

The electrical measurements were made by means of a suitably shielded electrometer connected to D and sensitive to about 500 div. per volt. The potentials were applied and maintained by means of dry cells and suitable potentiometer connections, and were measured by a Siemens and Halske standard voltmeter.

Method.—The procedure in making measurements was essentially that employed in accordance with the Lenard method.

A field V_1 was impressed between A and B, Fig. 1, in such direction as to accelerate the electrons from A through the gauze B; a field V_2 was maintained between B and C in such direction as to oppose the passage of these electrons in the region BC and just enough larger than V_1 to prevent the electrons from reaching C. The departure from the Lenard method consisted in the maintainance of a third and constant field V_3

between C and D throughout the measurements, but just as in the Lenard method the rate of charging up of D was measured for different values of the voltage V_1 , $V_2 - V_1$ being maintained constant. The shape of the current curve thus obtained and its intercept with the voltage axis was, as in the case of the Lenard method, used as a basis for the interpretation of the results.

The function of V_3 was to control the field between C and D, it being possible to maintain it either in the same direction as V_2 or in the opposite direction, thereby furnishing a means of distinguishing between a photoelectric charging up of D, and a charging up due to the production of positive ions in the region BC. For if V_3 be made smaller than V_2 , positive ions formed in the region BC will be able to reach D and consequently will have a tendency to charge it positively whether V_3 be either in the same or opposite direction to V_2 . Whereas, if the atoms of the mercury vapor are stimulated to emit radiation, both C and D will be in the path of such radiation, and would consequently be capable of emitting photo-electric electrons, so that D would charge up due to this cause, and the direction of this charging up of D would be determined by the direction of the field V_3 . If V_3 were in the same direction as V_2 electrons would be extracted from D and driven to C (or through it into the region BC beyond), while if V_3 were in the opposite direction to V_2 , the emission of electrons from D would be prevented, and part of the electrons emitted from C would be carried to D, causing it to charge up negatively. The relative rates of charging up of D for these two directions of V_3 , for any given voltage V_1 , would of course depend on the relative strength of electron emission of C and D under these conditions. It is evident that they would follow the same law of increase with increasing values of V_1 , since the intensities of the radiation falling on C and D should always be in the same ratio.

It is evident that if C and D are connected together we would have the equivalent of the regular Lenard method, and we see why in this case we would have no means of distinguishing, from the shape of the current curves, as to whether it is caused by radiation from the impacted atoms or to actual ionization of the gas. For, if the charging up of D were due to radiation, the intensity of electron emission from CD would be proportional to the number of atoms stimulated to emit radiation by impact, whereas if it were due to positive ions from region BC, the number of such ions would be proportional to the number of impacts resulting in ionization.

The procedure then in the application of this method for the purpose of distinguishing between these two causes, consists in maintaining a

field V_3 in a desired direction between C and D. The field V_3 is small compared to V_2 . The field V_1 and V_2 are applied in their proper directions, the difference $V_2 - V_1$ being kept constant, and the rate of charging up of D for different values of V_1 is measured. The current voltage curves, for V_3 in the same or opposite direction to V_2 , may be thus obtained and compared. Should the curves show a negative charging of D when V_3 is oppositely directed to V_2 , we may conclude that at least the effect of radiation is greater than that of ionization, and if the curve continues to increase in the negative direction for increase of voltage V_1 , we must attribute this increase to impacts resulting in radiation, for the tendency of ionization would be to cause an increase of current in the positive direction.

The method can be further extended to the study of radiation alone, by making V_3 greater than V_2 and in the opposite direction to it, thus preventing the positive ions that may be formed in the region BC from reaching the collecting electrode D. The charging up of D in this case will be due to the electrons emitted from C by the ultra-violet radiations and carried to D by the field V_3 . The shape of the negative current curve with different values of V_1 will then serve as a basis for an interpretation of the nature of the radiation emitted by

the atoms of mercury vapor when impacted at various voltages.

Results.—For the purpose of making measurements in mercury vapor liquid mercury was introduced into the measuring vessel and contained in the part marked "To B," Fig. 1. The heat from the electron source A was sufficient to produce the desired pressure of mercury vapor for most measurements, but the vessel was enclosed in a heat insulating box when higher pressures were desired. The pressures usually employed were probably less than .01 mm., estimating from the temperature of the vessel at the time of making the observations.



The diffusion pump was kept running continuously to carry off any traces of

other gases than mercury vapor. The quantity of permanent gas present was always too small to give a reading on the McLeod gauge.

Fig. 2 shows the current curves obtained in accordance with the regular

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Lenard method (C and D connected together), where (a), (b) and (c) were obtained with decreasing electron emission from A, and over increasingly wider range of voltages. Curve (a) shows the sharp break at 4.9 volts, and is the same kind of curve as that previously obtained by Goucher. Curve (b) shows a marked increase of the current between 6 and 7 volts, while curve (c) shows this same increase and in addition a discontinuity at 9.8 volts and a very sharp rise in current intensity at This value 10.3 volts is very close to 10.4 volts as cal-10.3 volts. culated from the head of the Paschen series. The discontinuity at 9.8 volts which occurs at twice the value 4.9, is what should be expected in consideration of the elastic nature of the impacts of electrons having an energy less than that due to 4.9 volts; and this would be true whether the energy lost at 4.9 volts were transferred into radiation or produced ionization. This energy loss would occur again at twice this voltage, viz., 9.8 volts, producing an increase either in the intensity of the radiation or ionization at values beyond this.



The curves obtained, when the charging up of D alone was measured, with a field V_3 of 1.5 volts maintained between C and D, are shown in Fig. 3. Curve (b) was obtained with V_3 in the same direction as V_2 , and curve (a) with V_3 in the opposite direction to V_2 . Since curve (a) shows a negative charging of D, increasing with increase of applied voltage V_1 up to a voltage of 10.3+, where there is a sharp positive increase, we can fairly attribute the effects below this point to a photo-electric emission of electrons from The production of positive ions in region C. BC would cause an increasing tendency to make D charge positively with increasing values of V_1 . Since curve (b), up to 10.3+ volts, shows a positive charging of D in accordance with practically the same law of increase as shown in (a), we can likewise attrib-

ute this part of the curve to photo-electric emission of electrons from D. We may conclude from these results that the corresponding portions of the curves obtained by the regular Lenard method (Fig. 2) were also due to photo-electric action on the collecting electrode caused by radiation from the impacted atoms of mercury vapor.

The strong positive charging of D in both cases, (b) and (a) Fig. 3,

above the value 10.3+ volts, we can attribute only to the production of positive ions in the region *BC*, and since this value, within the limits of experimental error, is equal to the value calculated from the frequency of the shortest wave-length of the spectral series, viz., 10.4 volts, it is fair to conclude that this latter is the true ionizing potential of mercury vapor.

Since the parts (a) and (b) of the curves (Fig. 3) are due to radiation, the question arises as to the cause of the rise of these curves between 6 and 7 volts. Attention has been called to the fact that the other strong line in the Paschen series is the wave-length $\lambda = 1849$ Å. This line was sought for by McLennan but not found. The value of the voltage corresponding to this line as calculated from the quantum relation is 6.7 volts. It seems probable that the increase in the intensity of the radiation between 6 and 7 volts is due to this cause.



Since the curves obtained show that the radiation occuring at 4.9 volts will produce a sharply defined discontinuity at twice this value (9.8 volts), we would expect that if additional radiation were emitted when electrons lose their energy at 6.7 volts, such electrons would be capable of losing their energy a second time at twice this voltage, viz., 13.4 volts, and consequently there should be a second rise in the radiation curves beginning at this voltage.

For the purpose of testing this point V_3 was made large (about 20 volts) and in the opposite direction to V_2 , and a curve showing the negative charging of D with increasing values of V_1 over a range greater than 13.4 volts was obtained. The curves obtained with this arrangement of voltages are shown in Fig. 4, where (a), (b) and (c) are for decreasing electron emission from electron source A. The dotted lines show the points

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at which rises in the curves should take place on the assumption that the two lines $\lambda = 2536.7$ Å and $\lambda = 1849$ Å, are produced at their respective voltages. The shape of the curve (c) certainly indicates the existance of such effects.

The fact that there appears to be no marked increase in radiation at the ionizing voltage (10.4) is quite significant. It indicates that the energy of the impacting electron had gone into separating the electron from the sphere of action of the atom, and in so doing had produced no radiation. This suggests that the strong increase in radiation coincident with the production of the many lined spectrum observed by McLennan and by Richardson is due to recombination and not to ionization. It should be noted that the pressure of mercury vapor in these experiments was small, and that the chances for recombination are therefore small as compared to the conditions employed by those experimenters.



The foregoing interpretation of the results obtained for mercury vapor is more easily understood by a consideration of the schematic diagram, Fig. 5, where A represents the equipotential source of electrons and B the gauze through which these electrons are accelerated by the field V_1 . The arrows represent the directions in which electrons would move in the various fields. The extra gauze is represented by C, and D is the collecting electrode. The fields V_2 and V_3 are maintained between BC and respectively. The difference CD $V_2 - V_1$ is kept constant and just

large enough to prevent electrons from A reaching C. The field V_3 is also constant and arranged to carry electrons from C and D or vice versa as represented by the arrows.

Consider the possible history of electrons with increase of voltage V_1 . At all voltages an electron may at this low pressure take a path as represented by (1) in which it makes no collisions with the atoms. If it does however make such collision and the energy is less than a given minimum corresponding to a voltage V_0 (4.9), the impacts are elastic as shown by Franck and Hertz, and the path of an electron making such impacts would be represented by (2), where the circles represent impacted atoms. When V_1 becomes equal to the minimum voltage V_0 at which

the electron will lose its energy, and if it is assumed that this energy will appear as radiation, some of this radiation will fall on both C and D causing photo-electric emission of electrons. These latter electrons will move in the field V_3 according to its direction (a or b). This situation is represented by (3) in the figure.

As V_1 is increased beyond V_0 an electron is capable of producing radiating atoms in an increasingly wider range on either side of the gauze B, thus proportionately increasing the intensity of the radiation reaching C and D. This situation is represented by (4) and (5). When V_1 becomes equal to $2V_0$, impacts half way between A and B will cause the electron to lose its energy, but it will be capable of again acquiring enough energy to cause another atom to radiate in the region of the gauze B, as represented by (6); so that beyond $2V_0$ some of the electrons would have this double capacity for causing atoms to radiate and therefore we should expect a corresponding increase in the intensity of radiation at a value of V_1 equal to $2V_0$.

If ionization takes place at or beyond B in the region BC, the positive ions so formed would be carried to D irrespective of the direction of V_3 , so long as this latter is smaller than the fraction of V_2 run through by the positive ion before reaching C. Therefore at this point we should expect a tendency for D to charge positively irrespective of the direction of V_3 . This situation is represented by (7). The transport of positive ions to D can be prevented however by making V_3 larger than V_2 so that no positive ions can reach D from the regions BC as shown in (8). The effects due to radiation alone can thus be studied even at large values of V_1 .

It may be objected that since V_2 is slightly greater than V_1 , electrons photo-electrically emitted from C or D would be capable of producing positive ions in the region BC before those from A could do so. This is of course true, but the number so doing is so small that it does not mask the effect under these experimental conditions. This was shown experimentally by increasing the difference $V_2 - V_1$, and also by increasing the pressure of the mercury vapor. There was an appreciable tendency to charge positively below 10.3 volts. The point at which the curve started to rise depended on $(V_2 - V_1)$, but in no case did it mask either the discontinuity found at 9.8 or 10.3 + volts, which are of course independent of $(V_2 - V_1)$. It may also be objected that since V_3 is large compared with V_1 and V_2 , that it would be capable of producing ions and additional radiation in the region CD. But since these ions and radiation could only be produced by the electrons emitted from C by the action of the radiation from the impacted atoms in AB and BC, such ionization and radiation would tend to increase the magnitude of the breaks in the curves,

which occur at particular values of V_1 . The results of these experiments may be summarized as follows:

(a) Radiation is emitted without ionization at an impact voltage of 4.9 volts. This voltage corresponds to the frequency of the first line $\lambda = 2536.7$ Å. of the Paschen combination $\nu = 2p - mS$, as has previously been pointed out.

(b) An increase in the intensity of the radiation takes place at an impact voltage of about 6.7 volts. This voltage corresponds to the frequency of the first line ($\lambda = 1849$ Å.) of the principal series $\nu = 1.5S - mP$ of this combination.

(c) Ionization by impact, without an apparent increase in radiation, occurs at an impact voltage of about 10.4 volts. This voltage corresponds to the head or shortest wave-length of this same principal series.

These results are of considerable interest when considered from the point of view of the Bohr theory of the atom. The definiteness of the results are due to the fact that the impacts in mercury vapor are perhaps completely elastic. That is, an electron loses no energy at impact with a mercury atom, unless either radiation or ionization is produced, in which case the entire energy of the electron goes into the radiation or the ionization, and none is absorbed by the atom.

When the atom is impacted by an electron running through 4.9 volts, its energy is transferred to an electron of the atom, lifting it we may suppose from its equilibrium position to some ring farther from the nucleus, and storing this energy in the potential form. Upon the return of this electron to its equilibrium position this energy appears as radiation $(\lambda = 2536.7 \text{ Å}.)$ in accordance to the relation $Ve = h\nu$.

When the atom is impacted by an electron having an energy corresponding to 6.7 volts, an electron in the atom is lifted from its position of equilibrium to some other ring still farther from the nucleus, and its energy stored in the potential form. Upon the return of this electron, its energy appears as radiation ($\lambda = 1849$ Å.) in accordance with the above energy relation.

One considerable difficulty with this view of the process of emission of radiation is that the other lines of this spectral series should appear at their corresponding voltages. They apparently are not produced in sufficient intensity to affect the curves obtained in these experiments. The intensities of these other lines are weak compared to the intensities of the two strong lines just referred to, when the radiation is observed from the usual electrical discharge in mercury vapor. If the energy emitted at each frequency corresponded to its voltage ($Ve = h\nu$), then

all the lines should be intense, and their intensities should progressively increase toward the head or shortest wave-length of the series.

When the atom is impacted by an electron having energy corresponding to 10.4 volts, an electron in the atom is lifted entirely from the atom and removed from its sphere of influence. This electron is then free and the atom is ionized. No radiation is then produced, as the electron does not return to the atom. When the conditions are such that this (or some other) electron may return to the atom (recombination) then radiation is emitted. Experiments on the electrical discharge in mercury vapor indicate that under these conditions not only is the Paschen spectral series emitted, but the entire mercury spectrum including the visible.

Much of the phenomena of electrical discharge in gases indicate that the greater part of the emission of radiation takes place at recombination and not at ionization. We might mention for illustration the fact that the most intense light from the usual vacuum tube discharge is emitted from the cathode glow, where the electrical field is small, the concentration of ions greatest and the recombination of the ions is far in excess of their rate of production; while on the other hand in those parts of the discharge in which the ionization is in excess of the recombination the emission of light is small. Some recent direct experiments of Child¹ indicate also that a part at least of the emission of light from mercury vapor is due to recombination of the ions.

Hydrogen.

Introduction.—It seemed desirable to apply the method employed for mercury vapor to an investigation of hydrogen as well, on account of its theoretical interest in connection with the Bohr theory of the atom. The value of the ionizing potential for hydrogen has been found by Franck and Hertz² and also Pavlow,³ using the regular Lenard method, to be 11 volts. This is in agreement with some recent work of Bishop,⁴ using the same method, who also has found by extending the current curve over a wider ange of voltage, that there is apparently a second type of ionization at 15.8 volts. Neither of these values are in accord with the theoretical voltages, calculated from the Bohr Theory. The theoretical value yielded by this theory would be that corresponding to the head or shortest wave-length of the series given by

$$\nu = N\left(\frac{\mathbf{I}}{T_{2}^{2}} - \frac{\mathbf{I}}{T_{1}^{2}}\right),\,$$

where $T_2 = I$. $T_1 = I$, 2, 3 which is the series observed by Lyman.

¹ PHYS. REV., Jan., 1917.

² Franck and Hertz, Deutsch Phys. Ges., Vol. 15, 1913.

⁸ Pavlow, Proc. Roy. Soc., Vol. 90, 1914.

⁴ Bishop, not yet published.

Using the value of N,

$$N = \frac{2M^2me^4}{h^3} = 3.26 \times 10^{15}.$$

as given by the Bohr theory, we can calculate the different frequencies of this series; and from the $Ve = h\nu$ relation can calculate the value of voltage corresponding to the different members. This gives a value IO.2 volts as that corresponding to the first line or longest wave-length, and I3.6 volts as that corresponding to the shortest wave-length. This value then in the light of the Bohr theory should be the ionizing voltage. It therefore seemed desirable to redetermine the values for hydrogen by the application of this method to see whether or not the effects obtained at II volts were due to radiation and not to ionization; and whether either the radiation or ionization had any connection with the above values calculated from the Bohr theory.

The apparatus was the same as that used for the investigation of mercury vapor. A stream of hydrogen was continuously passed through the observation vessel by means of the palladium tube P. This was heated by a gas flame and the pump was kept running. The pressure of the hydrogen could be maintained as desired by regulating the flame that heated the palladium tube.

The vessel was kept free from mercury vapor by means of liquid air applied to the liquid air trap between the vessel and the pump.



The complete elimination of mercury vapor could be tested by the disappearance of the radiation effects characteristic of mercury vapor below 10 volts which have just been described.

Results.—With the pressure of about .01 mm. and the potential V_3 small and arranged so as to draw electrons from *C* to *D*, the potentials V_1 and V_2 were arranged to give curves of same type (*a*, Fig. 3) as found in mercury vapor. With this arrangement of V_1 , V_2 and V_3 , if there were no ionization and only radiation, a negative current would have been

observed. The curves actually obtained were all positive and are shown in Fig. 6, where a, b, c and d represent results with diminishing electron emission from equipotential source A. This indicates that

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experiments as showing ionization by impact at 11 volts. They also agree with the results of Bishop who found a break in the curve at about 15.8 volts, indicating a second type of ionization at this voltage. These curves (Fig. 6) might be due to ionization alone or to a combined effect of ionization and radiation, if the ionization effect were greater than the radiation effect.

The existence of a radiation without disturbance due to ionization may be tested for by an arrangement of potentials similar to that by which the curves (Fig. 4) were obtained in mercury vapor. The potential V_3 was made larger than V_2 (it was made about 20 volts) and directed so as to stop and turn back the positive ions com-



ing through C toward D. At the same time, the photo-electric electrons



emitted by radiation falling on C would charge D negatively.

The curves thus obtained are shown in Fig. 7, where a, b and care curves for diminishing electron emission from the electron source A. These reults reveal the striking fact that there are two types of radiation from hydrogen. The one type occurs at the ionization potential of 11 volts and the other at 13.6 volts.

The effects due to radiation may be increased and at the same time those due to ionization may be decreased by increasing the pressure of the hydrogen. The curves in Fig. 8 were obtained with a pressure of .3 mm. Curve *a* was obin the same direction as V_2 , while

tained for V_3 equal to 1.5 volts, and in the same direction as V_2 , while

a' was obtained with V_3 at 1.5 volts and in the opposite direction to V_2 . The curve a shows the combined effects of ionization and radiation, while curve a' shows the difference between the ionization and the radiation effects.

The curves b, b' were similarly obtained at lower pressures, where the radiation effects were not so strong as at higher pressures. The ionization and radiation effects nearly neutralize (b') until a voltage of about 15.8, where the second type of ionization begins, when the ionization predominates.

At the pressure of .3 mm., the radiation and ionization effects just neutralize from 11 to about 13 volts when the radiation predominates to about 15.8 volts at which point the second type of ionization sets in, and then the ionization effects predominate.

These experiments show the following facts:

(a) Both ionization by impact and emission of radiation occur at 11 volts.

(b) A second type of ionization by impact without increase of radiation occurs at about 15.8 volts.

(c) A second type of radiation without an increase of ionization is emitted at 13.6 volts.

These facts show a greater complexity than the simple Bohr theory of the atom would predict, but are not inconsistent with it.

As has been indicated in a previous paragraph, by means of this theory together with quantum relation the voltage corresponding to any frequency may be readily calculated.

The voltage corresponding to the head or shortest wave-length of Lyman series $(T_2 = 1 \text{ and } T_1 = \infty)$ is 13.6 volts. The voltage calculated in the same way for the tail or longest wave-length of this same series $(T_1 = 2)$ is 10.2 volts.

There is thus a marked difference in the behavior of hydrogen and mercury vapor. This latter gas showing radiation at a voltage corresponding to the longest wave-length and ionization without radiation at the head of the series. There is no radiation from hydrogen at 10.2 volts, which corresponds to the tail or longest wave-length of the series. This may be due to the fact that the radiation of this frequency is very weak or that some of the energy of the impacting electron is transformed into kinetic energy of the hydrogen atom. This is quite probable since the impacts in hydrogen are not elastic as in mercury vapor.

The occurrence of a new type of ionization by impact at 15.8 volts instead of 13.6 volts which might be expected can also be accounted for on the hypothesis that the hydrogen atom has a certain affinity for an electron. As the electron is displaced from the inner ring by the impact, the radiation emitted on its return will correspond to the change in the potential energy caused by the impact. When the impacting energy is that due to 13.6 volts the electron is lifted to the outer ring or boundary of atom and on its return emits the radiation of highest frequency. But this electron when displaced to the outer ring will not be free as in case of the mercury atom. If the hydrogen atom has an affinity for an electron (non-elastic), it will require an additional energy to separate the electron entirely from the atom (ionization). This additional energy will be represented by the difference in voltage (15.8-13.6). This difference of 2.2 volts is thus a measure of affinity of a hydrogen atom for an electron. An important result is the production of ionization at II volts. This fact presents some difficulty in view of the Bohr theory, but it may be due in some way to the diatomicity of hydrogen. We may perhaps assume that at the II volts impact, the two atoms are separated one from the other, and that the electron is taken away from one atom and attaches itself to the other in this process, the one becoming a positive and the other a negative ion.

It is hoped that we may be able to examine other diatomic non-elastic gases, to determine if they behave in a similar manner.

Phœnix Physical Laboratory, Columbia University, April, 1917.