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THE MEASUREMENT OF THE RESONANCE, RADIATION, AND IONIZATION POTENTIALS OF SEVERAL GASES AND VAPORS.

By Paul Edward Boucher.

Synopsis.

Minimum Resonance, Radiation and Ionization Potentials for Various Gases.—A special vacuum tube was used which embodied a modification of K. T. Compton's variable-area electrode by being so designed that either a gauze or a plate electrode could be slid into the position of the fourth electrode. The resonance potentials were obtained from the difference in voltage between successive peaks of the resonance curves; the ionization potentials from Lenard current-voltage curves corrected as to zero by the resonance curves; the relative importance of radiation and ionization at various voltages from the ratio of the Lenard currents obtained with the plate, to the corresponding currents obtained with the gauze electrode having only one fourth the area. The critical potentials in volts, accurate to about 0.1 volt except for toluene, are as follows:

Gas.	Resonance Potential.	Radiation Predominant.	Ionization Potential.
Hydrogen	10.1	10.1 to 13.6	13.6; 15.6
Nitrogen	8.4	8.4 to 15.8	15.8
Oxygen	8.0	None detected	14.0
Ether ($C_4H_{10}O$)	6.6	8.1 to 10.1	13.6
Benzene (C_6H_6)	6.0	None detected	9.6
Toluene (C_7H_8)	6.2 ± 0.2	" "	8.5 ± 0.5
Xylene (C_8H_{10})	6.5	" "	10.0
Chloroform ($CHCl_3$)	6.5	" "	11.5

The results for the resonance potentials for H_2, N_2 and O_2 agree with those obtained by Foote and Mohler, but the values for the corresponding ionization potentials are about 1 volt higher than theirs. The fact that no radiation was detected in the case of O_2 and of all the vapors except ether is rather remarkable; but it may be due to the method used.

A. Introduction.

A CONSIDERABLE amount of research has been carried out on the radiation and ionization potentials of various gases and vapors. The problem has been attacked in several ways but the results are not

in such good agreement as could be desired. The Bohr theory has been applied only to the hydrogen and helium atoms with much success. As time goes on we may expect extensions of this or other theories to other elements and even to compounds. The development of a satisfactory theory rests upon the accuracy with which the radiation, resonance, and ionization potentials can be determined. In this paper the writer describes methods and gives the results in which the critical potentials of several simple gases and compounds have been measured.

Some preliminary work was carried out, in which several ionization tubes of various designs were constructed and tested. Only the final form of the apparatus will be described here.

B. APPARATUS.

The problem of distinguishing between radiation and ionization is one of some difficulty. Davis and Goucher[1] have used a modification of the Lenard method in which they reversed the direction of the retarding field between two of the electrodes. A photoelectric effect due to radiation would give a current the direction of which would depend only on the direction of the retarding field, while a positive ion current due to ionization would be obtained with the retarding field in one particular direction. Other observers using the same method have not obtained consistent results.

K. T. Compton in the Philosophical Magazine for November, 1920, describes a three-electrode tube, having a variable area receiving electrode. This electrode consists of a cylinder closed at one end with a piece of foil and at the other with a piece of fine gauze. Either end could be turned towards the cathode, and thus the area exposed to radiation could be changed and a consequent variation in photoelectric current proportional to the area exposed might be expected. If the effect were one of ionization then a variation in the electrode area would not change the current.

The principle of a variable area electrode was employed, though the design was entirely different from that of Compton's. Fig. 1 will give an idea as to its construction. It was a four-electrode tube, though most of the time it was used as a three-electrode tube, two of the electrodes being connected together. The filament A, the platinum cylinder B, and the gauze C were mounted on the glass stopper T. This large glass stopper was fitted to the main part of the tube by a very fine ground glass joint. A small amount of grease was placed around the lower part of the joint, but several days would elapse before the grease could be

[1] PHYSICAL REVIEW, Vol. 10, No. 2, August, 1917, p. 101.

noticed working its way towards the vacuum. During the latter part of the work, the grease was entirely removed and the joint was sealed in with a mixture of beeswax and rosin. The ground joint was 8 cms. from the cathode, so that it did not become appreciably warm. Because of the large size of the opening, the entire assembly of the electrodes, *A*, *B*, and *C*, could be removed at will for alteration or repair.

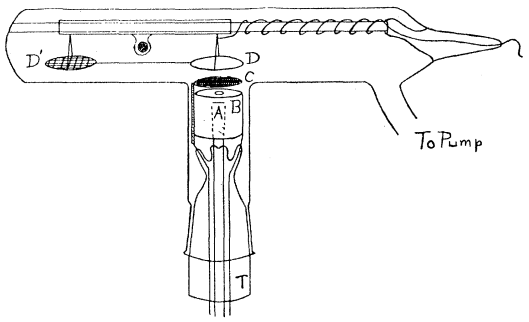

Fig. 1.

The cathode *A* was a piece of platinum foil 1 cm. in length, cut narrow at the center, so that the central portion became much hotter than the ends, thus furnishing the larger portion of the supply of electrons and hence approximating to an equipotential source. It was coated with lime and baryta by giving it several coats of sealing wax and heating it at a high temperature in air before being placed in the tube.

The platinum cylinder was 2 cms. long, 2.5 cms. in diameter, and closed at one end except for a circular opening 0.5 cm. in diameter. The cylinder was thus slipped over the cathode so that the small hole was about 3 mms. directly above the cathode. A fine gauze placed over the small hole was found to improve the operation of the tube.

A small glass stem furnished both the support and the means of insulation for the fine gauze electrode *C*. This electrode was placed 6 mms. distant from the cylinder.

The innovation, the electrode of variable area *DD'*, consisted of a platinum foil disk of 3 cms. diameter, and a very coarse gauze disk of the same diameter. These were connected by a stiff wire 5 cms. long, and the whole was suspended from a glass sleeve. A glass rod fixed permanently in the tube, formed the track upon which the glass sleeve could be moved back and forth. A small piece of soft iron, enclosed in glass, was sealed to the movable electrode at *E*. Thus by means of an electromagnet outside the tube, the electrode could be moved so that either the solid disk or the coarse gauze was directly above the electrode *C*. It was

thought by placing these parts of the electrode 5 cms. apart, that while one disk was directly above C, the other would be too far away to receive any appreciable effect either due to radiation or ionization. The meshes of the coarse gauze were about 6 mms. square. The total effective area of one side that would be exposed to radiation was 7 square cms. for the solid disc, and 1.87 square cms. for the gauze. Thus the ratio of their effective areas was about 3.78. So that if the current received were entirely due to radiation incident on the electrode, it would be almost 4 times larger for the solid disc than for the gauze. A fine coil of platinum wire formed the flexible lead to the outside of the tube. All parts were made of platinum, so that before being connected to the pump, the entire tube was washed several times in nitric acid, rinsed in ammonia and distilled water and then dried in an electric oven.

C. METHODS EMPLOYED.

Three methods of operation were employed with tube No. 4. Figure 2 shows the connections which were essentially the same for the three methods. The cathode A was heated by four 7-volt Edison storage batteries. This number was found to be advisable in order to obtain steady electron currents, because from 4 to 6 amperes of current were required to raise the cathode to the desired temperature. This source of current was found to be fairly constant. During most of the work, a piece of fine gauze was stretched across the small hole in the cylinder B. In the preliminary tryout of the tube, the cylinder was removed, but the results were very unsatisfactory and it was replaced. C is the fine gauze and DD' is the movable electrode by which the area exposed to radiation could be varied. B and C were connected together most of the time.

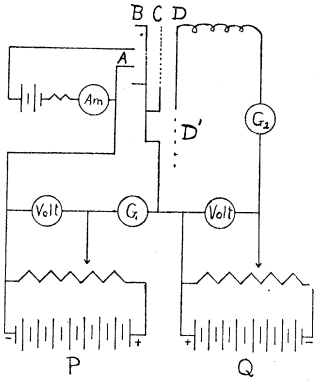

Fig. 2.

The methods employed are called the Lenard, the ratio, and the resonance methods. The Lenard and the ratio methods were used simultaneously, that is, data by which ratio curves were plotted, were obtained from the Lenard readings. Battery P furnished the accelerating potential V_a, which was applied between the cathode and BC. For the Lenard method battery Q furnished the retarding potential V_r, which was applied between the variable area electrode DD' and BC. This potential was always larger than the highest value of the accelerating

potential used, usually about 30 volts. Thus BC was charged plus with respect to A, and electrons from the cathode would move to BC. Some would pass through the gauze covered opening into the space BC, where they would travel at a constant velocity, since the electric field in BC was zero. Those electrons which did not collide with atoms or molecules in BC and possessing sufficient velocity would pass through the fine gauze C into the space CD. Here however the large retarding potential V_r would prevent any electrons reaching D. Let us suppose that the electrons have attained a velocity V_a sufficient for them to cause the atoms they collide with to give off radiation. Then some of this radiation will fall on the movable electrode DD', and due to what is called the photoelectric effect, electrons will be emitted from DD' and due to V_r will pass from DD' to BC, and we will have a current measured by the high sensitivity galvanometer G_2. This special Leeds and Northrup high sensitivity galvanometer had a sensitivity of 5×10^{-11} amperes per mm. deflection. Now the value of the radiation current will depend on the area of the electrode exposed to radiation. Since the ratio of the area of the solid disc to the coarse gauze is about 3.8 we should expect the current to the disc to be almost four times that to the coarse gauze, provided the effect is purely one of radiation. On the other hand if the velocity of the electrons is sufficient to produce ionization by collision, then the positive ions formed will go to the electrode DD', and we will have a current indication on the galvanometer in the same direction as for radiation effects. However if we vary the area of the electrode DD', there will be no change in the value of the current since the ionization does not depend on the area of the electrode exposed. Thus we have a means for distinguishing between radiation and ionization. The procedure in obtaining the necessary data for the ratio test was to take first a reading of the Lenard current with the disc end of the movable electrode above C, then by means of an electromagnet move the gauze end above C, and again read the current value, the accelerating and retarding potentials meanwhile remaining constant. This procedure was continued for each value of accelerating potential applied. Dividing the current value to the disc by the current value to the coarse gauze we obtain the ratios of the currents for the various V_a's applied. And we can conclude, at least with our present knowledge of the subject of photoelectric and ionization effects, that if the ratio approaches 4 in value, the effect is entirely due to radiation; if it becomes 1, then it is due to ionization, while if the ratio has some intermediate value between 1 and 4 both ionization and radiation are present.

The only change necessary to obtain resonance currents is to make the

retarding potential V_r small, say 1 to 5 volts, instead of 30 volts as in the Lenard method. The collisions between electrons and the atoms of some gases appear to be elastic up to a certain velocity. Beyond this point, the collisions become inelastic, that is the colliding electrons give up their energy to the atoms or molecules, which in turn is used to remove one of the atom's electrons from its stable position to an unstable one, and thus radiation of frequency n is produced when the electron falls back into its stable position. Thus when inelastic collisions take place the colliding electrons lose their velocity. If the retarding potential is small and the accelerating potential is increased from zero, the electrons will acquire a velocity which will enable them to reach the electrode DD' against the retarding potential. When inelastic collisions take place, however, some of the electrons lose their velocity and these are unable to reach DD' against the retarding potential and a consequent decrease in electron current takes place. But as the increase in the accelerating potential is continued these electrons again increase in velocity and the electron current begins to increase in value once more. This increase continues, as the potential goes up, until the electrons have acquired a velocity such that inelastic collisions again take place, and we have a second decrease in current. As many as four resonance points in a current voltage curve have been obtained.

It is found that the gas pressure at which resonance curves may be obtained is limited in range. The best resonance curves are obtained between gas pressures of about 0.1 mm. to 2 or 3 mms. No doubt the distance between the electrodes is a factor in obtaining resonance curves, though just how it would affect the critical pressure is not known. The resonance potential may thus be accurately found by taking the difference in accelerating potential between two consecutive resonance points. It should be remembered that an atom or molecule does not necessarily give off radiation at its resonance potential.

The initial correction due to several factors, the initial velocity of the electrons, the contact difference of potential between the cathode and the receiving electrodes, the potential drop along the filament, may be obtained from the resonance curves. In most cases the potential at which the first resonance peak is obtained, is not equal to the difference between two resonance peaks. For any gas the difference between two resonance peaks is found to be always the same no matter what conditions prevailed. The writer found considerable variation in the applied potential difference at which the first resonance peak occurs. Mohler and Foote[1] have published some work on the "Ionization and Resonance

[1] Scientific Papers of the Bureau of Standards, No. 400.

Potentials of some Non-metallic Elements," in which they obtained the first resonance peaks with applied accelerating potentials of smaller value than the resonance potentials as read from the difference of two succeeding resonance peaks. In practically all the work reported in this paper, the initial applied accelerating potentials for the first resonance peaks were either equal to or greater than the resonance potentials. The explanation of this is not clear. It may perhaps be due to contact difference of potential in the cathode itself. We need not know the magnitude of the corrections in order to obtain the proper correction for the Lenard curves. This correction was obtained by taking the difference between the resonance potential and the applied potential at which the first resonance peak begins, and adding or subtracting it as the case may be to the ionization and radiation potentials obtained by the Lenard method.

The general procedure for obtaining the radiation and ionization potentials of any gas was as follows: The tube was first heated to about 300° C. in an electric heater, and the cathode was also heated to a high temperature to help free the electrodes and glass from occluded gas. Liquid air was placed on the trap and the pump was started. This treatment was continued for several hours with a new tube, and was always repeated for an hour or more before each day's work was begun. After such treatment the Gaede pump would give vacuums of the order of 10^{-4} mms. The gas to be tested was then admitted to the desired pressure, and by means of a Geissler tube and an Adam Hilger direct-reading spectroscope, the purity of the gas was tested. If not satisfactory it was pumped out and refilled. Readings were never recorded until the currents became constant in value. After a set of readings was taken, several potentials were rechecked and if the current values varied more than a few mms. deflection on the galvanometer the data were rejected. For any gas pressure data for the resonance curves were first taken and then that for the Lenard and ratio curves.

For admitting the vapors, a bulb connected to a three-way stopcock was sealed on close to the electrode tube. A little of the liquid was poured into the bulb, then it was frozen by liquid air, and all the gas was pumped out above the frozen liquid. The stopcock was then closed, the liquid air removed, and the pure vapor could be admitted as desired. Some difficulty was experienced in admitting the proper amount of vapor. Due to the sudden expansion of the vapor on entering the vacuum, some would condense on the walls of the tube, and considerable time would be required to obtain the desired pressure. It was found however that by first getting a large electron current in vacuum and then just admitting

enough vapor to cause this current to decrease, that the desired pressures could be obtained much more quickly.

D. EXPERIMENTAL RESULTS.

The experimental results obtained in measuring the radiation and ionization potentials of several gases and vapors will now be described in the order performed.

1. *Hydrogen.*

Hydrogen for this test was prepared by the action of caustic potash on aluminum. It was found very convenient to store the gas in a tank under water pressure, so that if any leakage should take place, it would be only loss of hydrogen. A calcium chloride tube was inserted between the storage tank and the ionization apparatus. This tube could be exhausted before admitting hydrogen. The apparatus was always washed out several times with the gas in question before adjusting the

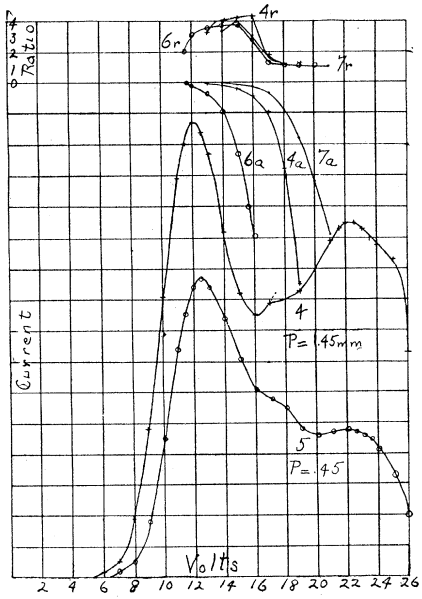

Fig. 3.

pressure for a test. Liquid air was always kept on the trap during these tests. The purity of the gas was tested by examining its spectrum.

Some characteristic curves obtained with hydrogen gas are shown in Fig. 3. Curves 4 and 5 are resonance curves, obtained at the same pressure, but at different filament temperatures. Curves 4*a*, 6*a*, and 7*a*

are Lenard curves obtained at the same pressure but at different filament temperatures. These are the current values measured to the disc of the movable electrode while obtaining the two sets of data from which the corresponding ratio curves were plotted.

The resonance curves give these results:

Curve.	1st Res. Pt.	2d Res. Pt.	Difference.	Correction.
4.....	11.5	21.6	10.1	10.1 − 11.5 = − 1.4
5.....	12.0	22.0	10.0	10.0 − 12.0 = − 2.0

Curve 4 gives a break at 17 volts, and adding the correction (− 1.4 volts) to this gives, 17.0 − 1.4 = 15.6 volts, which is the ionization potential as determined from the resonance curves. Lenard curves 4*a* and 7*a* both have sharp increases in current at 17.0 volts. Referring to the ratio curves this is evidently the potential where strong ionization predominates. Applying the correction we have 17.0 − 1.4 = 15.6 volts for the ionization potential of hydrogen. Curve 6*a* gives a resonance potential at 11.6 − 1.4 = 10.2 volts. Thus it will be seen that the resonance and ionization potentials obtained by the three methods check very well indeed. The break in the resonance curves due to ionization at 15.6 volts was not obtained in all curves. The ionization at this potential evidently prevents the second resonance peak from being as high and sharp as the first. This can be readily explained by the fact that when ionization sets in both plus and minus ions are formed. Remembering that the resonance currents consist simply of electrons possessing sufficient velocity to go against the small retarding potential applied between the movable electrode and *BC*, it will be readily seen that any sudden introduction of positive ions would tend to diminish the electron current, for the positive ions would be attracted by the retarding field to the movable electrode. If the effect were strong enough we might get a complete reversal of current. This has been obtained with some of the vapors worked with and will be referred to again.

The ratio curves deserve further consideration. Radiation and some ionization appear to exist at 10.2 volts. As the accelerating potential is increased the effect becomes principally one of radiation though some ionization is no doubt present. Ionization begins to increase at about 15.0 volts on the ratio curves. Adding the correction (− 1.4) to 15.0 gives 13.6 volts as the potential at which ionization begins to supercede radiation. At this potential the ratio begins to decrease rapidly from 4 until it reaches a value of almost 1.0 at 17.0 − 1.4 = 15.6 volts.

Final Results.

Radiation and some ionization was found at	10.1 ± 0.1 volts.
Radiation predominates between	10.1 to 13.6 volts.
Ionization begins to increase at	13.6 volts.
Strong ionization begins at	15.6 volts.

It is interesting to compare these values with those given by the Bohr theory for hydrogen.

Bohr's theory gives:

Resonance potential	10.16 volts.
Ionization potential of the atom	13.54 volts.
Ionization potential of the molecule	16.26 volts.

There is good agreement between the radiation and resonance potentials, and the first ionization potentials. But the strong ionization found at 15.6 volts does not check quite so well with 16.26 volts as predicted by Bohr's theory. Compton and Olmstead,[1] who first used the ratio method, give 10.8 volts for the resonance potential, 13.4 volts an additional critical velocity, and 15.9 volts the point where intense ionization sets in. The latter two values check fairly well with those found, but there is considerable difference between 10.8 and 10.1 volts.

2. *Nitrogen.*

Nitrogen gas was prepared by heating a solution of ammonium chloride and sodium nitrite in a hot water bath. It was passed through a red hot copper coil and collected against pressure in a storage tank. As before an air tight connection through a calcium chloride tube was used for admitting the gas into the apparatus. Phosphorus pentoxide and liquid air removed the other impurities. The spectrum checked well with that given by Georges Salet in his "Analyse Spectrale."

Some trouble was experienced at first due to what has been called by some writers, polarization effects. Difficulties of this nature have been reported by other observers for various gases. The nature of the trouble seems to be obscure. The character of the resonance and Lenard curves was not affected, but some of the first ratio curves showed that the gauze apparently received more current than the disc. This is difficult to account for, unless the disc was exposed a long time to a freshly coated filament, and some kind of an insulating layer was deposited on it. However this trouble was eliminated by removing the filament base, recoating the filament, and heating all platinum parts to a white heat with a gas flame. The electrodes were replaced and the movable electrode was bombarded by electrons from the hot cathode by applying a potential difference of 50 volts. This trouble was never repeated in the subsequent work.

[1] PHYSICAL REVIEW, Vol. 17, No. 1, Jan., 1921, p. 45.

Fig. 4 shows the type of results obtained. Curve 3 shows three distinct resonance points. In some of the curves four resonance points were obtained. This curve gives a resonance potential between the first two peaks of 8.4 volts. Subtracting from this value the value at which the first resonance point begins, gives an initial correction of -3.2 volts, which as explained before takes care of all corrections. The Lenard curve $3a$, at the same pressure (0.4 mms.), gives the first indication of current at 11.5 volts, and a sharp change in slope due to ionization at 19.0 volts. Adding the correction, -3.2 volts, gives 8.3 volts for the resonance potential and 15.8 volts for the ionization potential.

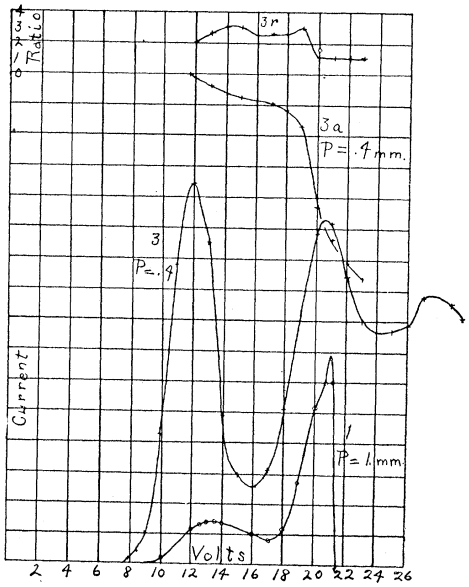

Fig. 4.

Curve $3r$ shows the ratio of the plate to the gauze current. This ratio is greater than 1 up to 19 volts, where it suddenly drops to a value of 1. It however indicates some ionization as well as radiation before the ionization potential is reached.

Curve 1 shows the arcing potential. It gives a resonance potential of about 8.5 volts and a consequent initial correction of -3.5 volts. Adding this to the observed potential at which arcing sets in, 20.5 volts, gives the arcing potential as 17.0 volts. The retarding potential used for this curve was only 5 volts, yet here we have an interesting case in which the increase of the accelerating potential from 20.5 to 21.0 volts gives a complete reversal of current, the galvanometer indicating a large positive current instead of an electron current. The magnitude of the

current was too large to measure on the scale. An intense bluish glow was observed when this break in the current curve took place. By using lower pressures and smaller retarding potentials, curves of type 3 were obtained without arcing setting in.

Using the frequency corresponding to the wave-length, = 1492.8 Å., of the isolated doublet in the nitrogen spectrum, observed by Lyman,[1] in the quantum relation, $Ve = h\nu$, we obtain $V = 8.27$ volts. The potential, 8.3 volts, obtained agrees fairly well with this calculated radiation potential. The limiting spectral line corresponding to the ionization potential of nitrogen has not been identified. With the ionization potential of nitrogen equal to 15.8 volts, this limiting spectral line should have a wave-length equal to 782.0 Ångstrom units.

Final Results.

Resonance potential of nitrogen	8.4 ± 0.1 volts.
Radiation predominates between	8.4 and 15.8 volts.
Ionization potential of nitrogen	15.8 volts.

3. *Oxygen.*

An oxone generator was used to generate the oxygen gas, which was said to be 99.4 per cent. pure. It was collected in the storage tank and admitted into the apparatus through a calcium chloride tube. Sometimes the spectrum would show a red line corresponding with that of hydrogen, but this would soon disappear with a hot cathode. Figure 5

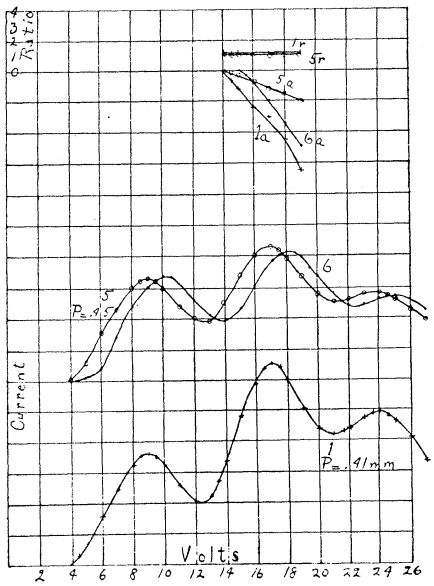

Fig. 5.

[1]Lyman, The Spectroscopy of the Extreme Ultraviolet, p. 113.

shows resonance, Lenard and ratio curves. The best resonance curves were obtained between pressures of 0.5 and 0.1 mm. Three resonance peaks were easily obtained. Curves 1 and 5 give resonance peaks starting at 8, 16, and 24 volts. The true resonance potential is then 8 volts, and there is no initial correction to apply to the corresponding Lenard and ratio curves. Hence the Lenard curves, 1*a* and 5*a*, give the ionization potential as 14.0 volts. It will be noted that no indication of current was found before 14.0 volts. It was sometimes thought that an indication of current could be detected at 13.7 volts, but this is not certain. The increase at 14 volts however was very definite. There is no indication of another ionization potential in the Lenard curves at a higher potential. Mohler and Foote[1] found resonance at 7.9 volts, ionization at 15.5 volts, but no Lenard indication of current before 15.5 volts. The resonance potential checks with that found in this investigation, but there is a difference of 1.5 volts in the ionization potentials. Hughes and Dixon[2] obtained what they called an ionizing potential at 9.2 volts for oxygen. They also state that the curve rises slowly from the axis for several volts, then begins to increase more rapidly. So that it is possible that there is a radiation or ionization effect before 14 volts which is too feeble to be detected in the Lenard method by the galvanometer used. The ratio curves give a value of 1.0 for all accelerating potentials, which means that the current is principally due to ionization from 14 volts on.

Curve 6 was taken immediately after Curve 5. The shift in the position of the curve was caused by reversing the direction of the heating current through the cathode. With Curve 5 the negative end of the accelerating potential was applied to the plus side of the cathode, and reversing the heating current for Curve 6, was the same as applying the accelerating potential to the negative side of the cathode. The resonance peaks of Curve 6 occur at accelerating potentials of about 1.2 volts greater value than those for Curve 5, and this was found to be equal to the potential drop along the filament due to the heating current. Hence we see that the accelerating potentials as read from the voltmeter for Curve 5 are about 0.6 volt less and those for Curve 6 are about 0.6 volt greater than they would have been if there was no potential drop along the filament.

Curve 6 gives 8.0 volts for the resonance potential, and an initial correction of about $8.0 - 9.0 = -1.0$ volt, which added to the corresponding Lenard Curve 6*a*, gives 14.0 volts for the ionization potential, which agrees with the values obtained from the other curves.

[1] Bureau of Standards Publications, No. 400, Oct. 14, 1920.

[2] PHYSICAL REVIEW, Vol. 10, No. 5, 1917, p. 502.

Final Results.

Resonance potential of oxygen	8.0 volts.
Radiation was not detected at any potential.	
Ionization potential of oxygen	14.0 volts.

4. *Ether* ($C_4H_{10}O$).

Ethyl ether, prepared by Squib for anaesthesia purposes, was poured into the special bulb for admitting the vapors. With the ether frozen by liquid air, the gas above it could be pumped out to a pressure of less than .00075 mm. Then by closing the three way stopcock to the bulb and removing the liquid air, the vapor could be admitted as desired. Pressures between 0.2 and 0.6 mm. gave the best results.

Figure 6 shows some typical curves. Curves 1 and 2 give resonance

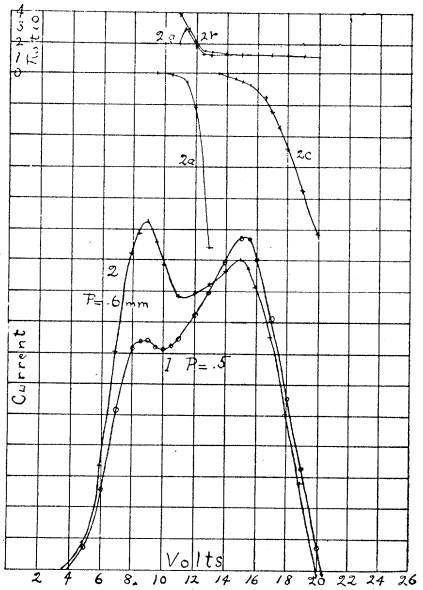

Fig. 6.

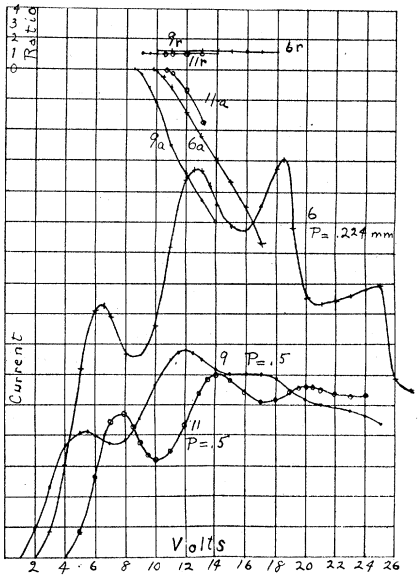

Fig. 7.

potentials of 6.6 and 6.7 volts respectively. The initial correction is − 1.4 volts. Beyond the second resonance point the current decreases rapidly, passes the zero axis and increases in the opposite direction. This effect is supposed to be due to two causes; one a large production of positive ions by ionization by collision, and the other, a decomposition or a chemical action of some kind taking place. It was found that the electron currents were steady in value until the second resonance point was passed. At this point the current would slowly decrease even with a constant accelerating potential, a phenomenon which indicates that some other effect besides ionization by collision is present. It may be

in ether, a compound consisting of carbon, hydrogen, and oxygen, that some kind of decomposition takes place when the molecules collide with electrons having a velocity equivalent to the accelerating potential at which the second resonance peak is produced.

The Lenard Curve *2a* starts at 9.5 volts, and adding the corresponding correction of − 1.4 volts, gives 8.1 volts as the potential at which current is first indicated. Perhaps a more sensitive current measuring device would have indicated a current at the first resonance potential, 6.6 volts. There is a large increase in current at 11.5 − 1.4 = 10.1 volts. Curve *2c* was taken at a lower cathode temperature and it shows a rapid increase at about the second resonance point, 15.0 − 1.4 = 13.6 volts. It is interesting, too, that at large values of accelerating potential, the Lenard currents also decrease with time.

The ratio curves indicate both radiation and ionization up to about 11.5 volts. From here the ratio decreases to a value of 1.0 at 12.5 volts. It is noteworthy that, since oxygen and hydrogen are both constituents of ether, the first indication of the Lenard current, 8.1 volts, agrees with the resonance potential of oxygen, and the increase at 10.1 volts is very close to the resonance potential of hydrogen. Of course additional information will be required before we can determine just what part of the ether molecule is affected when radiation or ionization is produced.

Final Results.

Resonance potential of ether	6.6 ± 0.1 volts.
Radiation and ionization were found at	8.1 volts.
Ionization predominates at	10.1 volts.
Strong ionization was found at	13.6 volts.

5. *Benzene (Benzol)* (C_6H_6).

The benzene used was guaranteed to be of the highest purity and crystallizable by Merck and Co. The benzene vapor gave less trouble than ether. Very little time was required to obtain steady currents.

Fig. 7 gives typical curves for benzene vapor. No difficulty was experienced in obtaining four resonance peaks. It was found that with retarding potentials of 3 volts or more, only two resonance peaks could be obtained, for the electron current beyond the second resonance peak would decrease to zero value and increase in the opposite direction as in the case of ether. The first indications of resonance in Curve 6 are at applied accelerating potentials of 6, 12, 18, and 24 volts, which gives the resonance potential as 6.0 volts with no initial correction to be applied to the corresponding Lenard curves. Curve 9, obtained at a higher vapor pressure, gives first indications of resonance at 5, 11, and 17 volts

and thus a resonance potential of 6.0 volts and an initial correction of 6.0 − 5.0 = + 1.0 volt.

The corresponding Lenard curves, 6*a* and 9*a*, start at 9.7 and 8.5 volts respectively. Curve 6*a* needs no correction, while Curve 9*a* has an initial correction of + 1.0 volts to be added to 8.5 volts thus making it 9.5 volts. The Lenard curves give no further indication of a critical potential above 9.5 volts. The value of the ratio curves is approximately one at all accelerating potentials, which shows the effect is due principally to ionization.

Before taking the data for Curve 11, the cathode was removed and examined. It was found to be covered with a deposit of carbon, sootlike in appearance. A black deposit of this nature was never noticed while working with hydrogen, nitrogen, or oxygen. Subsequent removals of the cathode while working with xylene have also shown a black deposit. This deposit seems to give a fairly large supply of electrons. The cathode was then recoated with sealing wax and replaced. The curves taken immediately afterwards like Curve 11 required a larger applied initial accelerating potential to produce the first resonance peak than did Curve 9, which was taken at approximately the same gas pressure before the cathode was recoated. So that it would appear that an oxide coated filament requires a larger potential to separate the electrons from it than one with a carbon deposit. Subsequent removals and recoating of the cathode tend to substantiate this statement. Curve 11 gives resonance at 7, 13, and 19 volts and consequently a resonance potential of 6.0 volts, with an initial correction of 6.0 − 7.0 = − 1.0 volt. The Lenard Curve 11*a* starts at 10.5 volts and adding the correction gives 9.5 volts as the ionization potential.

Final Results.

Resonance potential of benzene	6.0 volts.
Radiation was not detected at any potential.	
Ionization potential of benzene	9.6 ± 0.1 volts.

6. *Xylene* (C_8H_{10}).

Xylene vapor gave similar results to that of benzene. The currents were steady except at accelerating potentials of about 20 volts or more. At these higher potentials both the resonance and the Lenard currents exhibited decreases in value while at a constant accelerating potential. This indicates that some other effect besides ionization is present at these higher potentials.

Fig. 8 gives samples of the curves obtained with xylene vapor. In Curve 5 resonance begins to set in at accelerating potentials of 8.0, 14.5,

and 21.0 volts. This gives 6.5 volts as the resonance potential with an initial correction of −1.5 volts. Curve 2 shows only two resonance

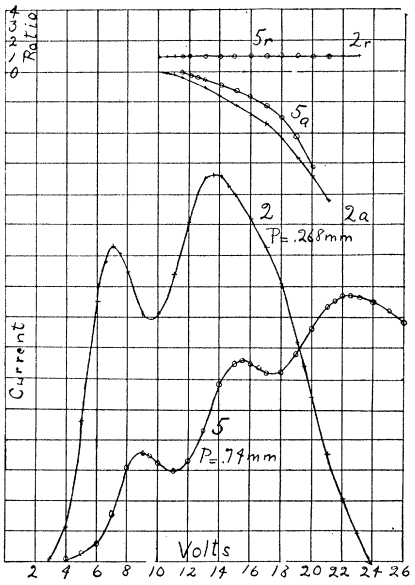

Fig. 8.

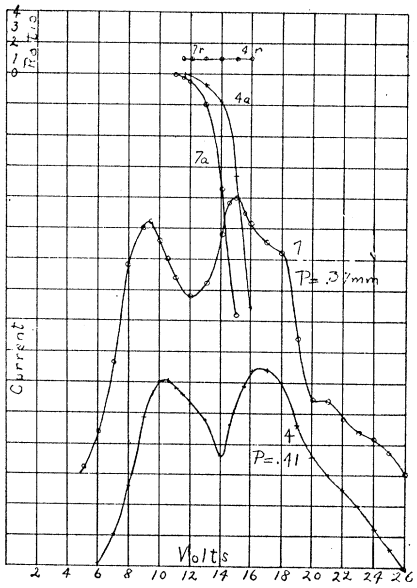

Fig. 9.

peaks beginning at 6.5 and 13.0 volts. The difference gives 6.5 volts as the resonance potential and no initial correction to apply to the corresponding Lenard and ratio curves.

Lenard Curve 5*a* begins at an accelerating potential of 11.5 volts and adding the proper initial correction, − 1.5 volts, gives 10.0 volts as the ionization potential. Curve 2*a* with no initial correction needed, also gives 10.0 volts for the ionization potential.

The ratio curves with a constant value of one, give no indication of radiation at any accelerating potential.

Final Results.

Resonance potential of xylene	6.5 volts.
Radiation was not detected at any potential.	
Ionization potential of xylene	10.0 volts.

7. *Toluene* (C_7H_8).

Some trouble was experienced while working with toluene vapor. The ionization tube had developed a leak, which necessitated the rebuilding of the glass stopper electrode assembly. With vapor present, a large initial accelerating potential of 5 to 6 volts was required to obtain a measurable electron current against a retarding potential of 1 or 2 volts.

The currents were steady until the first resonance peak was passed. Then they were somewhat erratic in their variations at a constant accelerating potential. Sometimes the current deflection would increase a few mms., then decrease a few mms., but always finally coming to rest at a definite position. It was impossible at any vapor pressure to obtain three resonance peaks, though curve 7 gives some indication of a third resonance peak at about 20 volts.

Some characteristic curves of toluene vapor are shown in Fig. 9. Curve 7 indicates resonance setting in at 8.5 and 14.5 volts, which gives a resonance potential of 6.0 volts with an initial correction of -2.5 volts. Curve 4 gives 6.5 volts for the resonance potential with an initial correction of $6.5 - 9.5 = -3.0$ volts.

Lenard Curve 4*a* starts at 11.5 volts and applying the proper correction gives 8.5 volts for the ionization potential. Curve 7*a* also gives $11.0 - 2.5 = 8.5$ volts.

The ratio curves give no indication of radiation. In fact, except for the large initial correction, toluene vapor behaves in a manner similar to that of benzene and xylene. These three belong to the benzene group, and therefore might be expected to give similar results.

Final Results.

Resonance potential of toluene ..... 6.25 ± 0.25 volts.
Radiation was not detected at any potential.
Ionization potential of toluene ..... 8.5 ± 0.5 volts.

8. *Chloroform* ($CHCl_3$).

Commercially pure chloroform was used during this test. The filament had been freshly coated before admitting the vapor. After working several hours the filament was examined and no traces of carbon deposit could be detected. The electron currents obtained in chloroform vapor were always steady and apparently no decomposition of the vapor took place.

Fig. 10 shows some typical chloroform curves. Curve 2 gives a resonance potential of 6.5 volts with a correction of + 1.0 volt, and likewise Curve 4 gives a resonance potential of 6.5 volts with a correction of + 1.5 volts.

The Lenard Curves 2*a* and 4*a* give respectively 10.5 and 10.0 volts, both of which with the proper corrections, give 11.5 volts as the ionizing potential at which the Lenard current is first detected.

The ratio test gave a value of one for all accelerating potentials, showing that radiation was not present in a measurable quantity.

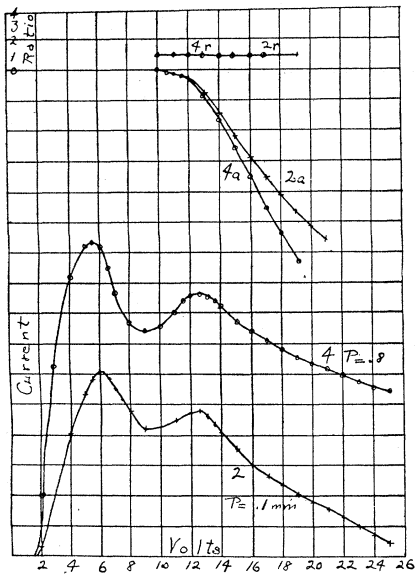

Fig. 10.

Final Results.

Resonance potential of chloroform ..... 6.5 volts.
Radiation was not detected at any potential.
Ionization potential of chloroform ..... 11.5 volts.

The resonance potentials of hydrogen, nitrogen, and oxygen agree well with those obtained by Foote and Mohler,[1] who used the same method. The ionization potentials of these three gases as found in this investigation using the Lenard method, are respectively about one volt lower than those given by Foote and Mohler. This discrepancy may possibly be attributed to the method of making initial corrections, a difference in galvanometer sensitivity, and the design of the tube.

The indication of radiation in hydrogen as given by the ratio curves agrees well with that given by the ratio curves of Compton and Olmstead.[2] Strong radiation was found to predominate between the resonance and ionization potentials of nitrogen, while no radiation was detected in oxygen.

[1] Scientific Papers of the Bureau of Standards, No. 400.

[2] PHYSICAL REVIEW, Vol. 17, No. 1, Jan., 1921, p. 45.

E. CONCLUSION.

Table of Results. (*In volts.*)

Gas or Vapor.	Resonance Potential.	Radiation Predominates.	Ionization Potential.
Hydrogen—H_2	10.1 ± 0.1	10.1 to 13.6	13.6 15.6
Nitrogen—N_2	8.4 ± 0.1	8.4 to 15.8	15.8
Oxygen—O_2	8.0	No radiation detected.	14.0
Ether—$C_4H_{10}O$	6.6 ± 0.1	8.1 to 10.1	13.6
Benzene—C_6H_6	6.0	No radiation detected.	9.6 ± 0.1
Toluene—C_7H_8	6.2 ± 0.25	No radiation detected.	8.5 ± 0.5
Xylene—C_8H_{10}	6.5	No radiation detected.	10.0
Chloroform—$CHCl_3$	6.5	No radiation detected.	11.5

So far as is known the critical potentials of the vapors used have not been heretofore determined. The resonance potentials for the vapors have about the same values, all lying between 6 and 7 volts. The ionization potentials also occur at a limited range of accelerating potential lying between 8 and 10 volts. Radiation was detected only in the case of ether. If it is present in the other vapors it is too small to be detected by the method used.

It should be noted that the results of this investigation indicate that in many cases inelastic collisions between the electrons and atoms take place without a measurable quantity of radiation being given off. Either this is due to a lack of sensibility in the detecting device, the method of measurement used, or the energy absorbed by the atom from the colliding electron is dissipated in some unknown manner.

Hughes and Dixon [1] found the ionization potentials of acetylene C_2H_2, methane CH_4, ethylene C_2H_4, and ethane C_2H_6, to be between 9.5 and 10.0 volts, which is of the same order as the ionization potentials of the vapors measured in this investigation. So that the hydrocarbons so far measured have approximately the same ionization potential.

The ionization potentials of the compounds are less than those of the simple elements of which they are composed. At least they are less than those of hydrogen and oxygen, the ionization potential of the carbon molecule not being known. This result might be expected from a consideration of the theory of the structure of the molecule. For

[1] PHYSICAL REVIEW, Vol. 10, No. 5, Nov., 1917, p. 495.

instance in a molecule containing a large number of electrons, the repulsive forces of neighboring electrons acting on any one electron will weaken the attractive force between it and the positive nucleus. So that such a molecule could be caused to give up one of its electrons with a smaller input of energy than a molecule containing say, only one or two electrons. No definite conclusions can as yet be drawn as to what part of the molecule is ionized. The loss of an electron by a molecule may mean a rearrangement of the remaining electrons about the nucleus, or it may mean the loss of an electron from one particular atom in the molecule.

In concluding the writer wishes to express his thanks to Dr. H. A. Wilson, under whose direction this investigation was carried out.

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HOUSTON, TEXAS.
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