IONIZATION BY COLLISIONS OF THE SECOND KIND IN THE RARE GASES

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Abstract

A positive ray apparatus was used to investigate the products of ionization by electron impact in mixtures of helium, neon, and argon. The variation with pressure of the ratio of the two types of positive ions present was investigated in detail for three cases. Case 1: A mixture of half helium and half neon was investigated up to 0.15 mm pressure. The ratio He^+/Ne^+ was found to decrease regularly between 0.03 mm and 0.15 mm. At 0.03 mm the mean free path is approximately equal to the dimensions of the apparatus. The suggested reaction is: $Ne+He^+\rightarrow Ne^++He$. Case 2: A mixture of half neon and half argon was investigated throughout the same pressure range. The ratio Ne^+/A^+ decreased regularly between 0.05 mm and 0.15 mm, but this decrease was less rapid than that of the ratio in Case 1. The suggested reaction is: $A+Ne^+\rightarrow A^++Ne$. Case 3: This mixture was half helium and half argon, and the pressure range was the same as in the first two cases. The ratio He^+/A^+ remained constant within the limits of experimental error. Case 3a: A mixture of 15 percent helium and 85 percent argon was also investigated as there were theoretical grounds for believing that the rate of variation of He^+/A^+ with pressure would be greater in such a mixture. In that case the ratio He^+/A^+ was found to decrease slightly. The suggested reaction is: $A+He^+\rightarrow A^++He$.

The observed effects are best explained by a type of collision of the second kind which is equivalent to ionization by positive ions. To account for the results obtained an electron must be transferred from an atom to an ion at a certain fraction of the collisions between an atom and an ion of higher ionizing potential. The results obtained at low pressures corroborated the values for the probability of ionization in these gases obtained by K. T. Compton and C. C. Van Voorhis.

IN CONSIDERING certain experiments of Lind and Bardwell,[1] Professor K. T. Compton suggested the possibility of ionization by positive ions of high ionizing potential, probably as the result of collisions of the second kind. The present research was prompted by the belief that such a process might play an important rôle in many of the phenomena of ionization in gases and that it might be investigated by the modification of Dempster's positive ray apparatus used by H. D. Smyth[2] and Hogness and Lunn.[3] The rare gases were selected for the first experiments, as they are monatomic and have well known ionizing potentials, and consequently the results obtained from them would probably be the most easily interpreted. It was well known that the intensities of the peaks in a positive ray apparatus fell off rapidly at high pressures because of collisions of the ions with the atoms or molecules of the gas and subsequent deflection or neutralization. Hence it was thought that secondary effects of the type looked for would be expected to appear in the region just before the peaks were extinguished by

[1] Lind and Bardwell, Science, Dec. 25, 1925, Vol. LXII, page 593.

[2] H. D. Smyth, Phys. Rev., **25**, 452 (April, 1925).

[3] Hogness and Lunn, Phys. Rev., **26**, 786 (Dec., 1925).

the increased pressure. These effects would probably be intimately connected with the ionizing potentials of the two gases present. For they presumably represent the tenacity with which an electron is held in the atomic structure. If an ionized helium atom collided with a neutral neon atom it is conceivable that, because of the intensities of the fields involved, an electron would be transferred from the neon atom to the helium ion. The resulting bodies would then be a helium atom and a neon ion. The reverse of this process would not occur as the electron would then be originally attached to that atom which had the greater affinity for it. There would be no way of detecting any effects which might take place during the collision of an atom with an ion of its own kind. Hence the result which would be observed, in case collisions of the above kind took place, would be that the number of neon ions would be increased at the expense of the number of helium ions. The same reasoning would lead to the conclusion that argon ions would be produced at the expense of neon ions in mixtures of those two gases. Effects corresponding to the above were observed under various conditions, but the probability of the transfer occurring was not found to bear any simple relation to the ionizing potentials of the gases. While this investigation was in progress Hogness and Lunn[4] published the results of certain experiments they had conducted with argon and nitrous oxide during which they had incidentally observed effects of the same nature as those contained in this paper.

Apparatus and Procedure

The apparatus used is shown in Fig. 1. It is essentially the same as that used by Smyth[2] with only minor alterations. Chamber A, the high pressure region in which the ionization occured, was quite heavily shielded as was also the path between that and chamber B where the magnetic deflection took place. The shielding was thought necessary as rather large magnetic fields were used during some parts of the investigation and it was desired that the effect of changes in the field should be negligible except in chamber B. The distance between the slit, S_1, maintaining the pressure difference and the collimating slit, S_2, was made as small as was consistent with good evacuation from the upper outlet. The filament was placed very close to the first gauze, G_1, in order that the chance of a collision between an electron and an atom in that region might be reduced to a minimum. The filament itself was placed inside a tube the lower end of which supported G_1 and G_2. The tube was solid above G_1, but there were openings between G_1 and G_2. It was found convenient to have two gauzes during part of the work to investigate and interpret certain effects which were met. The filament was of tungsten. The width of S_1 was about 0.05 mm, that of S_2 was about five times as great. The gases to be used were mixed and stored in a system in which the pressure could be varied between convenient limits, and were then admitted to chamber A through capillary leaks. A McLeod gauge was situated as close to chamber A as possible. The evacuating system consisted of two single stage diffusion pumps backed by a double stage and an

[4] Hogness and Lunn, Phys. Rev., **28**, 849, abstract (1926).

oil pump. The large metal-to-glass seal was made by grinding the parts together and covering the joint with both DeKhotinsky and Picein cements. This joint proved quite satisfactory under the fluctuation in temperature to which it was subjected. It was found necessary to wind a cooling coil around the outside of chamber A which contained the filament.

As the apparatus could not be baked out it had to stand under vacuum for a day or two before the nitrogen, oxygen, water vapor, etc. adsorbed

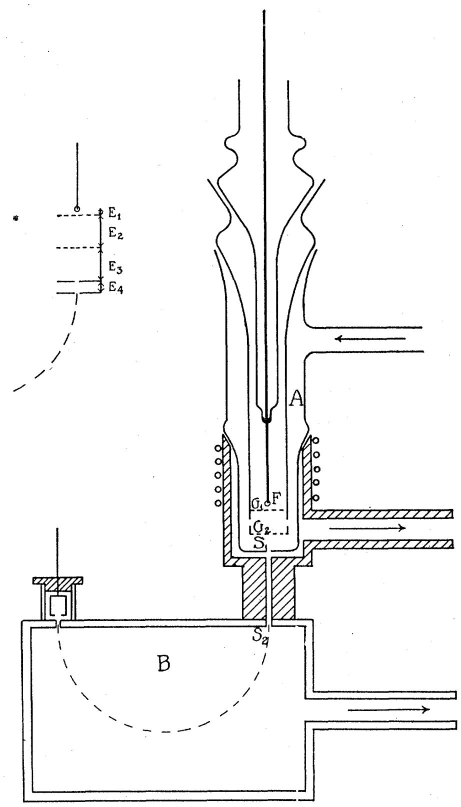

Fig. 1. Diagram of apparatus.

on the walls were reduced to a negligible quantity. Then after preliminary runs in hydrogen the behavior of pure helium was investigated under various conditions. At the high pressures used the amount of ionization was found to vary nearly linearly with the emission. In the final procedure the variable was the pressure and every change in pressure necessitated a slight change in the filament current in order to keep the emission constant. The fluctuation of the emission from one run to the next was very slight but sufficient to account for the greater part of the irregularity of the curves obtained. As E_1, the accelerating voltage for the electrons, was increased the ions began to appear very soon after the critical potential was passed, but the amount of ionization did not rise very rapidly at first and the values of E_1 used during the work were in the neighborhood of twice the critical potentials. E_2 and E_3 the accelerating voltages for the positive ions were kept of the order of five volts in the final measurements as it was found that larger values introduced complicating effects which will be discussed later. The curves that follow are not strictly comparable as it was necessary to change the magnetic field for different gases and it was found, as will be mentioned later, that the ionization as measured by the electrometer was not independent of the magnetic field used.

The variation of the area under the peak with pressure was investigated and the results for helium, neon, and argon are given in Fig. 2. As would be expected the forms of the curves when the ordinates are multiplied by the proper constant are approximately the same. The constant probably depends on the value of E_1 used and the ionizing potential of the gas. The means of several runs were taken and the discrepancies could be accounted

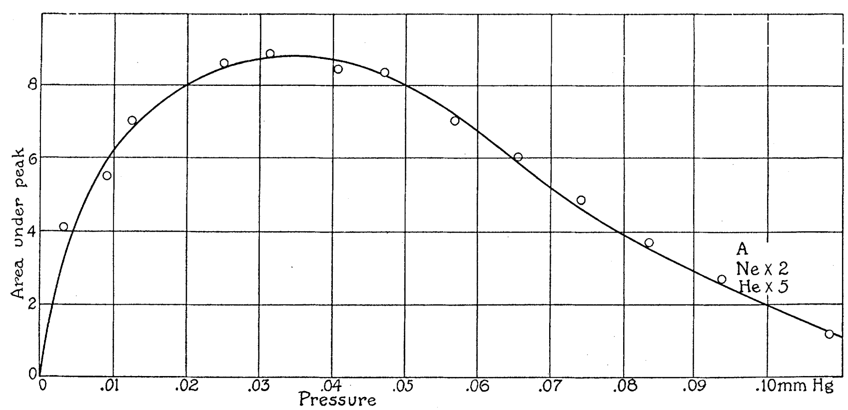

Fig. 2. Variation with pressure of the area under the peaks of positive ray analysis curves in A, He, and Ne.

for by the inevitable slight variations of voltages and filament emission. The abscissas are the pressures and the ordinates are measured in arbitrary units. A maximum of ionization occurs when the pressure is between three and four hundredths of a millimeter. The decrease in ionization after that point is presumably due to collisions with gas atoms resulting in deflection or neutralization, and it is therefore in that region that any secondary effects should be expected.

Several procedures were tried, such as taking runs at constant total pressure with varying mixtures of helium and neon, or with a constant partial pressure of one of the gases and varying the partial pressure of the other. These experiments showed in a qualitative way that some such an effect as the one looked for was actually taking place but they did not lend themselves to accuracy of measurement or ease of interpretation. The procedure finally adopted, as least equivocal and best adapted to the particular investigation, was to admit the gases in known and nearly equal proportions and to vary the total pressure. The secondary effects would not be expected to occur below three hundredths of a millimeter pressure and should come more into evidence as higher pressures were reached. In this method the only variable was the pressure and it was susceptible of quite accurate measurement.

Results

The first attempts were made using potentials for E_2 and E_3 in the neighborhood of fifteen or twenty volts. It was found that under these conditions the effects were complicated by having all the peaks double. The duality of the peaks was found to vary only with the potentials E_2 and E_3. If these potentials were large the peaks were widely separated and as they were decreased the peaks became indistinguishable when E_2 plus E_3 was in the neighborhood of twenty volts. If E_3 was small and its direction reversed the extraneous peak was very much reduced. This and other evidence of a similar nature pointed to the theory that the second peak was produced by photoelectrons emitted from G_2 and S_1 and accelerated upward towards G_1. This effect was eliminated by reducing E_2 and E_3 till their sum was well below the ionizing potential of any gas used. This still left the currents measured by the electrometer of a convenient order of magnitude. Other sources of slight error or irregularity were investigated and their effects reduced as much as possible.

The gases were thoroughly mixed in the reservoir by a method of contraction and expansion and also allowed to stand for some time after mixing before the runs were taken. Furthermore the possibility of a change in the ratio of the gases on passing through the capillary leaks into chamber A was considered. That is, it was thought that there might be a differential effect between the capillary method of pressure limitation and the slit method at S_1 in favor of one of the gases. This effect was investigated and found not to exist within the limits of experimental error. Any error due to minor irregularities in the mixture was greatly reduced by taking the mean of a series of observations. All the results were converted into the form of ratios and hence were independent of the fact that there is probably not an exact correlation between the area under the peaks and the number of ions present. However, the variation in size and shape of a peak with the magnetic field as a source of error will have to be mentioned again in the case of helium and argon.

By far the largest and most serious possibility of error is due to stray ionization present in chamber B. The electrometer was adjusted so that its natural drift when the filament was not glowing was extremely small. But as soon as ions were produced in A the drift increased. It is very probable that a small fraction of the ions entering B instead of continuing in a circular path are scattered from the beam. Some of these ions enter the Faraday cylinder and cause a deflection of the electrometer. This effect is more marked at low values of E_4. And the possibility of error in that region was further enhanced by slight traces of N_2 and H_2O which could not be completely eliminated. For equal areas of peaks the height as measured by the current to the electrometer varies to a first approximation as E_4, so that the total error due to these effects became more serious with a gas of high atomic weight such as argon. Or more particularly when the discrepancy between the atomic weights of the two gases used was large. For if the atomic weights were not widely different the difficulty could be overcome by increasing the magnetic field and hence the corresponding value of E_4 for the peaks which would decrease the error due to scattered ionization. This will have to be mentioned again in the case of argon and helium.

The first gases used were helium and neon. The result in the case of a mixture of fifty percent of each (by volume) is shown in Fig. 3. The pressures plotted are the total pressures, the partial pressure of each gas being half of

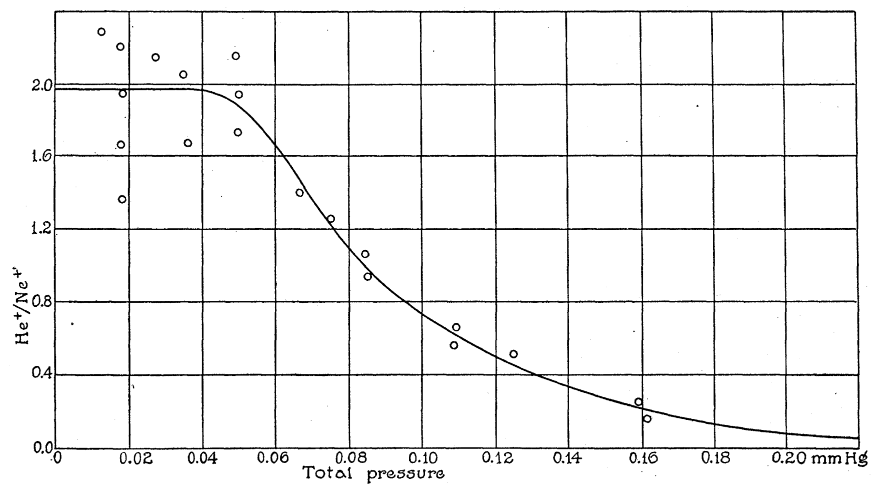

Fig. 3. Ratio of He^+ to Ne^+ for various pressures of a 50 percent mixture of He and Ne.

the pressure shown. The ordinates represent the ratio of the helium ions to the neon ions, as obtained by taking the areas under the peaks representing the two gases. E_1 was fifty volts and E_2 and E_3 were five volts apiece. The emission from the filament was maintained as nearly as possible at one milliampere. In this case the most convenient magnetic field to use with the available limits for E_4 was about 1700 gauss. In the region of pressure below five hundredths of a millimeter the ratio fluctuated rather widely. There seems to be no really adequate explanation for this. The most probable cause is that more difficulty was experienced in keeping the filament emission at a constant value in this region. The mean, however, remained practically constant. After the pressure passed five hundredths of a millimeter, approximately, the ratio dropped showing a predominance of neon ions. This is about the pressure judging from Fig. 2 at which any secondary effects should become noticeable. This is also the point at which the effect should occur from a more direct point of view. The distance between G_1 and S_1 was approximately two centimeters, and the pressure at which effects due to collisions should become evident would be that at which the mean free path was of about this length. This should occur in these gases at about five hundredths of a millimeter. From this point the curve drops in a fairly regular fashion, and apparently approaches a lower value asymptotically. In the case of helium and neon the final value, if one exists, seems to be a very low one. It is probably closely related to the process of exchange of an electron from an atom to an ion outlined above. The difference between the original and final value of the ratio may even be a measure of the probability of the transfer occurring. It was not possible to carry these observations much above fifteen hundredths of a millimeter as the peaks had become very small by the time that pressure was reached. Also, for the same reason, the observations were less accurate as the drift of the electrometer due to scattered ionization had become a very appreciable fraction of the area of the peak. That was allowed for but it could not be done with great accuracy.

The next mixture used was that of neon and argon. In some ways this was a more favorable mixture to work with in a positive ray apparatus than

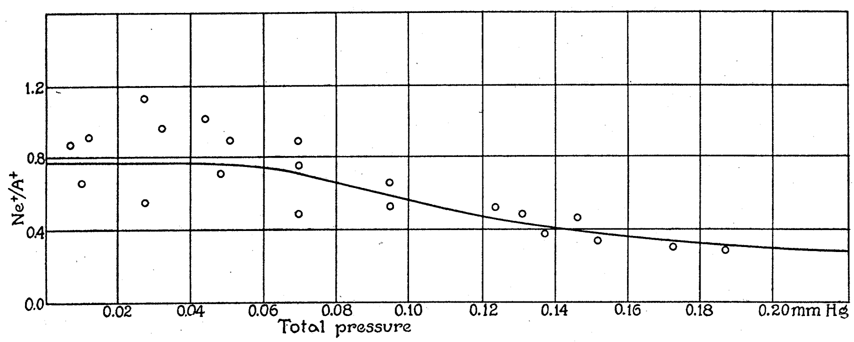

Fig. 4. Ratio of Ne^+ to A^+ for various pressures of a 50 percent mixture of Ne and A.

the previous one for the ratio of the atomic weights is 5:9 instead of 1:5. The reason that the value of this ratio effects the accuracy was mentioned above. Also the ionizing potentials are slightly lower, and the difference between them is about twice that in the previous case. The results for this mixture are shown in Fig. 4. As before the abscissas represent the total pressures and the mixture contained equal proportions of each gas. The ordinates are again the ratios of the areas under the peaks, but they are not strictly comparable to the ordinates in Fig. 3 for the magnetic field was about 3000 gauss in this case and the ionization as measured by the electrometer was not independent of the magnetic field. This curve shows the general characteristics of Fig. 3. The values of the ratio at lower pressures fluctuate rather widely as before. The most distinctive feature is that the change in the ratio of the ions with pressure is very much less than in the case of helium and neon. It also looks as if the slope approaches zero at higher pressures, but the evidence for this is not very conclusive.

The third mixture investigated was that composed of half helium and half argon. The conditions under which these observations were taken were as nearly as possible those of the previous runs. E_1 was fifty volts, E_2 and E_3 were five volts apiece, and the emission was kept at one milliampere. The magnetic field first used was about 2000 gauss. Approximately the same range of pressures was covered and with the same procedure, but within the limits of error no departure from the original value of the ratio of helium to argon was observed. However, the results were less convincing than in the two previous cases for the fluctuation in the actual areas of the peaks at constant pressure was considerably larger. This was due to the particular gases used for they were the least satisfactory ones to investigate by this method, the ratio of the atomic weights in this case being 1:9. Hence the argon appeared at a comparatively low value of E_4 and had a broad low peak much less susceptible to accurate measurement than the helium one. The particular difficulty, of course, was due to the electrometer drift caused by the scattered ionization in the argon region. Attempts were made to find a more satisfactory method of procedure. The most promising one was to investigate the behavior of one of the peaks, in this case the argon one, with

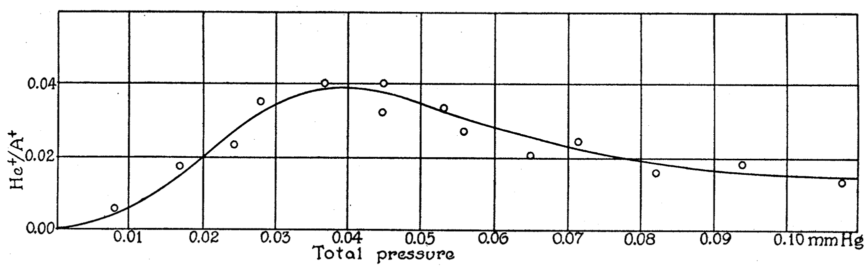

Fig. 5. Ratio of He^+ to A^+ for various pressures of a mixture of 15 percent He—85 percent A.

variation in the magnetic field and consequent variation in E_4 at different pressures. This was done and curves were obtained relating the peak area to the value of E_4 at which it was obtained. These were found to depend slightly on the pressure. With these data the two peaks of helium and argon could be measured at different magnetic fields such that the E_4 values at which they appeared were of the same order. By this means the area under the argon peak could be measured more accurately and its value extrapolated back to the value which it would have if measured at the same magnetic field as that used in obtaining the helium peak. This method yielded more consistent results and was presumably of greater accuracy. However, no change in the ratio of the peaks, within the limits of error, could be observed as the pressure was varied.

From simple kinetic theory considerations it can be seen that if this effect takes place as assumed, the rate of variation of the ratios: $He^+/(He^+ + A^+)$ and $A^+/(He^+ + A^+)$, with pressure should be greatest when the ratio of helium to argon is small. Acting on these considerations a mixture of 15% helium and 85% argon was investigated. The conditions were almost the same as in the other experiments and the results are shown in Fig. 5. The ratio increases to a maximum at about .03 mm as would be expected from consideration of the partial pressure of the gases. After that point the ratio decreases slightly tending to show that the argon ions are being increased at the expense of the helium ions. Further evidence that this effect is taking place is given by the shapes and positions of the peaks. As the pressure increases beyond about .03 mm the He peak decreases in area but remains of the same shape and in approximately the same place. The argon peak decreases slightly but also broadens out and extends to higher values of E_4 showing that the region of production of argon ions is moving from G_1 toward S_1. The evidence thus indicates that the process observed in the other mixtures occurs in a mixture of helium and argon though it is much less probable.

Discussion

The outstanding result of these experiments is that this type of ionization by positive ions apparently does occur. Further experiments have been made with mixtures of the rare gases and gases whose molecules are diatomic. These results will form the subject of a later paper, but they tend to confirm the evidence contained in this one. If this effect occurs at a certain fraction of the collisions in any mixture of ionized gases it should have an important bearing on almost all discharge tube phenomena. A rough estimate of the probability of this electron transfer can be made from the slopes of the curves but the data are as yet insufficient to justify the publication of a numerical value.

The shapes of the curves in Figs. 3 and 4 further suggest that the probability of the transfer of an electron from an atom to an ion is not connected in a simple way with the electron affinities of the two gases involved. In fact, it even seems that though a difference in ionizing potential is necessary to cause such a transfer, yet the smaller this difference the more likely such a transfer is to occur. For the difference in ionizing potential between neon and argon is twice that between helium and neon. If this is so, and it is a result consistent with those of other experiments on collisions of the second kind, it accounts for the smallness of the effect in the case of helium and argon. For in this case the difference in ionizing potential is three times that in the case of helium and neon. These remarks apparently also apply to diatomic gases.

It should also be mentioned that the possibility of explaining the observed effect on the basis of a limiting speed for electrons in a mixed gas was considered. At sufficiently high pressures inelastic impacts would prevent the electrons from gaining sufficient energy to ionize the gas with the higher ionizing potential. However, such a situation could only exist when the length of the electron mean free path was of the order of the distance from the filament to G_1, which from the constants of the apparatus would occur at a pressure of about 1.5 mm. This is very much higher than any pressure used.

Finally it might be mentioned that the mean values obtained for these ratios below three hundredths of a millimeter are in fairly good agreement with the values obtained by Compton and Van Voorhis[5] for the probability of ionization in these gases. It was mentioned above that the area under the peak is probably not an accurate measure of the ionization in chamber A and also that the peak area varied with the values of magnetic field and E_4 used to obtain it. The points on the curves given here all represent runs in which the magnetic field was kept constant and the value of E_4 was varied. The behavior of peak area with magnetic field was investigated and from these results Figs. 3 and 4 can be replotted in such a way that the points represent runs in which E_4 is kept constant and the magnetic field varied. If this is done the shapes of the curves remain the same but the actual values of the ordinates are slightly different. And the ratios at low pressures when these ordinates are used are in quite good agreement with the same ratios calculated from the Compton and Van Voorhis results at the appropriate E_1.

My thanks are particularly due to Professor K. T. Compton and Professor H. D. Smyth for the suggestion of the present investigation and for their invaluable assistance and helpful interpretations during the work.

Palmer Physical Laboratory
Princeton, New Jersey
February 5, 1927

[5] Compton and Van Voorhis, Phys. Rev., **27**, 724 (June, 1926).