IONIZATION BY COLLISIONS OF THE SECOND KIND IN MIXTURES OF HYDROGEN AND NITROGEN WITH THE RARE GASES

By Gaylord P. Harnwell

Abstract

The effect of the presence of a rare gas in ionized hydrogen and nitrogen was studied by means of a positive ray analysis of the products of ionization. The variation with pressure of the types of ions found was investigated in some detail for both hydrogen and nitrogen in the presence separately of helium, neon and argon. In all of the mixtures studied the evidence tends to support the view that a type of collision of the second kind takes place at which an atom is ionized by colliding with an ion of an atom of higher ionizing potential. Thus at high pressures corresponding to a large number of collisions the equilibrium is displaced in favor of the atom of lower ionizing potential. The following equations can be predicted from a knowledge of the ionizing potentials and they are all supported by the experimental evidence obtained:

$He^+ + H_2 = He + H_2^+$	$He^+ + N_2 = He + N_2^+$
$Ne^+ + H_2 = Ne + H_2^+$	$Ne^+ + N_2 = Ne + {}^{17}N_2^+$
	$Ne + {}^{24}N_2^+ = Ne^+ + N_2$
$A + H_2^+ = A^+ + H_2$	$A + N_2^+ = A^+ + N_2$

Where ${}^{17}N_2^+$ and ${}^{24}N_2^+$ represent respectively the nitrogen ions produced at the expense of seventeen and twenty-four volts.

The situation for nitrogen is seen to be more complicated than that for hydrogen. In the latter case the evidence shows that the equations listed above are in the order of increasing probability. This tends to support the view that the probability of the transfer's occurring is an inverse function of the difference in ionizing potentials. The phenomena can not be interpreted as accurately in the case of nitrogen. However, the formation of ${}^{24}N_2^+$ by Ne^+ (24.5) was found to be the most probable of all the processes occurring in nitrogen and the results obtained with the other rare gases as far as they can be interpreted are also in accord with this view.

THE work forming the substance of this paper is a continuation of an investigation undertaken to detect any evidence for ionization at collisions of the second kind in mixtures of the rare gases.[1] A very short résumé of the previous results and the mechanism suggested to account for them will serve as an introduction to the rather more complicated situations found to exist in mixtures of the rare gases with hydrogen and nitrogen. The positive ray apparatus was the same as that used in the previous experiments. It was described in detail in the paper cited, so here it will be necessary only to outline the method of investigation employed.

In a partially ionized mixture of two monatomic gases there will be three general types of collisions taking place: atoms will collide with atoms, atoms will collide with ions, and ions will collide with ions. The second type of collision may be divided into two classes: an ion may collide with an atom

[1] Gaylord P. Harnwell, Phys. Rev. **29**, 683 (May 1927).

of higher ionizing potential, or an ion may collide with an atom of lower ionizing potential. In the latter case the ion has a greater electron affinity than the atom and there may be a certain probability of an electron being transferred from the atom of small electron affinity to the ion of the atom of large electron affinity. As this interchange would not be reversible the effect of a large number of collisions would be to increase the number of ions of lower ionizing potential at the expense of those of higher ionizing potential. As the number of collisions would be proportional to the pressure, if a curve representing the ratio of the ion of higher ionizing potential to the ion of lower ionizing potential were plotted against the pressure it should commence to drop at a pressure at which the mean free path of an ion was comparable to the dimensions of the apparatus and continue to fall as higher pressures were reached. Also the slope of the curve should be a measure of the probability of the electron transfer outlined above. Mixtures of helium and neon, neon and argon, and of helium and argon were investigated for evidence of this effect and the following equations, given in the order of their probability, account for the results obtained:

$$He^+ + Ne = He + Ne^+$$
$$Ne^+ + A = Ne + A^+$$
$$He^+ + A = He + A^+$$

Considering these equations from the point of view of the ionizing potentials of the gases it will be seen that the interchange is most probable in the case of helium and neon where the discrepancy between the ionizing potentials is least and least probable in the case of helium and argon whose ionizing potentials are the most widely separated. This is of particular interest by analogy with the thermodynamic argument developed by Klein and Rosseland[2] for collisions of the second kind between atoms and electrons where it is shown that the probability of an energy transfer is greatest when the energy to be transferred is least. The argument as there given is not absolutely conclusive nor is it strictly applicable to the present conditions but it is of interest in the light of the above results. One further point should be mentioned, namely that the probabilities of ionization of these rare gases as deduced from the experimental curves were in good agreement with the values obtained by K. T. Compton and C. C. Van Voorhis.[3]

As has been mentioned the apparatus was described in detail in a previous paper.[1] The ions were produced by the usual method of electron bombardment in a region whose pressure could be varied and then drawn into a region of very low pressure and analyzed by a magnetic field. The ion stream was detected by an electrometer and the current taken as a measure of the number of ions of that particular mass emerging from the high pressure region. The analyzing runs were made by varying the accelerating voltage (E_4) for the positive ions. The areas under the peaks obtained by such a run, and plotted on a mass scale ($1/E_4$), were taken as representing the number

[2] O. Klein and S. Rosseland, Zeits. f. Physik **4**, 46 (1921); also Franck, Anregung von Quantensprüngen durch Stösse, Page 210 et seq.

[3] Compton and Van Voorhis, Phys. Rev. **27**, 74 (June 1926).

of ions of the particular type present in the high pressure region. The variation of this quantity with the pressure existing in the ionizing chamber, as measured by a McLeod Gauge as close to the apparatus as possible, was the relation investigated. As the pressure was increased the area under a peak, when a pure rare gas was in the chamber, increased up to a certain pressure due to the actual increase in the number of ions produced and then decreased showing that some of the ions produced were being scattered from the beam before they could emerge from the high pressure region. Consequently at high pressures the ions reaching the electrometer were mainly those produced near the slit which separated the high from the low pressure regions. At sufficiently high pressures the electrons were not able to ionize close enough to the slit so that any of the positive ions could be drawn out and the area under the peak reduced to zero.

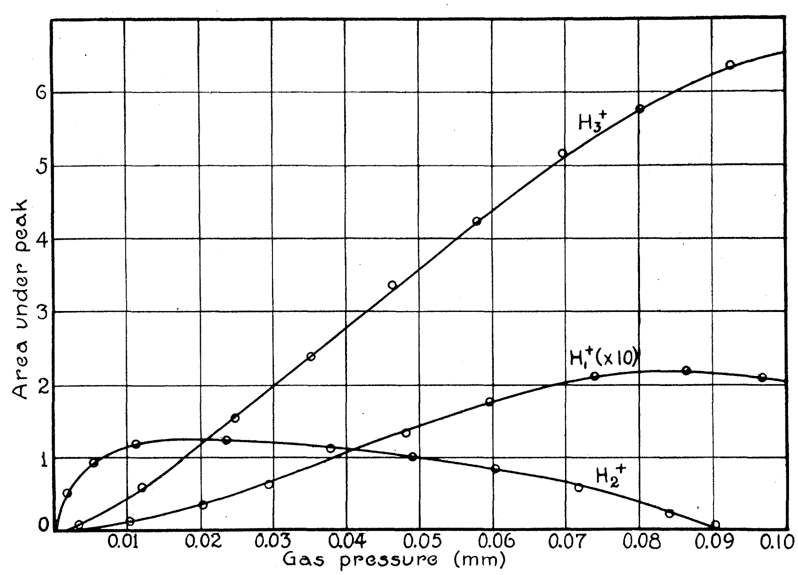

Fig. 1. Effect of pressure on the nature of the positive ion in hydrogen.

In dealing with a diatomic gas the observed phenomena become more complicated as can be seen from Figs. 1 and 2. It is quite well established from the work of H. D. Smyth[4] and of Hogness and Lunn[5] in hydrogen and nitrogen that the primary product of ionization is the molecular ion and that such ions as N_1^+ and H_3^+ are formed as a result of a secondary process. Any ionized hydrogen molecule apparently can dissociate, but the case is slightly different for nitrogen. Hogness and Lunn[5] have shown that two types of N_2^+ exist one having been produced at the expense of twenty-four volts of energy and the other at the expense of seventeen. The former $^{24}N_2^+$ is capable of dissociating into N_1^+ but the latter, $^{17}N_2^+$, is not. Also there

[4] H. D. Smith, Phys. Rev. **25,** 452 (April 1925).

[5] Hogness and Lunn, Phys. Rev. **26,** 44 (1925); **26,** 786 (1925).

is very good evidence for believing that H_3^+ is a secondary and not a tertiary product, that is, that the majority of it is produced directly from H_2^+, and not by way of H_1^+. The above reactions are represented by these equations:

$$H_2+H_2^+=H_3^++H_1$$
$$H_2^+=H_1\ +H_1^+$$
$$^{24}N_2^+=N_1\ +N_1^+$$

These equations are well illustrated by Figs. 1 and 2. The primary product would be expected to predominate at low pressures where collisions are very infrequent and to behave in that region very much like a rare gas peak. This is what is observed, the primary product rising sharply from the origin. However, as soon as the pressure reaches a value such that an appreciable number of the ions collide before emerging from the high pressure region the character of the phenomena changes. It no longer resembles the

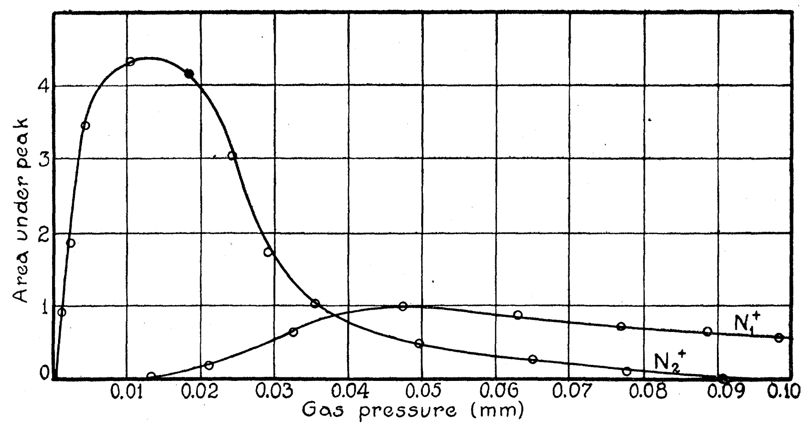

Fig. 2. Effect of pressure on the nature of the positive ion in nitrogen.

rare gas case for the secondary products appear in large quantities and the primary products drop very rapidly. At sufficiently high pressures the primary product entirely disappears though the secondary products are still present. This means that the primary product is only formed in the region so far removed from the slit from which the ions are drawn that it can not reach it without making several collisions at each of which it is likely to be deflected or dissociated. The secondary products on the other hand are formed nearer the slit at one of these collisions and continue toward the slit. There is less chance of their being deflected from the beam, and they are more stable so that there is also less chance of their being dissociated. These phenomena are very evident in both hydrogen and nitrogen. There are two secondary products in hydrogen, H_1^+ and H_3^+, the latter greatly predominated under the conditions which existed in the ionization chamber. The accelerating potential for the ionizing electrons was well above twenty-four volts so in the case of nitrogen N_1^+ is present. When the electrons had only had twenty volts of energy the N_2^+ peak behaved exactly as a rare gas peak and no N_1^+ was observed.

In obtaining the curves of Figs. 1 and 2 and in all that follow the ionizing electrons have fallen through fifty volts, the field drawing the positive ions out of the high pressure region is four volts per centimeter, and the length of this region is about two and a half centimeters. The abscissas in all but Figs. 7, 8 and 9 represent total pressure, and in curves representing the characteristics of mixtures the observed pressure has been multiplied by

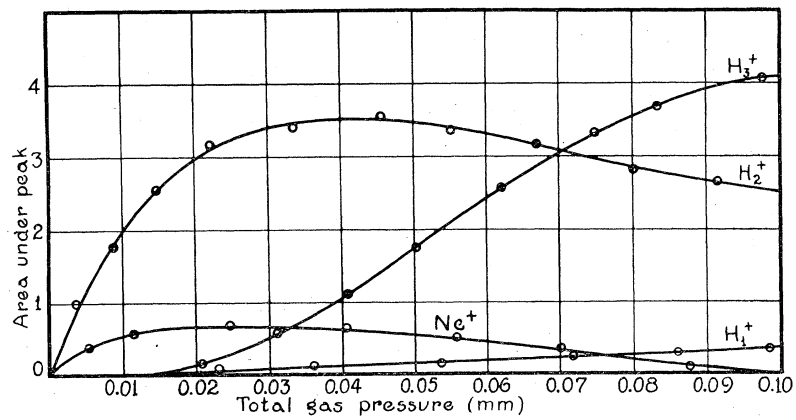

Fig. 3. Effect of pressure on the nature of the positive ion in mixtures of hydrogen and neon.

the ratio of the mean free path in the pure diatomic gas to the mean free path in the mixture so that the abscissae are directly proportional to the number of collisions and the curves are comparable with one another. Also all results refer to mixtures in which the two constituents are present in equal proportions unless otherwise stated.

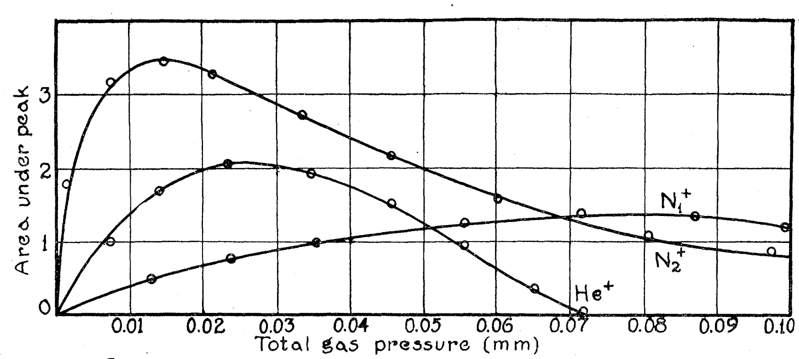

Fig. 4. Effect of pressure on the nature of the positive ion in mixtures of nitrogen and helium.

Figs. 3, 4, 5, and 6 represent the results obtained with mixtures of hydrogen and neon, nitrogen and helium, nitrogen and neon, and nitrogen and argon. The curves obtained with hydrogen and helium and with hydrogen and argon are not reproduced here as the same general phenomena are observed in the analogous curves with nitrogen. The ordinates of all these curves as directly calculated from the experimental data represent the amount of the particular ion that is drawn out of the region of high pressure in the ionization chamber. In the cases of the curves representing the rare gases in the mixtures these ordinates have been too large to be represented on these diagrams. Hence they have been reduced in such a proportion that they bear the same ratio to the ordinates of the primary product of ionization

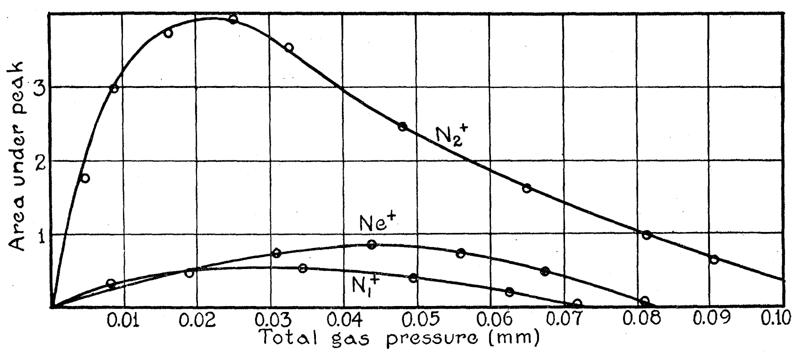

Fig. 5. Effect of pressure on the nature of the positive ion in mixtures of nitrogen and neon.

in the diatomic gas at low pressures as the probabilities of ionization of the two gases as given by the work of Compton and Van Voorhis.[3] The justification for this procedure is that the ordinates of the curves obtained in mixtures of the rare gases with one another were about in proportion to their probabilities of ionization, at low pressures. And the curves obtained by plotting the value of the electrometer current do not represent the ions produced

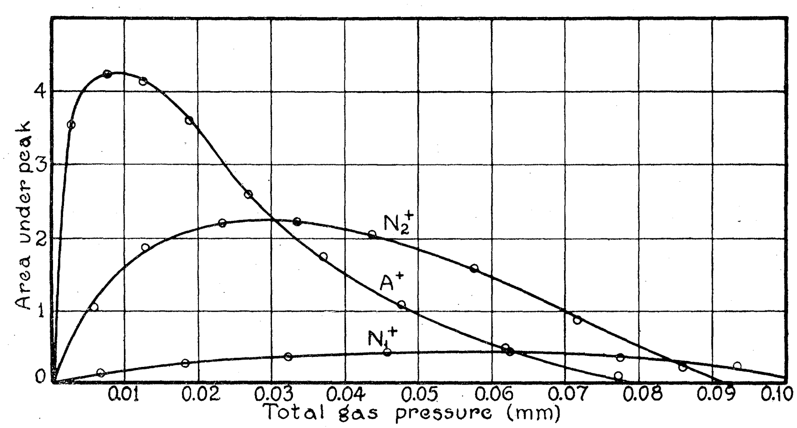

Fig. 6. Effect of pressure on the nature of the positive ion in mixtures of nitrogen and argon.

but only those which pass through the high pressure region. Hence the natural assumption is that the monatomic and diatomic ions are produced in the proportions found by Compton and Van Voorhis but that the probability of a monatomic ion passing through the high pressure region and remaining in the beam so that it will be recorded by the electrometer is greater than for a diatomic ion. There is other evidence that this is the correct explanation, particularly that obtained from the position of the maximum of the rare gas curve, for the shape of the curve is a function of the probability of ionization and also of the probability of deflection or neutralization. From a consideration of the shapes of these curves in hydrogen and nitrogen it can be seen that the probability of deflection is less in hydrogen than in nitrogen, as would be expected. However, in the following analysis of these curves the rare gas curves are less important than the curves representing the primary and secondary products of ionization in the diatomic gas.

The ionization potentials of the gases used are approximately as follows:

$$He = 24.5 \text{ volts} \qquad H_2 = 16 \text{ volts}$$
$$Ne = 21.5 \qquad N_2 = 17 \text{ and } 24$$
$$A = 15$$

And if the interchange of an electron at a collision between an atom and an ion is completely determined by the electron affinities or ionizing potentials involved it would be expected that the processes taking place would be represented by the following equations; where N_2^+ represents both types of ion:

$$He^+ + H_2 = H_2^+ + He \qquad He^+ + N_2 = N_2^+ + He$$
$$Ne^+ + H_2 = H_2^+ + Ne \qquad Ne^+ + N_2 = {}^{17}N_2^+ + Ne$$
$${}^{24}N_2^+ + Ne = Ne^+ + N_2$$
$$A + H_2^+ = H_2 + A^+ \qquad A + N_2^+ = N_2 + A^+$$

Where the type of N_2 ion is not specified either one can be considered as obeying the equation. Also, if the relation that the probability of a transfer is inversely proportional to the amount of energy in excess of that transferred is found to be as applicable in the case of diatomic as in the case of purely monatomic mixtures, it would be expected that the hydrogen equations as listed are in the order of increasing probability. The nitrogen equations represent a more complicated case and it is a little difficult to know just how the probabilities should run except that the first equation should be the most probable, on these simple assumptions, as the difference in ionizing potentials for ${}^{24}N_2$ and Ne is only of the order of half a volt.

The phenomena observed in the mixtures containing hydrogen will be considered first and for the purpose of simplifying the discussion a slightly different method of plotting will be employed. The abscissas again represent the pressure, in this case the partial pressure of hydrogen, and the values are corrected for the difference of free path in the various mixtures so that they are really proportional to the number of collisions. The ordinates represent the value of the ratio H_2^+/H_3^+, this is the ratio of the primary to the secondary product of ionization. The ratio $H_2^+/H_1^+ + H_3^+$ could be used, but H_1^+ was present in such small quantities that the difference between these two ratios would be inside the limit of accuracy of the experiment. It brings out in a very convenient way the processes taking place, for the only difference in the conditions under which the curves shown in Fig. 7 are obtained is in the type of collision possible to the two members of the ratio, that is whether the hydrogen can collide just with hydrogen or also with helium, neon, or argon. There will not be the possibility of the formation of H_3^+ at a rare gas collision for it can only be formed at a collision with another H_2 particle, hence the increased value of the ratio at high pressures in the mixtures will represent the secondary production of H_2^+.

The curve marked 1 in Fig. 7 represents this ratio under normal conditions when only hydrogen is present. The curve drops from a very high

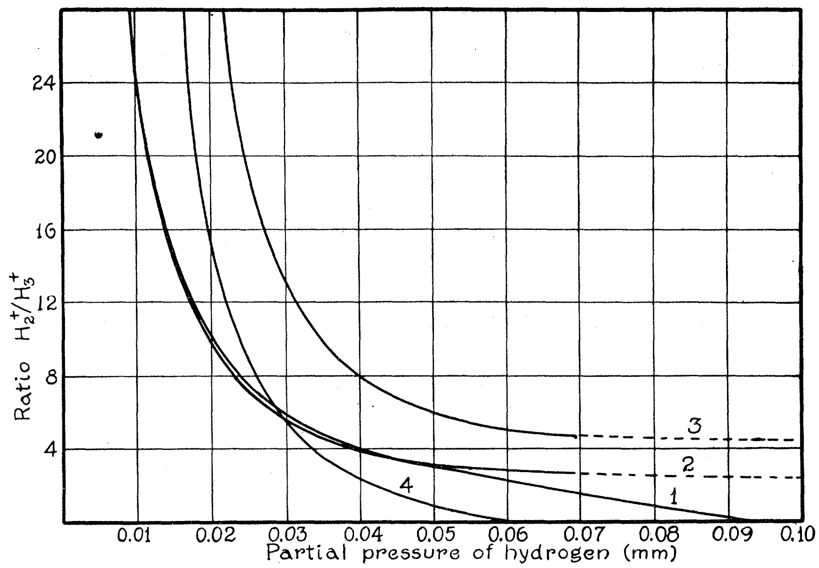

Fig. 7. Ratio of H_2^+/H_3^+ as a function of the partial pressure of hydrogen. Curve 1, in pure hydrogen; curve 2, in the presence of helium; curve 3, in the presence of neon; curve 4, in the presence of argon.

value at low pressures to zero at about nine hundredths of a millimeter. The reason that H_2^+ disappears is, as we have seen, that at that pressure the electrons from the filament are no longer able to ionize the hydrogen close enough to the low pressure region so that an appreciable amount of the ionized product can be drawn out without having suffered any collisions. H_3^+ being the secondary product and capable of surviving many collisions does not even reach its maximum value till after the H_2^+ has completely disappeared.

The curve marked 2 represents the variation of this ratio with pressure when helium is present in the ionization chamber. The character of this curve is quite different for pressures above five hundredths of a millimeter. Above that pressure as far as experimental points could be obtained the ratio H_2^+/H_3^+ remains practically constant. The interpretation of this is that H_2^+ is being produced near enough to the slit so that it can emerge from the high pressure region without having been dissociated. As we have seen, electrons are not able to do this, hence these hydrogen ions must have been produced by collisions with helium ions. There is the alternative possibility that they may have been produced by collisions with excited helium atoms. In the present apparatus the two possibilities can not be distinguished. However, as the life of an ion would be much longer than that of an excited atom the first explanation is much the more likely. The process occurring can be represented by the equation:

$$He^+ + H_2 = H_2^+ + He$$

The curve marked 3 represents the behavior of the ratio in the presence of neon. It is evident that the effect of neon is very similar to that of helium. The fact that this curve does not coincide with curves 1 and 2 at low pressures probably has little significance. It would be amply accounted for if the probability of deflection of an ion depended on the type of particle with which it collided. This is certainly very probable and it has not been previously allowed for. The chief difference between curves 2 and 3 is that the high pressure value of the ratio is considerably greater in the latter case. That is more H_2^+ is produced in neon than in helium for the same number of collisions. The equation would be similar to the helium one:

$$Ne^+ + H_2 = H_2^+ + Ne$$

The curve marked 4 represents the behavior of the ratio in the presence of argon. The shape of this curve differs greatly from that of the two preceding ones. It would appear that a reverse phenomenon is taking place. The two possibilities to account for a change in the ratio are: that H_3^+ is created at a collision with an argon particle or that H_2^+ is destroyed. The former is obviously impossible directly and probably may be entirely neglected. The latter is exactly what would be predicted by the argon hydrogen equation:

$$A + H_2^+ = A^+ + H_2$$

It is difficult to form an accurate idea of the probabilities of electron interchanges between hydrogen and the rare gases from Fig. 7. However, the ordinates of curves 2 and 3 at high pressures tend to show that the process associated with 3 is the more probable. The hydrogen curves analogous to Figs. 4 and 5, which are not reproduced here, bring this out much more clearly and also tend to show that the process associated with 4 is the most probable of all. This is exactly what would have been expected by analogy with the rare gas mixtures[1] as can be seen by referring to the ionizing potentials given above.

Fig. 8 gives the analogous curves for nitrogen. The ordinates represent the values of the ratio N_2^+/N_1^+, and the abscissas are the partial pressures of nitrogen. These curves are very similar to those in Fig. 7 except that curve 3 representing the ratio in the presence of neon is missing. By referring to Fig. 5 it can be seen that the ratio has an infinite value in that pressure range where the other curves are of the most interest. The neon case will be discussed separately. In this case also the fact that the curves do not coincide at low pressures is probably not of great significance due to the considerations mentioned while discussing Fig 7.

The curve marked 1 representing the ratio in pure nitrogen is very similar to the analogous curve in the case of hydrogen. Its behavior is almost identical throughout the entire pressure range. In this case also of course the ordinates represent the ratio of primary to secondary product, but the type of secondary product concerned is very dissimilar and Figs. 1 and 2 bear little resemblance to one another, hence it is rather remarkable that curves 1 in Figs. 7 and 8 should be so very much alike.

Curve 2 represents the ratio in the presence of helium. It is apparent that its behavior is very similar to the analogous curve in the case of hydrogen. The only differences are that the slope decreases more rapidly in the low pressure region of the curve and that the values of the ordinates approached almost asymptotically at high pressures are considerably greater

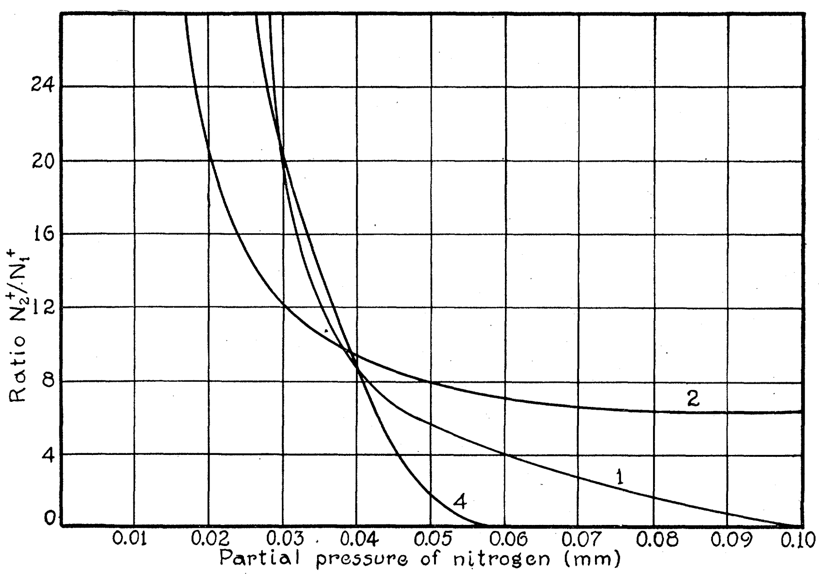

Fig. 8. Ratio of N_2^+/N_1^+ as a function of the partial pressure of nitrogen. Curve 1, in pure nitrogen; curve 2, in the presence of helium; curve 4, in the presence of argon.

than those of curve 2 in Fig. 7. These differences are such as to be most easily accounted for by assuming a larger value for the probability of ionization of a nitrogen molecule when it collides with a helium ion than for the probability of ionization of a hydrogen molecule at a similar collision. This is in a general way what would be predicted from the ionizing potentials if it is true that the transfer is more likely when the energy to be transferred is smaller. The difference, however, should be very small for $^{17}N_2^+$ but very large for $^{24}N_2^+$. The equation representing the transfer would be analogous to the hydrogen one:

$$He^+ + N_2 = N_2^+ + He$$

The phenomena, however, are rather more complicated in the case of nitrogen. In the first place the secondary product entering into the radio plotted in Fig. 7 can not be increased at collisions between H_2^+ and the rare gas particles. This is not true in the case of nitrogen. For N_1^+ can be formed at any collision of $^{24}N_2^+$, if indeed a collision is necessary at all. In the second place two types of primary product are possible in the case of nitrogen, namely: $^{24}N_2^+$ and $^{17}N_2^+$. The former can dissociate at a collision, or possibly spontaneously, into N_1^+. However, without more accurate knowledge of the probability of formation of the two types of primary product and of the probability of dissociation of $^{24}N_2^+$ only qualitative interpretations of the data that have been obtained are possible. The quantity of N_1^+ observed is probably a measure of the amount of $^{24}N_2^+$ present but the details of the dissociation such as the necessary conditions and probability of occurrence are not known. Hence the curves in Fig. 8 represent a more complicated situation than those in Fig. 7, and the main interest in this method of plotting is in the possibility of comparison between the two figures. Considering curve 2 of Fig. 8 in more detail it is seen that the numerator of the ratio can be increased by an increase in either primary product but that the production of one of these also automatically increases the denominator, hence it would be difficult without accurate knowledge of the probabilities involved to predict the form curve 2 would take. More information is given, however, by Fig. 4, which represents the variation of the ions with pressure in a mixture of nitrogen and helium. From this figure it can be seen that both N_1^+ and N_2^+ exist in larger quantities at high pressures than in pure nitrogen: this is what would be expected if they are produced at collisions with helium ions. The fact that a large amount of N_1^+ is observed at high pressures is very significant for it shows that a very large proportion of the nitrogen ions produced by the helium ions are of the type $^{24}N_2^+$. This is interesting from at least two points of view. In the first place it definitely places this ionization potential of nitrogen below the ionization potential of helium. In the second place it shows that the first of the following equations is much more probable than the second:

$$He^+ + N_2 = {}^{24}N_2^+ + He$$
$$He^+ + N_2 = {}^{17}N_2^+ + He$$

This is of interest from the point of view of the energy interchange occurring.

Curve 4 in Fig. 8 representing the variation of the ratio with pressure in the presence of argon is of some interest by comparison with the analogous curve in Fig. 7. The forms of the two curves are very similar, the outstanding difference being that the decrease is more rapid for the nitrogen ratio. This is exactly what would be expected from the foregoing considerations. N_2^+ would be decreased in accordance with the equations:

$$A + {}^{24}N_2^+ = A^+ + N_2$$
$$A + {}^{17}N_2^+ = A^+ + N_2$$

The latter being by far the more probable. Also N_1^+ would be increased by the collisions between $^{24}N_2^+$ and A^+ and also probably at a certain number of collisions with neutral argon; in fact, the validity of the first equation is rather doubtful. It is difficult to obtain much more information from Fig. 6.

However, it can be seen by a comparison of Figs. 2 and 6 that the rate of decrease of N_2^+ is much more rapid at high pressures when argon is present (all pressures given are total pressures) than in pure nitrogen. This is less true for N_1^+. If of any significance at all this may be taken as supporting the second rather than the first equation just given.

Fig. 5 represents the results obtained in a mixture of nitrogen and neon. The most striking difference between it and Figs. 4 and 6 is seen to be the behavior of the N_1^+ ion. The secondary product of ionization actually disappears before the primary one. This has not been true in any of the preceding mixtures. The cause of this is probably contained in the equations:

$$Ne^+ + N_2 = {}^{17}N_2^+ + Ne$$
$$Ne + {}^{24}N_2^+ = Ne^+ + N_2$$

According to these equations the only N_2^+ ion formed by a collision of the second kind with a neon ion is the type of ion not capable of dissociation. Hence at high pressures the only ions produced near enough to the analyzing chamber to be able to emerge from the high pressure region and be detected are N_2^+ ions. This was not true in the case of the helium mixture for in that case the ${}^{24}N_2^+$ was produced in large quantities and it could dissociate giving N_1^+. In addition to this effect the presence of neon according to the second equation tends to decrease N_1^+ by decreasing ${}^{24}N_2^+$. These are exactly the phenomena which are observed. The N_1^+ ion decreases more rapidly than in any other mixture and disappears at a comparatively low pressure. On the other hand the N_2^+ ion is apparently little effected by the presence of

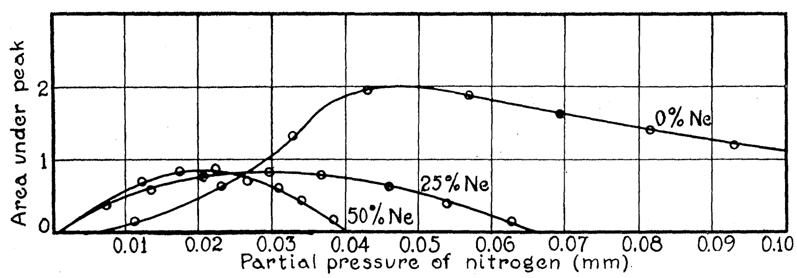

Fig. 9. Effect of mixtures of neon on the number of N_1^+ ions.

neon. Making the proper change in abscissae N_2^+ behaves much as it does in pure nitrogen. The effect of neon is about half way between that of helium and that of argon. This is just what would be expected from the equations for N_2^+ is increased at one type of collision and decreased at the other. Little can be said of the relative probabilities of these processes except that they must be of the same order of magnitude and probably roughly equal. From a consideration of Figs. 4, 5, and 6 it can be seen that by far the most probable of these ionizing processes that we have been considering is the production of ${}^{24}N_2^+$ by He^+. The difference in ionizing potentials in that case is of the order of half a volt.

Fig. 9 has been included to show the very striking way in which N_1^+ decreases in the presence of neon. The ordinates represent the area of the

N_1^+ peak and the abscissa are the partial pressures of the nitrogen. N_1^+ is greatly decreased in the presence of 25 percent neon and still further when the neon is increased to 50 percent. This is exactly the result predicted by the second equation. If a sufficient number of collisions occurred the two equations could be considered together:

$$Ne + {}^{24}N_2^+ = Ne + {}^{17}N_2^+$$

Thus it can be seen that the equilibrium at high pressures would be displaced greatly in favor of the stable form of N_2^+. It might also be mentioned that the N_1 ionizing potential though not known accurately is certainly below that of Ne and reactions involving N_1 may be completely neglected.

Conclusions

From the detailed and rather complicated analysis of the experimental results two main conclusions become evident. The first is that at a certain number of collisions between an atomic or a molecular ion and an atom or ion of lower ionizing potential an electron transfer will occur. In all the mixtures of gases that have been studied so far no exception to this has been observed. The processes expected to occur at a collision can be predicted from a knowledge of the ionizing potentials of the atoms or molecules involved. Secondly the probability that a given transfer will occur appears to be an inverse function of the difference between the ionizing potentials involved. By far the most probable transfers seem to be those in which the ionizing potentials of the two gases concerned are nearly equal. When there is a large amount of excess energy the probability of the process occurring is very much smaller.

In conclusion I want to express my deep gratitude to Professor K. T. Compton and Professor H. D. Smyth for their interest and helpful suggestions during this work.

Palmer Physical Laboratory,
Princeton, New Jersey,
March 24, 1927.