The Probability of Collision for Slow H^+, $(H^1H^1)^+$, $(H^1H^2)^+$, $(H^2H^2)^+$, $(H^2)^+$ and He^+ Ions in Argon

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The probability of collision P_c for slow H^+, $(H^1H^1)^+$, $(H^1H^2)^+$, $(H^2H^2)^+$, $(H^2)^+$ and He^+ ions in argon has been measured. The energy range studied was 225 to 4200 volts for the H^+ and $(H^1H^1)^+$ ions, 225 to 1300 volts for the $(H^1H^2)^+$, $(H^2H^2)^+$ and He^+ ions and 300 to 1225 volts for the deuteron hydrogen molecular ion $(H^1H^1)^+$ beam. The probability of collision for the $(H^1H^1)^+$ ion decreased from a value of $P_c=56$ at 225 volts to a minimum value of 48 at 784 volts with a subsequent increase to $P_c=57$ at 3840 volts. The proton curve increases from $P_c=38$ at 225 volts to $P_c=46$ at 4220 volts. It gradually flattens out at the higher voltages. The $(H^1H^2)^+$ and $(H^2H^2)^+$ curves remain nearly constant at $P_c \cong 41$ and 39, respectively, while the He^+ curve decreases from $P_c=28$ at 225 volts to 24 at 1225 volts. The curve obtained by using a deuteron hydrogen molecular ion beam shows two distinct minima at 380 volts and 806 volts. The percentage of $(H^1H^1)^+$ ions in the beam was estimated to be 15 percent. The $(H^1H^1)^+$ and H^+ curves, and the $(H^1H^1)^+$, $(H^1H^2)^+$, $(H^2H^2)^+$ and He^+ curves are grouped separately for comparison, and the probable processes in each case are discussed. It is significant to note that the heavier isotopic molecular ions have a longer mean free path in argon than the lighter $(H^1H^1)^+$ ion. A possible source of the discrepancies between the results of different authors in this field is discussed.

INTRODUCTION

If a positive ion is sent into a gas, there is a certain chance that it will reach a point, a given distance in the direction of its initial velocity, in its original condition. The chance is known to be an exponential function of the pressure, distance and a term called the probability of collision,[1] P_c which depends on the process involved and is a function only of the nature of the ion, its velocity and the nature of the gas. The unit of P_c is cm²/cm³ or 1/cm. It may be interpreted either as an area per cubic centimeter per unit pressure at 0°C or as a number of collisions per unit ion current per unit path length per unit pressure at 0°C. The latter interpretation is used throughout this paper. The effective area q for a single atomic collision is found by dividing P_c by the number of atoms per unit volume per unit pressure. If the unit of pressure is one mm Hg at 0°C and the unit of volume one cubic centimeter then $q=0.281 \times 10^{-16} P_c$ cm². The mean free path is given by $1/P_cp$ where p is the pressure in mm Hg at 0°C. A determination of P_c and a knowledge of the process involved is very important in the study of gaseous discharge phenomena.

The first quantitative measurements of P_c were made for slow protons in hydrogen. Aich[2] in 1922 found that the collision radius of an H_2 molecule and a 25-volt proton was approximately the same as the kinetic theory value of the radius of the H_2 molecule.

In 1925, Dempster[3] studied the nature of the collisions between H^+, H_2^+, He^+ ions and helium atoms. He concluded that no ionization was produced by 900-volt protons and that the decrease in intensity of a proton beam in helium was due chiefly to small angle scattering, and not to neutralization. Neutralization of the He^+ ions usually occurred upon the first collision while the H_2^+ ions were for the most part dissociated. The direction of the dissociated H^+ ion was at a small angle to that of the parent H_2^+ ion. G. P. Thomson[4] likewise found appreciable small angle scattering for protons of 5000 to 25,000 volts energy in hydrogen, helium and argon.

The next important measurements were made in 1930 by Holzer.[5] He found a variation of P_c with ion velocity when H^+, H_2^+ and H_3^+ ions were sent into hydrogen gas. The velocity range corresponded to a change in energy of 60 to 850 volts. The probability of collision for the H_3^+ ion was found to be smaller than the corresponding value for the H_2^+ ion. He concluded that the absorption of H_2^+ by hydrogen was due to

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[1] R. B. Brode, Rev. Mod. Phys. **5**, 258 (1933).

[2] W. Aich, Zeits. f. Physik **9**, 372 (1922).

[3] A. J. Dempster, Proc. Nat. Acad. Sci. **11**, 552 (1925).

[4] G. P. Thomson, Phil. Mag. **1**, 961 (1926).

[5] R. E. Holzer, Phys. Rev. **36**, 1204 (1930).

neutralization while the important factor in the absorption of H^+ and H_3^+ was scattering. Holzer[6] later reported some measurements for H^+, H_2^+ and H_3^+ ions in argon and helium but did not give the magnitudes of his values.

In 1931, Ramsauer, Kollath and Lilienthal[7] measured the probability of collision for protons in H_2, He, A, N_2 and Ne for ion energies of 30 to 2500 volts. When P_c was plotted against the velocity of the protons in root volts, a minimum between $(V)^{\frac{1}{2}}=40$ and $(V)^{\frac{1}{2}}=50$ was observed for most of the gases studied. Their curve for hydrogen is in complete disagreement with Holzer's curve. Ramsauer, Kollath and Lilienthal also found a large variation in the magnitude and slope of their curves as the slit dimensions in the scattering cylinder were decreased. These variations were more marked at the lower velocities.

The present experiment was undertaken in an attempt to explain some of the discrepencies in this field and to investigate the variation in the mean free path of ions having the same number of external electrons but different masses.

Apparatus and Experimental Procedure

Diagrams of the experimental apparatus and circuit are shown in Figs. 1 and 2. They are for the most part self-explanatory, thus only a few details will be given.

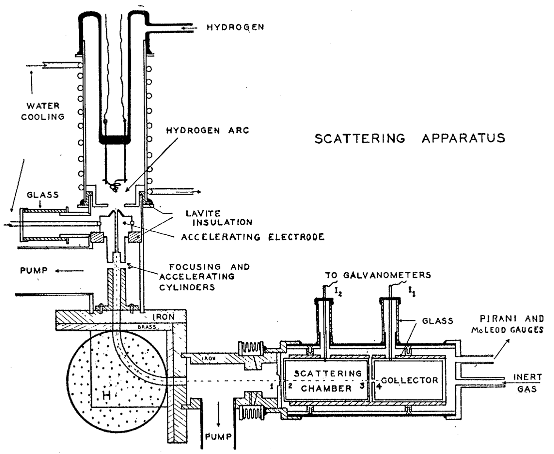

FIG. 1. Scattering apparatus.

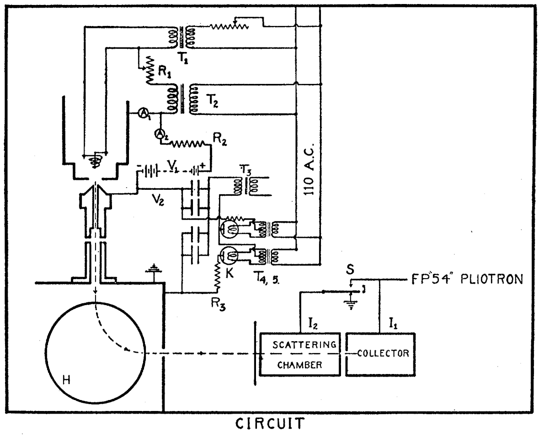

FIG. 2. Circuit.

A hot cathode a.c. arc was used to produce the ions. It was housed in a water-cooled brass cylinder insulated from the rest of the apparatus by means of a hardened lavite ring. A 20-mil spiral tungsten filament was used for a cathode. The pressure control of the gas in the arc was effected by steady flow through capillary leaks from reservoirs. A pressure of approximately 5×10^{-3} mm Hg was used. The ions were drawn from the arc by means of a water-cooled copper electrode placed at a negative potential (V_1) of 400 to 700 volts with respect to the filament. There was a 2-mm hole in this electrode which allowed some of the ions to pass through it into a region maintained at a low pressure by means of a 40-liter per sec. Apiezon oil pump. The ions were next accelerated or retarded to the desired velocity by means of an applied potential difference between the first electrode and a grounded iron cylinder shown in Figs. 1 and 2. The potential V_2 was supplied by a voltage doubling circuit shown in Fig. 2. The path of the beam was shielded from stray magnetic fields by means of the iron cylinder through which the ions passed and additional external iron shielding.

The magnetic field, calibrated by means of a test coil and Grassot fluxmeter, was found to be roughly proportional to the current flowing in the coils of the magnet when care was taken to reverse the magnetic field before measurement. When the ion beam emerged into this magnetic field, its constituent ions described different cir-

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[6] R. E. Holzer. Pasadena meeting of the Am. Phys. Soc., June 15, 1931. Phys. Rev. **38**, 585A (1931).

[7] C. Ramsauer, R. Kollath and Lilienthal, Ann. d. Physik **8**, 709 (1931).

cular paths, the radius of any one of which was determined by the mass, charge and velocity of the ions in that path and by the magnetic field strength. If the field strength was so adjusted that the radius of curvature of a particular ion path was 5.21 cm, then these ions passed through the quarter circle into a field free region just preceding the scattering chamber and collector.

The scattering chamber was 4.3 cm in diameter and 8.41 cm long, and the collector was 7.0 cm deep. They were both held in position and insulated by means of short lengths of glass tubing, care being taken that there was no resistance to flow of gas in the region immediately surrounding the cylinders. The areas of the openings were:

Area of aperture No. 1 = 0.33 sq mm
" " " " 2 = 0.50 " "
" " " " 3 = 2.0 " "
" " " " 4 = 7.1 " "

The first aperture was made small so that differential pumping could be used and in order that a beam of small cross section would enter the chamber. The area of the third aperture must be quite small or the measurement of P_c for ions will have no significance, especially in the case where the process involved is one of small angle scattering.

Fig. 3 is a graph of the current received by the collector as the magnetic field was varied when ordinary hydrogen and also deuterium were used in the arc.

The equation which expresses the fraction of the initial number of ions that still remain in a beam after it has traversed a distance x through a gas is:

$$I_x/I_0 = e^{-P_c p x}.$$

p represents the pressure in mm Hg at 0°C and P_c the probability of collision. For use in the experimental determination of P_c the equation may be written in the following form:

$$I_1 = [I_1 + I_2] a_s e^{-P_c p x}.$$

I_1 represents the current which reaches the collector when the scattering chamber is grounded, I_2 the current to the scattering cylinder, x the effective length of the cylinder and a_s the fraction of current which reaches the collector when no gas is flowing through the scattering chamber. The magnitude of a_s may be as small as 0.5 for the lower energies on account of the electrostatic spreading of the beam. This is especially true in accurate measurements where the third aperture is relatively small. The loss of ions from the beam because of the presence of a vapor will also contribute to the magnitude of a_s. The derivative of the above equation when expressed in logarithmic form

$$d[\log_e (I_1/(I_1+I_2))]/dp = -P_c x$$

does not contain a_s, and thus P_c may be calculated from the slope of an experimentally determined pressure *vs.* $\log_e I_1(I_1+I_2)$ straight line. Fig. 4 shows five of these experimental curves, each one of which corresponds to a different initial ion velocity. The pressures as marked on the plot have not been corrected for temperature, however this correction was made before computing P_c.

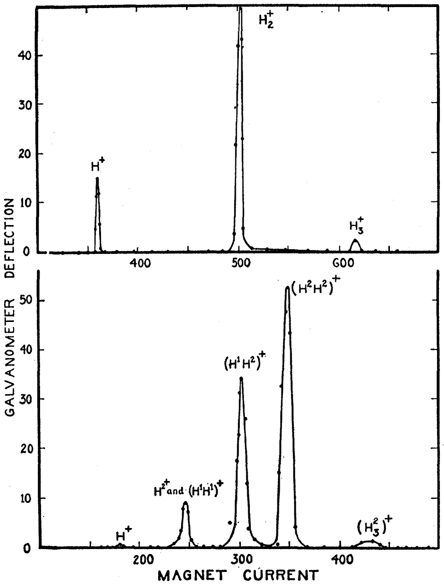

FIG. 3. Collector current as a function of the magnetic field for ordinary hydrogen and deuterium in the arc.

The procedure in determining a value of P_c for a given ion at a particular velocity was briefly as follows. After the tube had reached a steady state, the magnetic field was so adjusted that the maximum of one of the peaks was observed. The deflections of the pliotron galvanometer for I_1 and I_1+I_2 were recorded while the gas in the scattering chamber was maintained

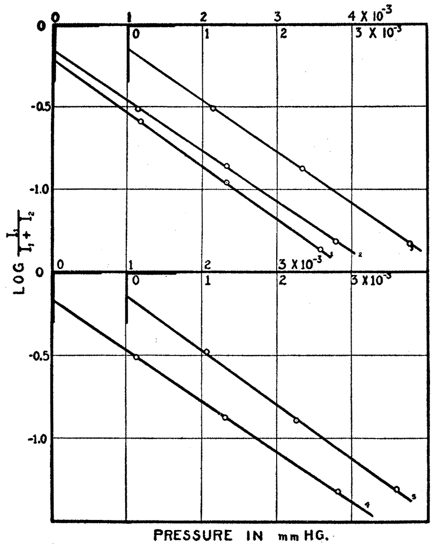

FIG. 4. Pressure *vs.* $\log_e I_1/(I_1+I_2)$ straight lines for the deuteron hydrogen molecular beam in argon.

constant at p_1 (measured by a McLeod gauge). In practice the value of I_1 was taken as the average of several trials. The pressure was raised by compressing the gas in the reservoir behind the leak to the scattering chamber. A Pirani gauge was used to indicate when equilibrium was again reached at the new pressure P_2, which was 1 or 2×10^{-3} mm higher than P_1, and again I_1 and I_1+I_2 were both recorded. The pressure was then raised to P_3 and the process was repeated. The data thus obtained were sufficient to determine a pressure *vs.* $\log_e I_1/(I_1+I_2)$ straight line from which P_c could be calculated. In those cases where a straight line could not be made to touch the three determined points and the pliotron showed signs of fluctuation the measurements were discarded. P_c was found to be independent of the pressure within the range studied.

It is clear from the above discussion of the differential method by which P_c is calculated that no error will be introduced by the presence of an unknown vapor in the scattering chamber, providing its vapor pressure remains constant. However, any impurity in the gas in which the measurements are made will obviously introduce an error. 99 percent pure argon was purchased and tested for impurities before being employed. The same gas supply was used for all measurements presented in this paper.

The Pirani and McLeod gauges were attached directly to the scattering chamber unit. No correction for flow resistance was necessary because of the construction of this unit and the position of attachment of these gauges.

RESULTS AND DISCUSSION

The results of the measurements are shown in Figs. 5, 6 and 7. Fig. 5 shows the number of collisions per cm path length per mm pressure at 0°C as a function of the velocity in root volts for $(H^1H^1)^+$ and H^+ ions in argon. The range in velocity studied corresponds to an energy range of 225 to 4200 volts. To change over to velocity in cm per second one can use the approximate equation $v=1.39\times10^6(V/M)^{\frac{1}{2}}$ cm/sec., where V is in equivalent electron volts and M in atomic mass units.

Upon a single encounter with an atom of the gas, a monatomic ion may be deviated from its original direction by scattering, or it may become neutralized, either continuing in the same or in a different direction. A diatomic ion may, in addition to the above, be dissociated. The products of dissociation may or not continue in the same direction.

Since the ionization potential of the (H^1H^1) molecule (15.9 volts),[8] is nearly equal to the ionization potential of argon (15.7 volts)[8] it appears that the neutralization of the $(H^1H^1)^+$ ion is very probably the process taking place and should account for at least the initial portion of the $(H^1H^1)^+$ curve.[9] The final rise is, however, difficult to interpret, as some other process such as dissociation may be taking place at these higher voltages. Further experiments in which the shape of the beam is studied at various pressures will have to be carried out before the nature of the collision can be definitely established.

The proton curve increases from $P_c=38$ at 225 volts to $P_c=46$ at 4220 volts. It gradually flattens out at the higher voltages. Previous experiments indicate that scattering is taking place in this case. Ramsauer, Kollath and

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[8] H. D. Smyth, Rev. Mod. Phys. **3**, 389 (1931).

[9] Holzer[6] has shown that a similarly shaped curve is obtained in this velocity region when $(H^1H^1)^+$ ions were sent into hydrogen gas and that the process involved was neutralization.

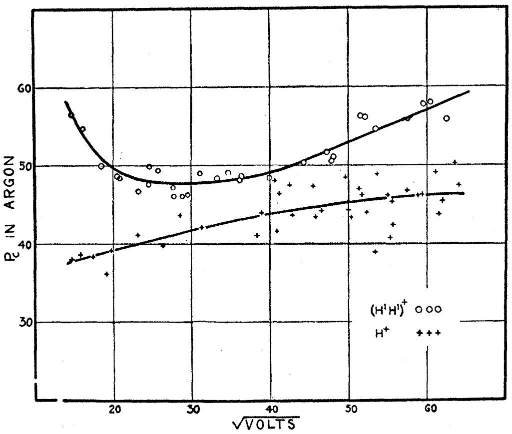

FIG. 5. Probability of collision, P_c.

Lilienthal[7] have definitely shown that there is no ionization by 2000-volt protons in argon and that scattering is important at the lower velocities. Ramsauer and Kollath[10] have since shown that for very low velocities practically all of the scattered protons continue in a direction at a small angle to their original direction. The work of G. P. Thomson[4] likewise indicates that there is appreciable small angle scattering for protons of 5000 to 25,000 volts energy in argon. An explanation of the positive slope found will undoubtedly involve a solution of the wave equation. It is not at all improbable that this curve may rise at still lower velocities and that there exists an effect for protons in argon similar to the Ramsauer effect for electrons.

The curves shown in Fig. 6 are for the $(H^1H^2)^+$, $(H^2H^2)^+$ hydrogen molecular ions and He^+ ions in argon. A portion of the $(H^1H^1)^+$ curve is replotted here for purposes of comparison. The value of P_c for the $(H^1H^2)^+$ ion is considerably smaller than for the $(H^1H^1)^+$ ion, while the value for $(H^2H^2)^+$ is only slightly less than that for the $(H^1H^2)^+$ ion. The heavier hydrogen molecular ions thus have a longer mean free path than the lighter $(H^1H^1)^+$ ion, and the variation for different ions is no simple function of the mass. It is also remarkable that P_c does not vary markedly with ion velocity over the range studied. Undoubtedly the same process is taking place in all three cases and is probably one of neutralization.

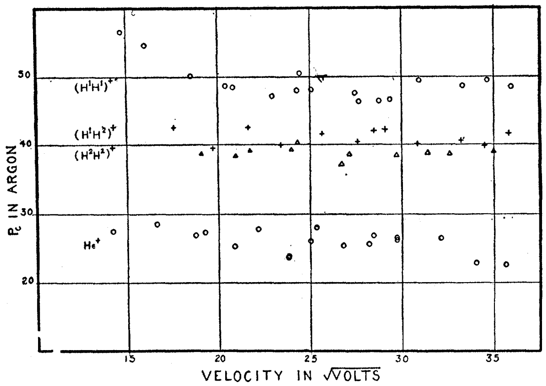

FIG. 6. Probability of collision, P_c.

The magnitude of P_c for the helium ion curve shows a slight uniform decrease over the range studied. Since the ionization potential of helium is so much greater than for the argon atom, it may be concluded that the process here is not one of neutralization but is probably one of scattering. Its mean free path in argon is much greater than that of the hydrogen molecular ions in the same velocity range.

Fig. 7 shows the curve obtained when the composite $(H^2)^+$, $(H^1H^1)^+$ beam was used. The percentage of $(H^1H^1)^+$ ions present was unknown although a study of the magnitudes of the different peaks when ordinary and heavy hydrogen were used in the arc indicates a value of 15 percent. This can only be considered as an exceedingly rough estimate. This peak was considerably broader and flatter on top than any of the others, thus slight fluctuations in the applied potentials or magnetic field did not affect the readings so markedly. The experimental points were not taken in any regular manner and each set of readings obtained was found to lie accurately on a pressure *vs.* $\log_e I_1/(I_1+I_2)$ straight line, consequently no points were discarded. Some of these curves are shown in Fig. 4. The end values of P_c are approximately the same as those for protons at the corresponding energy values and the average trend of the curve is likewise upward; however, two unexpected minima were observed. The minimum which occurs at 806 volts is much sharper and slightly deeper than that observed at 380 volts. The de Broglie wavelengths corresponding to these minimum values are $\lambda = 0.010$A and $\lambda = 0.0071$A.

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[10] C. Ramsauer and R. Kollath, Ann. d. Physik (5) **16**, 570 (1933).

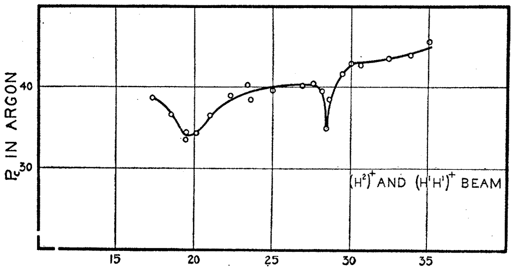

FIG. 7. Probability of collision, P_c.

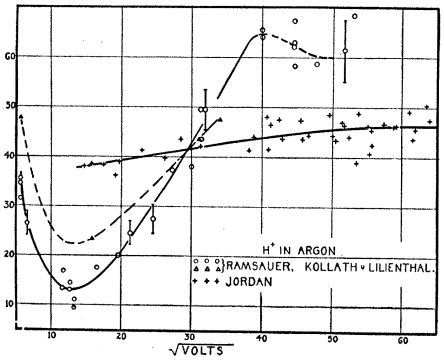

FIG. 8. A comparison of the data obtained by different authors for protons in argon.

The non-existence of such minima in the proton or the $(H^1H^1)^+$ curves shown in Fig. 5 is by no means established, for the fluctuations in P_c were sufficiently large to render a study of their fine structure impossible. A similar study using a pure deuteron beam is planned for the near future.

The only data available for comparison are those obtained by Ramsauer, Kollath and Lilienthal[7] for protons in argon. Fig. 8 shows the corresponding curves. A clue to the cause of the discrepancies which have occurred in this field is found in Ramsauer, Kollath and Lilienthal's own data. Using a slit aperture of 150 square millimeters area (which corresponds to the third aperture of 2 square millimeters area used in this experiment), they obtained the curve represented by the solid line. A circle with a stroke through it represents a possible variation in P_c due to an uncertainty in the pressure *vs.* log straight line. Using a smaller aperture area of 40 square millimeters they next obtained four points, three of which are well outside the limit of error of their previous measurements. These points are indicated by triangles. A curve (dashed line) which is similar in shape to their other one is drawn through them by the author. It will be noticed that this second curve approaches more closely to the one reported in this paper using a circular aperture of two square millimeters area. It is difficult to understand how data, obtained using slit apertures of such large area, can have any meaning, especially when the process involved is one of small angle scattering. Even for small aperture areas a slit introduces distortion since ions which are scattered at a small angle in the lengthwise direction of the slit can get through into the collector while those scattered in the opposite direction cannot. The amount of distortion would depend on the relative width and length of the slit. A well-defined circular beam of small cross-sectional area is also necessary if accurate measurements are to be obtained. If the process involved had been one of neutralization, an agreement would probably have been found regardless of the shapes or sizes of the apertures.

In conclusion, the author wishes to thank Professor R. B. Brode for many valuable discussions and comments and to acknowledge gratefully an appointment by the National Research Council which made the completion of this work possible.