IONIZATION OF GASES AS A FUNCTION OF THE ENERGY OF ELECTRON IMPACTS

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Abstract

Ionization of various gases by electrons of energy up to 300 volts.—Electrons were accelerated from a tungsten wire to a plane perforated electrode G, through which a small fraction passed into a space where they were all stopped by a retarding field between the perforated electrode and a plane parallel plate P connected to an electrometer, which collected all the positive ions formed on collision between the electrons and the gas molecules. *The fraction of the collisions resulting in ionization* as a function of the energy of impact is shown to be $f(V') = (1/2\alpha pD)[d(V_0P/E)/dV_0]$, where P/E is the ratio of positive ions produced to the number of electrons passing through the perforated electrode G, V_0 is the retarding potential between P and G and is somewhat greater than V' the maximum energy of impact, p is the pressure, D the distance apart of P and G, and α is the chance of collision per cm for 1 mm pressure which is assumed to have the Kinetic Theory value. For *helium*, *neon*, *argon*, *hydrogen*, *nitrogen*, and *methane*, $f(V')$ was found to increase very rapidly to a maximum value, after which there was a less rapid, though marked, decrease. The maxima occur at 147, 157, 80, 74, 101, and 80 volts for the gases in the order named, the maximum values being respectively .11, .14, .35, .21, .32, and .28. Even for the most favorable velocities, then, less than half of the collisions result in ionization.

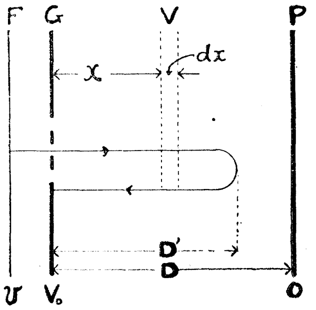
Radiation potentials of argon and carbon. A break in the argon curve suggests *L radiation for argon* at 250 volts impact energy, while a break in methane curve indicates a possible *K radiation for carbon* at 248 volts.

THE purpose of this investigation is to determine experimentally the percentage of molecules of a gas ionized by electron impacts as a function of the energy of impact. It is well known on the one hand that high speed electrons (β rays) pass through molecules much oftener without ionizing them than electrons having moderate speeds and are therefore to be regarded as inefficient ionizing agents, while on the other hand, electrons having energies below the ionizing potential do not ionize normal molecules at all. In between these limits, there must be a value of the impact energy at which the electron has its maximum efficiency as an ionizing agent.

Much work has been done on the measurement of the critical threshold energy which the electron must have in order just to produce ionization, the ionizing potential of course being a measure of this energy. Little is known, however, as to the percentage of collisions between electrons and molecules, which result in the formation of ions, at any value of the energy of impact.

This investigation is part of a general attack planned by one of the authors on the measurement of various effects as a function of the energy of impact of the electron on the molecule. Thus the distribution of the intensities in the spectrum has been studied as a function of the energy of impact for hydrogen[1] and helium,[2] and the dissociation of hydrogen[3] has been investigated as a function of the energy of electronic impacts.

It is hoped ultimately to get for a number of gases, as a function of the energy of impact of the electrons on the molecules, the percentage of collisions resulting in ionization, the percentage resulting in dissociation (for polyatomic gases), the distribution of intensities in the spectra and the intensity of the radiation which can be measured photo-electrically. The latter is, of course, merely a quantitative study of the effect started at the radiating potential and carried to much higher energies of impact. It is a makeshift for measuring the distribution of intensities in the spectrum in the extreme ultra-violet region as we have at present no easy way of measuring intensities of spectrum lines in this region. In all these experiments, the underlying idea is to study the effect of impact between an electron and a *normal* molecule, so that to avoid cumulative effects we have to work with as feeble electron currents and with as low pressures as is practicable.



[Fig. 1. Diagram of electrodes.

The arrangement employed for studying the ionization at different energies of impact was much the same as that used in the original Lenard method of studying ionizing potentials. Electrons are accelerated from a thermionic source F through very small holes in the electrode G (Fig. 1).

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[1] Hughes and Lowe, Phys. Rev. **21**, 292, 1923

[2] Hughes and Lowe, Proc. Roy. Soc. **104**, 480, 1923

[3] Hughes, Phil. Mag. **41**, 778, 1921. The results of this research are not strictly comparable with the others, since the results were given as a function of the terminal maximum electron energies, that is, the electrons used had a range of energies from zero up to a maximum. In the present investigation and in the spectrum researches the results are given as functions of the actual electron energies on impact.

Beyond G they are subjected to a retarding field between the parallel plane electrodes P and G. A small positive potential v is applied to F to prevent the electrons reaching P, which is at zero potential. The gas pressure is generally sufficiently low to ensure that only one electron in about ten collides with a molecule in the distance GP (9 mm) so that the chances of an electron making two collisions are less than one in a hundred.

Reducing the gas pressure, however, does not get rid of the secondary electrons produced on the right hand surface of G when the primary electrons strike it on their return journey. However, although the error due to not taking these secondary electrons into account is difficult to estimate, it is believed to be quite small.

Let E = number of electrons passing into the space GP per second; p = gas pressure.

The number of collisions per second between electrons and molecules in dx, is

$$dN=\alpha pE\,dx,$$

where α is the constant giving the number of collisions made by one electron in 1 cm path at 1 mm pressure.

The number of positive ions produced in dx is

$$dP=2dN\,f(V')$$

where V' is the energy, expressed in volts, of the electrons as they pass through dx, and $f(V')$ is the unknown function giving the fraction of collisions resulting in ions at this energy of impact, which is sought in this investigation. The 2 takes care of the ions formed on the return journey through dx.

Hence

$$dP=2\alpha pEdx\,f(V').$$

The relation between V', which measures the energy of the electrons at the equipotential surface x, and the potential V of that surface is

$$V'=V-v.$$

v may include, besides the potential of F, the correction due to initial velocities of the electrons from F, the contact potential difference, etc.

$$\frac{D-D'}{D}=\frac{v}{V_0}; \quad \frac{D-x}{D}=\frac{V}{V_0}; \quad dx=-\frac{D}{V_0}\,dV$$

$$P=-2\alpha\,p\,E(D/V_0)\int_{v_0}^{v}f(V-v)\,d\,V$$

$$P\,V_0=-2\alpha\,p\,ED\,[F(v-v)-F(V_0-v)]$$

$$d(PV_0)/dV_0=2\alpha\,p\,ED\,f(V_0-v)$$

Hence the required function

$$f(V_0')=f(V_0-v)=\frac{1}{2\alpha\, p\, D}\cdot\frac{d(V_0\, P/E)}{dV_0}. \tag{1}$$

To get it experimentally, we must measure the positive ion current P per unit electron current, passing into the space GP, as a function of the potential V_0 of the electrode G, then form the product $V_0\, P/E$, plot it against V_0 and differentiate graphically, or else plot successive differences

$$(V'_0P'/E'-V''_0P''/E'')/(V'_0-V''_0).$$

Apparatus and Method of Experiment

The final form of apparatus is shown in Fig. 2. It consisted of a pyrex tube 4 cm in diameter. The electrode G was a flat sheet of nickel hard soldered to a long cylinder of nickel so that the filament F was shielded from glass surfaces which might be at variable and indefinite potentials. The nickel cylinder fitted tightly into a glass tube of 3 cm diameter which was fused to the main tube at three points around the circumference. This permitted the gas to flow freely through the apparatus. In a region, 8 mm × 2 mm, in the center of G were drilled about 40 holes, .2 mm in diameter, through which the electrons passed into the space GP. A grounded nickel gauze inside the pyrex tube about G and P served to define the potential in the vicinity. In the helium experiments, helium was purified by passing through a charcoal tube in liquid air into a reservoir holding about 100 cc. From this reservoir it was passed into the apparatus through a fine capillary capable of transferring .2 cc per hour with a driving pressure of one atmosphere in the reservoir and a vacuum in the apparatus. Between the capillary and the experimental tube (Fig. 2) the helium was again purified, now at low pressure, by passing it through another charcoal tube in liquid air. When other gases were used, the charcoal in this liquid air tube was omitted. The other tubes

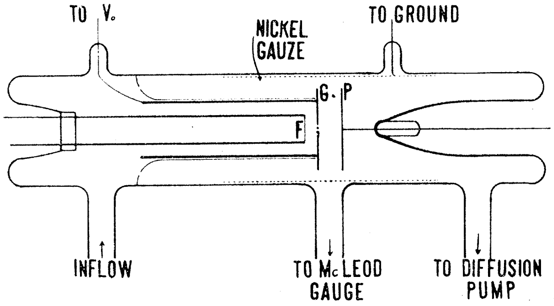

Fig. 2. Final form of apparatus.

leading to the pump and the gauge contained liquid air traps. All traps were left submerged in liquid air for the whole period during which any one gas was under investigation. The diffusion pump was in action continuously and a very steady pressure of gas was maintained in the apparatus.

Electron current. The total electron current from F to G was measured by means of a Leeds and Northrup galvanometer provided with a variety of shunts. To get the fraction of electrons passing through into the space GP, we arranged to measure simultaneously the electron currents to G and to P when the potentials of F, G, and P, were 0, V_0, and X volts respectively. Keeping V_0 constant and varying X, the number of electrons going to P increased rapidly as the value of X passed through V_0, and as X approached $2V_0$ the number of electrons became practically constant, showing a slight uniform linear increase with voltage beyond $2V_0$. The reason for this of course is that the electrons impinging on P excite secondary electrons at P having energies ranging all the way from zero to those of the primary electrons. These will only be held back completely when $X=2V_0$. The slight linear increase beyond $2V_0$ is due to the holes in G not being infinitely small, so that increasing the field considerably in GP pulls some more electrons through the holes. Since in the positive ion experiments the potential of P is zero, the obvious thing to do to get the actual fraction of the electrons passing through when $X=0$ is to extrapolate the almost flat linear portion of the curve back to the zero axis. This procedure was carried out for six different values of V_0 and a curve was drawn showing the number of electrons E passing through the holes in G as a function of the number going to G itself for different values of V_0, when $X=0$.

Positive ion current. The current to P was measured by means of a Dolezalek electrometer, shunted by an India ink resistance on cardboard sealed up in a glass tube. The values of the resistances were measured at frequent intervals to correct for slight progressive changes.

The plotted curves are the mean curves of at least four runs (generally eight) up and down the range of voltages. In certain cases, e.g., around certain voltages at which soft x-rays might be expected, as many as twenty runs were averaged to give the curve so as to show up any slight discontinuity which might be present.

The determination of the absolute value of $f(V')$ depends upon the values of D, α, p, and the gradient of the $V_0(P/E)$ curve. $D=.90$ ($\pm.03$) cm. α, the number of collisions made by an electron in moving 1 cm through the gas at 1 mm pressure, is the most uncertain of the constants used. According to the Kinetic Theory of Gases, an infinitely small particle, such as an electron, would make 7.95 collision per cm in helium at 1 mm pressure. A number of investigations by Lenard, Townsend, Compton, Meyer, and Ramsauer on the motion of electrons in gases, have led to numerical values for α. Unfortunately, these differ so much among themselves, and there seems to be no obvious reason why one should be taken in preference to the others, that we have decided to adopt the value given by the Kinetic Theory of Gases. Should future research on the motion of electrons in gases lead to a more acceptable value for α, the results in this investigation can easily be corrected by a suitable factor. At the pressure used for helium, .0048 mm, the collision frequency per cm path is $.0048 \times 7.95 = .0382$, which means that the chances of any electron making a *second* collision, may be neglected. The relative values of the collision frequency in the various gases used, are given in the following table together with the actual collision frequencies at 1 mm pressure.

Gas :	He	H_2	N_2	A	Ne	CH_4
Relative collision frequency :	1.00	1.54	2.96	2.77	1.6	3.64
Actual ($p=1$ mm) :	7.95	12.24	23.53	22.02	12.80	28.94

The actual energy of the electrons obtained with any applied voltage is not given accurately by that voltage minus v, the voltage applied to the filament. Corrections have to be made for initial velocities of emmission, contact potential difference, voltage fall along the filament, etc. The corrections were made by noting the values of the applied potential V_0 at which the discontinuities corresponding to the ionizing potential appeared. At these points, the actual values of the electron energies are given by the ionizing potential, and the necessary correction to get the electron energies at all points is therefore given by the difference between V_0 and the ionizing potential. In the curves shown, the electron energies, so obtained, are indicated as well as the values of V_0. The values of the ionizing potentials assumed are as follows, in volts: He, 24.5; Ne, 22.2; A, 16.0; N_2, 17.0; H_2, 16.2; CH_4, 13.9.

In each diagram will be found three curves. First, we have the experimental curve P/E, the absolute value being shown on the right hand ordinate. The second curve, showing $V_0(P/E)$, is obtained by multiplying each experimental value P/E by the corresponding V_0. The third curve $f(V')$ is obtained by graphical differentiation of the second curve, and its absolute value calculated from Eq. (1). The values of $f(V')$ are shown on the left hand ordinate of the curves.

Two diagrams are given for each gas, one showing the curves over the whole range, and one showing the curves over the earlier part of the range.

Helium and Neon

The helium was purified as described earlier in the paper. The neon was obtained from the Linde company, and was stated to be over 99 per cent neon. According to the company, there was not even a spectroscopic trace of helium in the neon. The curves for these two gases are given in Figs. 3a, 3b, 4a, 4b. The $f(V')$ curves are very similar in character, although the gases were certainly not alike as the viscosities of the

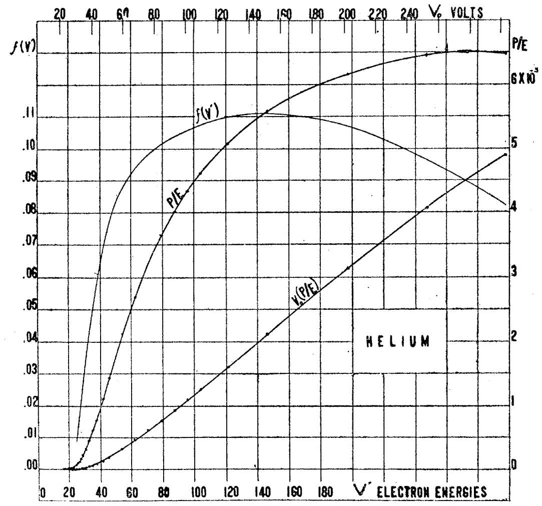

Fig. 3a

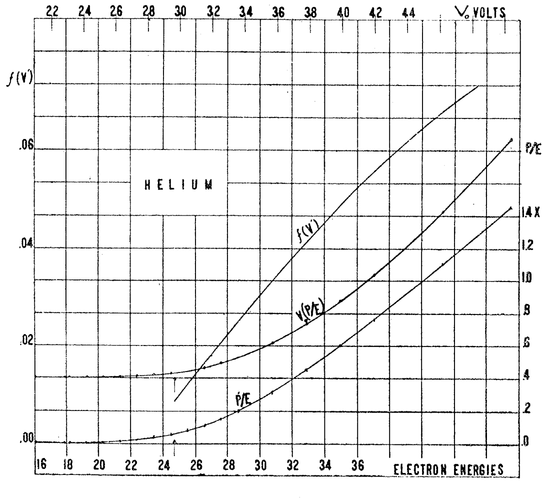

Fig. 3b

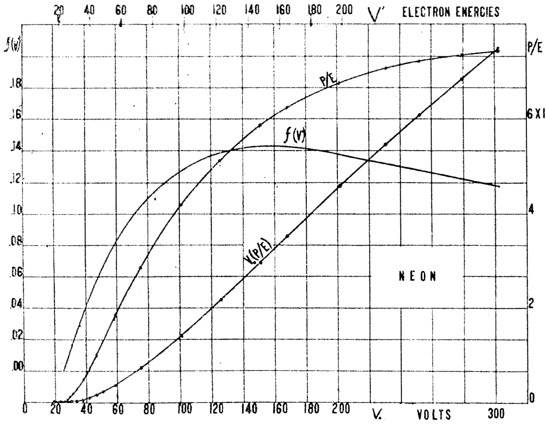

Fig. 4a

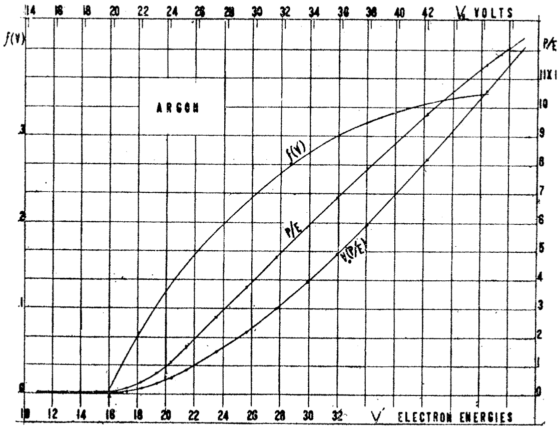

Fig. 5b

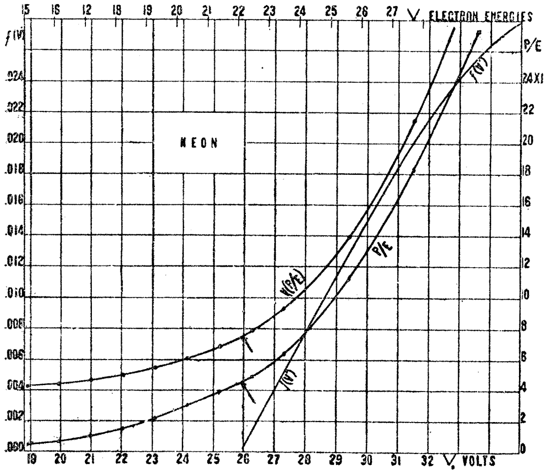

Fig. 4b

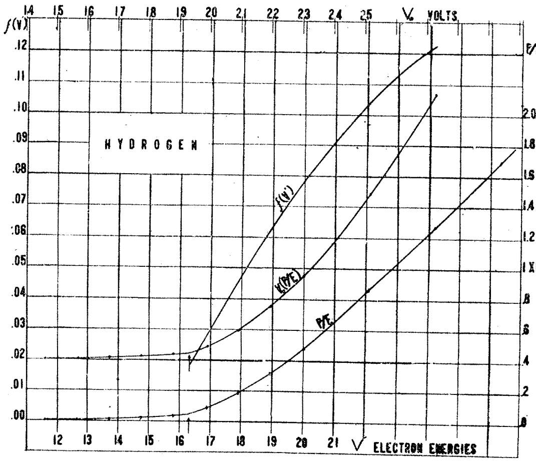

Fig. 6a

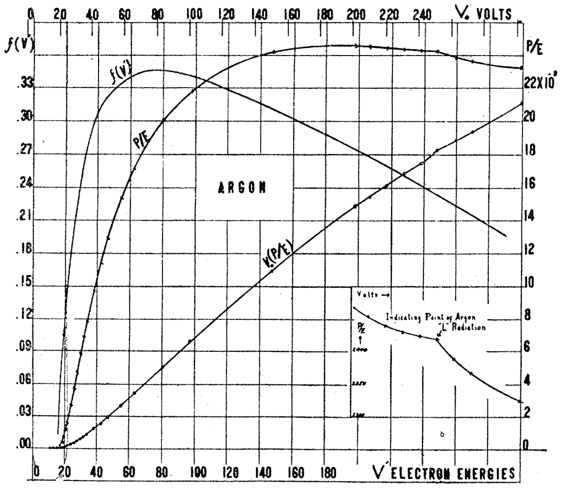

Fig. 5a

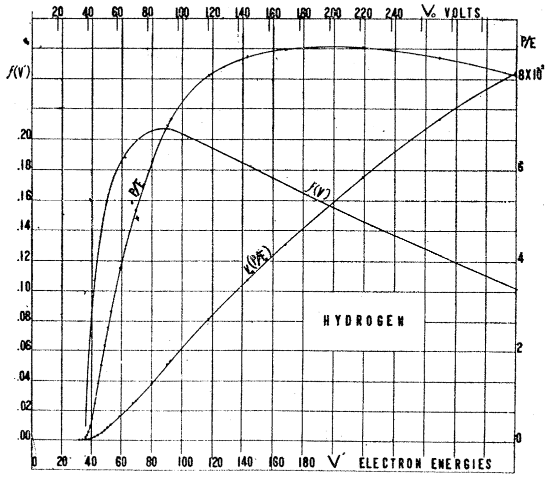

Fig. 6b

two gases, as indicated by the rate of flow through the apparatus, were widely different.

ARGON

Argon of purity 99.8 per cent was used. The results are shown in Figs. 5a and 5b. The maximum value of $f(V')$ for argon is higher than that

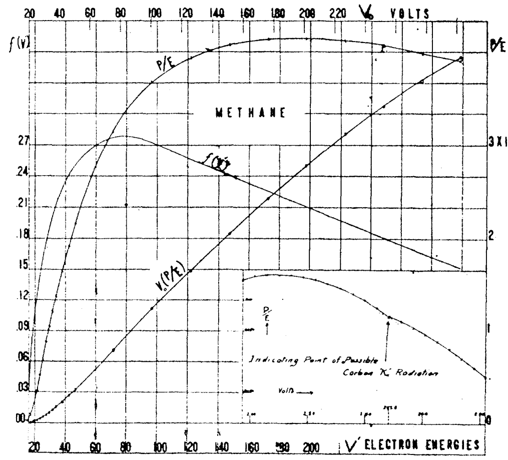

Fig. 7a

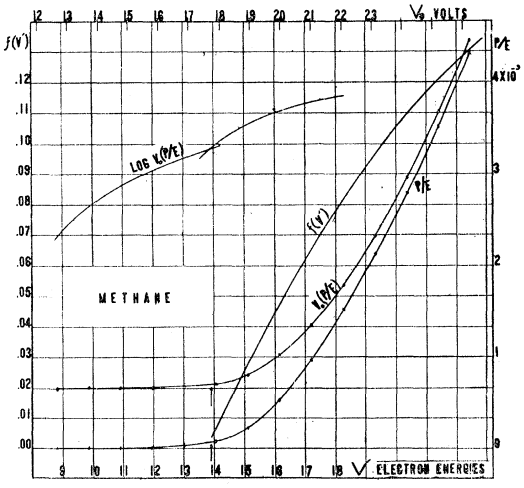

Fig. 7b

for any other gas investigated, and it occurs much earlier than with helium or neon. As a subsidiary experiment, a search was made for a possible discontinuity in argon, corresponding to the L radiation. In the lower right hand corner of Fig. 5a, will be found a large scale P/E diagram, showing a break at 250 volts.

Hydrogen, Nitrogen and Methane

The $f(V')$ curves for these three gases are similar to one another. To get the ionizing potential break in methane and in nitrogen, it was found that plotting log (V_0P/E) indicated the critical point more definitely than either the P/E or the V_0 (P/E) curve. A very carefully taken set of twenty runs between 200 and 300 volts in methane showed in the mean curve, a small but definite break at about 244 volts. This may be the K critical point for carbon.

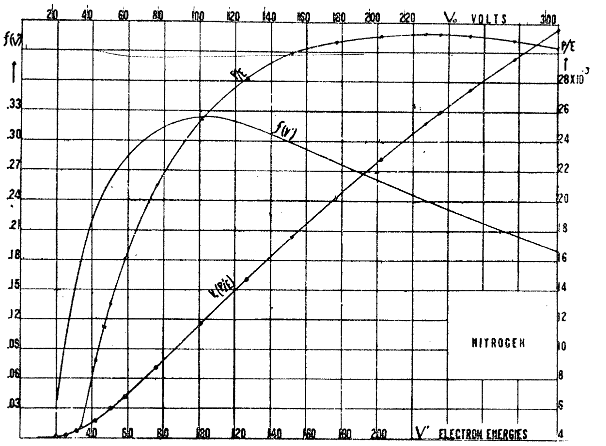

Fig. 8a

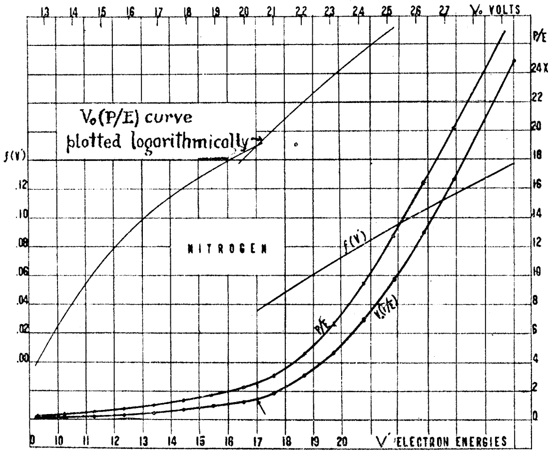

Fig. 8b

Discussion

In order to compare the $f(V')$ curves for the different gases, they are all plotted together, Fig. 9, as functions of the electron energies expressed in volts. The following observations may be made.

The maximum value of $f(V')$ for the polyatomic gases increases regularly with the molecular weight (2, 16, 28). The value of the electron energy at which $f(V')$ is a maximum, also increases regularly with increase of molecular weight. For the monatomic gases the maximum value of $f(V')$ also increases with increasing atomic weight (4, 20, 40), but no generalization as to the value of the electron energy at which $f(V')$ is a maximum can be made. The tendency, however, is for it to run in the opposite direction to that noted in the polyatomic gases.

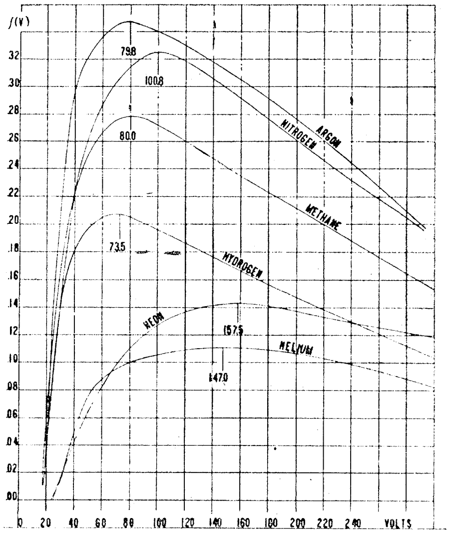

Fig. 9

The number of electrons per molecule is perhaps of more significance than the molecular weight. These run in the order 2, 10, and 14 for H_2, CH_4 and N_2; and in the order 2, 10, and 18, for He, Ne, and A. The same qualitative statements as made in connection with molecular weight will apply when we consider the number of electrons per molecule.

In argon, under the most favorable circumstances, one collision out of three results in ionization, while in helium the maximum proportion is one out of ten.

With the method employed, it is impossible to distinguish between positive ions and a photo-electron effect due to radiation. Except just above the ionizing potential, it is believed that the radiation effect may be considered negligible in comparison with the positive ion effect. Below the ionizing potential, the small apparent ionization is really due to a photo-electric effect at P excited by radiation produced between the ionizing and radiating potentials.

It is perhaps worth while stating, what has already been said in different terms, that the absolute value of these fractions is in doubt to the same extent as is the assumed value of the frequency of collisions between electrons and atoms.

Ramsauer[4] has recently published an account of his measurements on the collision frequency between electrons and atoms in argon and other gases. He finds, for example, that the collision frequency in argon is much *less* than the Kinetic Theory value for electron energies of the order of 1 volt, but increases rapidly to a maximum at about 12 volts where the experimental value is 4.4 times *greater* than the Kinetic Theory value. In the region overlapping that studied in this paper, the ratio of the experimental value to the Kinetic Theory value falls off to nearly unity at 100 volts. The values of the ratio at the voltages 16, 25, 36, 49, 64, 81, 100 are 3.8, 2.6, 1.5, 1.2, 1.1 and 1.06 respectively. This means that if we were to take Ramsauer's values in preference to the Kinetic Theory values, we should have to diminish the ordinates in these ratios. The effect would be more marked, the lower the voltage. The position of the maximum would hardly be affected, the shift being a few volts towards higher voltages. The values of $f(V')$ at the maximum would be diminished by about 10 per cent.

The curves have a number of characteristics in common. They all show a well marked maximum, preceded by a very rapid rise from the ionizing potential and followed by a distinct, though less rapid, fall. On the high voltage side, they all show (with the doubtful exception of Ne), a tendency to meet the abscissa axis at points between 600 and 700 volts. It would be interesting to carry out experiments in this region to see if, as suggested by the extrapolation, the ionizing power of electrons of this speed is almost zero.

The derivation of $f(V')$ shows that it varies inversely as the value of α, the frequency of collision between electrons and molecules per cm path at 1 mm pressure. Hence $\alpha f(V')$ is independent of the value of α, and *measures the number of positive ions produced per cm path at 1 mm pressure* when the electron is moving with energy V'. As there is considerable doubt as to the proper value to assume for the collision frequency, it is desirable to express the results in a form not dependent on α, and this is secured in Table I which gives the values of $\alpha f(V')$ whereas the curves give $f(V')$. Should these results be used for testing theories, the values given in the table are more accurate than those which could be measured

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[4] Ramsauer, Ann. der Phys. **72**, 346, 1923

from the curves. The values are given to three significant figures. This does not mean that the absolute values are correct to this extent, for there was an uncertainty of 3 to 4 per cent in determining *d* the distance between *G* and *P;* but the relative values at different electron energies are considerably more accurate. The numbers in brackets beside the symbols for the gases are the numbers of electrons per molecule.

TABLE I

Ions formed per cm path at 1 mm pressure, $a\,f(V')$

Energy	He(2)	Ne(10)	A(18)	H_2(2)	N_2(14)	CH_4(10)
300 volts	.648	1.502	4.14	1.264	4.460	4.36
280	.699	1.557	4.54	1.362	4.775	4.72
260	.744	1.608	4.83	1.463	5.100	5.05
240	.782	1.666	5.31	1.568	5.420	5.41
220	.815	1.710	5.68	1.678	5.650	5.74
200	.844	1.754	6.03	1.785	6.080	6.20
180	.867	1.800	6.36	1.902	6.425	6.43
160	.880	1.828	6.67	2.018	6.780	6.78
140	.881	1.820	6.95	2.137	7.125	7.14
120	.870	1.768	7.21	2.260	7.450	7.47
100	.846	1.651	7.45	2.376	7.640	7.82
80	.804	1.450	7.65	2.487	7.470	8.06
60	.730	1.130	7.48	2.518	6.880	7.80
40	.500	.630	6.74	2.280	5.580	6.79
35	.380	.480	6.36	2.153	4.96	6.28
30	.229	.320	5.56	1.947	4.09	5.55
29	.192	.287	5.35	1.882	3.89	5.37
28	.155	.255	5.13	1.825	3.68	5.20
27	.120	.220	4.88	1.755	3.47	5.00
26	.082	.180	4.61	1.670	3.24	4.80
25	(24.5)*	.140	4.31	1.600	3.02	4.55
24		.095	4.00	1.500	2.80	4.30
23		.044	3.67	1.383	2.54	4.02
22		(22.2)*	3.30	1.260	2.28	3.72
21			2.90	1.130	2.00	3.40
20			2.45	.980	1.72	3.05
19			1.90	.800	1.42	2.67
18			1.29	.595	.80	2.26
17			.45	.350	(17.0)*	1.80
16			(16.0)*	(16.2)*		1.28
15						.75
14						.10
						(13.9)*

*Ionization potential in volts.

It is clear that whether ionization occurs or does not occur on collision is not determined merely by whether the energy of the electron exceeds or does not exceed the ionizing potential, as has sometimes been tacitly assumed. When the electron has energies just above the ionizing potential, only the most favorable conditions at impact, e.g., those of orientation, yield ions. As the impact energy is increased, conditions of impact for ionization become less exacting, with a consequent increase in the number of collisions resulting in ions, until the maximum is reached. Beyond this point, even though the energy conditions are more than satisfied, the *time* during which the electron acts on the atomic system becomes less and less, with the result that fewer and fewer collisions result in ionization. Thus there are two factors concerned, viz., energy and speed. The ionizing potential measures the minimum energy necessary to produce ionization, even under the most favorable conditions, while the position of the maximum in these experiments gives a measure of the time of action between the electron and the molecule, resulting in the best yield of ions.

It seems impossible to handle the problem quantitatively at the present time. We may attempt a comparison of the time taken by the electron in the hydrogen *atom* (chosen for its simplicity) to move in its orbit from one end of the diameter to the other, with that of an electron shooting through the system. When the electron belonging to the atom happens to be travelling in the same direction as the electron shooting into the system, one would expect the disrupting effect of the impacting electron to be appreciable as long as they both traverse the atom in about the same time, but to decrease when the speed of the impacting electron takes it across the atom much faster than the electron belonging to the atom. According to Bohr's theory, the electron in the hydrogen atom moves from one end of a diameter to the other in its path around the orbit in $.7\times10^{-16}$ second. An electron having an energy 75 volts (giving maximum $f(V')$ for hydrogen), would traverse the diameter in $.2\times10^{-16}$ second, which is considerably shorter, though of the same order. It is of course admitted that these considerations are not strictly applicable to our work, as we are dealing with hydrogen molecules, not atoms. For want of satisfactory data on the molecule, we are forced to this makeshift.

Provided we consider the monatomic and the polyatomic gases separately, and make no intercomparisons, our results suggest that the maximum value of $f(V')$ (and indeed practically the whole curve) is higher, the more electrons there are in the molecule.

We wish to express our best thanks to Dr. E. F. Nichols for the opportunity of carrying out this investigation at the Nela Research Laboratories during the summer of 1923, and for giving us every facility and assistance in our work.

NELA RESEARCH LABORATORIES,
NATIONAL LAMP WORKS,
CLEVELAND, OHIO,
August, 1923.[5]

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[5] Received November 9, 1923—Ed.