THE RELATIVE IONIZATION IN DIFFERENT GASES FOR SLOW-MOVING ELECTRONS

By William P. Jesse

Abstract

A uniform beam of electrons was obtained by allowing thermions from a tungsten filament to fall through a given potential difference between the filament and a perforated plate and to pass through the plate into a short region devoid of strong electric fields. There, due to the energy acquired, they ionized the gas present, the positive ions being caught on a concentric ring element and the electrons themselves on a plate opposite the perforated plate. With the pressure low enough to prevent secondary effects the ionization was determined for electron energies ranging from 20 to 300 volts. With increasing electron energies the ionization in each gas was found to reach maximum at the following voltages: for He 140, Ne about 220, A 100, CO 120 and N_2 100 volts. For 200 volts the relative ionizations at 1 mm pressure, with reference to that in Ne taken as 1.0, are: H_2 .91, He .48, CH_4 3.5, N_2 3.2, CO 3.45, A 4.1. The results are in good agreement with those of Hughes and Klein, except that the value for argon is 0.7 higher. A second maximum was observed in each case at 350 to 400 volts which was probably due to secondary rays, but is not completely understood.

RECENTLY Dushman[1] and Found from their studies with the ionization gauge, using potentials between 125 and 250 volts, have concluded that, in general, ionization by electrons in various gases is approximately proportional to the number of electrons in their respective molecules. This result is rather surprising and difficult to understand because it implies that the chances for ionization depend only on the total number of electrons, irrespective of the fact that the energy necessary to knock out an electron from various atoms and from different parts of the same atoms, varies greatly. It seemed desirable, therefore, to study this result using slow-moving electrons of constant velocity throughout their path. After the investigation reported in this paper was completed, a paper by Hughes[2] and Klein dealing with the same subject, appeared. The results in general confirm those of Hughes and Klein, but differ in some respects. The method used differs from theirs in that the ionization was produced by electrons of approximately constant velocity.

[1] Dushman and Found, Phys. Rev. **23,** 734 (1924); also Dushman, The Production and Measurement of High Vacuum, Gen. Elec. Rev. (1922).

[2] Hughes and Klein, Phys. Rev. **23,** 450 (1924).

The general method employed was to obtain electrons of uniform velocity by allowing thermions to fall through a given potential difference, and then to pass these into a region devoid of strong electric fields, where owing to their speed, they were able to produce ionization in the gas present. The electrons themselves and any negative ions formed were collected on a plate and the positive ions, produced in the given region, were caught on another collector. For a given accelerating potential and gas pressure, the ratio of the positive ion current to the electron current gives a measure of the ionization in any particular gas. For a given gas the ionization could also be obtained as a function of the accelerating potential.

In order to observe the ionization due to the primary electrons alone, it was essential to use very low gas pressures, from 1 to 200×10^{-5} mm. Under these conditions only one in a large number of primary electrons actually made an ionizing impact. For the same reason the ionization produced by secondary electrons ejected from the atoms of the gas was a negligible part of the whole. The space charge in the region considered was kept quite low by using electron currents of the order of 20 microamperes.

Apparatus

After a preliminary trial of tubes of various designs, the following type was adopted (Fig. 1). The tube itself was 8 cm in diameter and was made of Corning G-702-P glass. The source of electrons was a tungsten filament T, welded to tungsten leads 1 mm in diameter. The filament was enclosed in a molybdenum cylinder C, 2 cm in diameter, and was placed close to a small circular hole through which the electrons passed. The diameter of this hole was 1.5 mm. The plate P was of molybdenum, and the collector M for positive ions was a tungsten wire bent to form a circle around the aperture. To protect the collector from the possibility of direct impact from electrons, a small cylinder was spot-welded to the larger cylinder and completely surrounded the hole. In most of the experiments, the distance from the plate to the top of the small cylinder was 7 mm, and this was considered the length of path from which positive ions were gathered. All the elements in the tube were supported by double leads in order that the latter might be further heated by an electric current during the process of baking the tube.

The tube was directly attached to a liquid air trap which was connected to a McLeod gauge and could be connected to a diffusion pump. A pressure as low as 10^{-5} mm could be read easily on the gauge. The apparatus

other than the tube was made of Pyrex glass so that it might be heated to drive off gases and moisture from the walls.

Electrical connections. During all the experiments the positive terminal of the filament was kept grounded. The cylinder and plate were maintained at the same potential and the combination was always kept positive with respect to the filament. The collector of positive ions

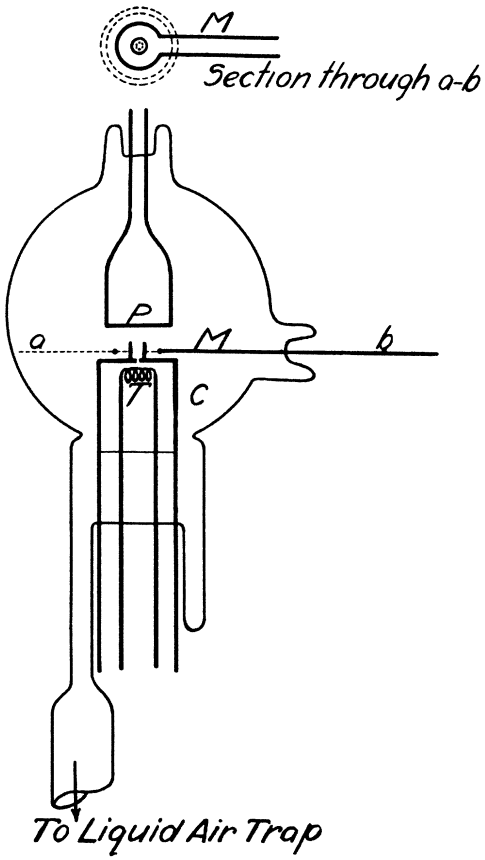

Fig. 1. Diagram of experimental tube.

was kept negative with respect to the filament. The electron current to the plate P was measured with a micro-ammeter, the positive ion current to the collector with a high sensitivity galvanometer. These instruments were calibrated from time to time during the course of the experiment.

Preliminary manipulation. The apparatus was so constructed that all parts could be surrounded by electric ovens and baked at a temperature of 450° C. As a rule such a general heating was necessary only occasion-

ally. Before every series of runs, however, the oven was placed over the tube and liquid air trap with only a few inches of the latter projecting beneath, and a temperature somewhat below the softening point of the glass was maintained for half an hour. The lower end of the trap was then immersed in liquid air and the heating continued for another half hour. During this latter period all the tungsten leads in the tube were heated to a dull red heat by means of an electric current, and a hand torch was played upon all parts of the apparatus outside the oven. The oven was then removed without disturbing the liquid air trap. Next the tube elements were heated to a bright red heat by means of a

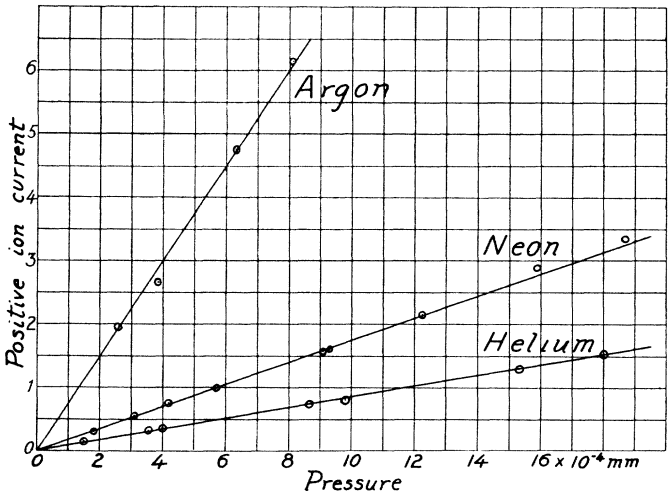

Fig. 2. Relation between positive ion current in galvanometer divisions and pressure, with 200 volts accelerating potential.

high frequency inductive-heating device, and then the trap was submerged as deeply as possible in the liquid air. During the course of the experiments the liquid air was always kept at this latter level.

In order to determine the efficacy of the treatment described above, control runs were taken during the course of the experiments to test for an evolution of gas from the apparatus. The system was pumped out and sealed off, and the filament allowed to remain lighted for a time equal to the average time of a run. No evidence of an evolution of gas was perceptible either by the McLeod gauge or by the registering of a positive ion current by the galvanometer.

Observations

The ionization in a gas was measured under two different sets of conditions—(1) when all quantities were kept constant except the pressure

(Figs. 2, 3); and (2) when all quantities were kept constant except the accelerating potential for the electrons (Figs. 4 and 5). In the first of these series of observations the cylinder and the plate were kept at the same potential of 200 volts positive with respect to the filament and the collector of positive ions 40 volts negative with respect to the filament. The electron current to the plate was kept constant by regulating the temperature of the filament. The pressures were read with the McLeod gauge, and the corresponding positive ion currents with the galvanometer.

Since the collecting ring drew positive ions from the region between the cylinder and plate, one might expect the energies of the ionizing electrons to be modified to a certain extent by the field due to the collector. To determine whether this introduced a serious error, preliminary runs

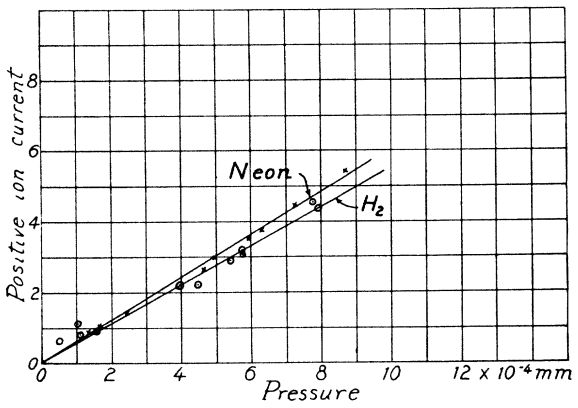

Fig. 3. Relation for hydrogen and neon between positive ion current, in galvanometer divisions, and pressure, with 200 volts accelerating potential.

were made with the collector at different negative potentials. These varied from -5 to -40 volts with respect to the filament. If the field due to the collector had much effect in accelerating the electrons, the curves shown in Figs. 4 and 5 should be shifted along the voltage axis as the collector potential was changed. No such shift was observed. The maximum with -5 volts was the same as for -40 volts. Moreover no important change was apparent in the early portion of the curves where the ionization changes rapidly with small changes in accelerating potential. The only difference between the curves taken at -5 and at -40 was that the ordinates throughout the latter were a few percent greater than in the former. Since no shift was observed on thus changing the collector potential, it was considered that, though a small field did exist between the cylinder and the plate due to the collector, the effect

of this field in accelerating the ionizing electrons introduced no serious error.

With the pressure of the gas so low that the electron in its passage could make ionizing impact with no more than one molecule, the positive ion current should be directly proportional to the pressure, and this was found to be the case, as is shown in Figs. 2, 3. In these experiments the value of the positive ion current was from 1/100 to 1/1000 of the electron current, so the chance of a second ionizing encounter was negligible. The effect of the ionization produced by the ejected electrons was, for the same reason, negligible.

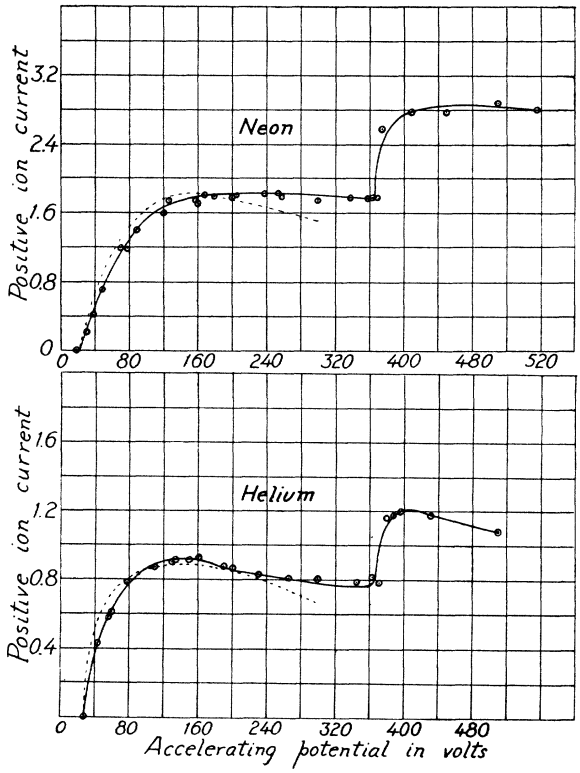

Fig. 4. Relation between positive ion current and electron energies in volts; pressure .001 mm.

When the speed of the electrons was varied by changing the accelerating potential and the other conditions were maintained constant the curves in Figs. 4 and 5 were obtained. These have all been reduced to a common pressure of 1/1000 mm. The ionization is seen to increase rapidly at first and after rising to a maximum to decrease slowly until

a sudden second increase takes place. The cause of the second sharp rise will be discussed later.

The neon used was obtained from the Linde Air Products Company and was considered by them to be very pure. It was examined spectroscopically in this Laboratory, especially with regard to the presence of helium, and neither visual observation nor a photograph gave any indication of impurities. Since neon was found to give quite consistent results, it was chosen as a reference gas and the relative ionizations in other gases were reckoned in terms of it. It may be said that the ratio between the ionization in two different gases was much more constant than the absolute magnitude of the ionization in either one. Once or twice it was necessary to open the tube to replace a burned out filament or for some other cause, and it was not possible to replace the elements in exactly the same position. This introduced a measure of uncertainty in the estimation of the length of electron path from which positive ions were drawn. Such a variation should affect the absolute values but not the relative values. The agreement obtained for the latter throughout the experiment was always very good.

The ionization voltage curve for neon, beginning at 20 volts, shows a gradual rise up to 150 volts and then an almost horizontal portion with an ill-defined maximum at about 220 volts.

The helium was purified by repeatedly passing it over charcoal immersed in liquid air until the spectrum showed nothing but sharp lines against a black background. Helium gave the least ionization of any gas used, the average ionization at 200 volts with respect to neon being 0.487. The curve for varying electron energy shows no ionization until 28 volts is reached. There is then a rise, sharper than in the case of neon, up to a maximum at 140 volts.

The argon used was obtained from the Nela Research Laboratory and originally contained something less than one-half percent of impurities. It was further purified by the action of an arc between calcium electrodes. The ionization in this gas was found to be quite large. The value at 200 volts, determined from a number of trials, was 4.15 times that with neon under the same conditions. With increasing electron energies ions were first formed at 18 volts and a maximum ionization was obtained at 100 volts.

Carbon monoxide was prepared by heating recrystallized oxalic acid in a glass tube. The water and CO_2 were removed by passage through phosphorus pentoxide, finely divided potassium hydroxide, and lastly

through a liquid air trap. The ionization of carbon monoxide at 200 volts was to that of neon in the ratio of 3.45 to 1. Ionization first became apparent at 20 volts (Fig. 5), after which the curve rose rapidly to a maximum at 120 volts. The rate of decrease after this maximum was much greater than in the curves heretofore examined.

Hydrogen was prepared by the electrolysis of phosphoric acid and was thoroughly dried by passage through phosphorus pentoxide and a liquid air trap. The gas was most difficult to work with on account of the rapid "clean-up" effect of the tungsten filament. Nevertheless, for the

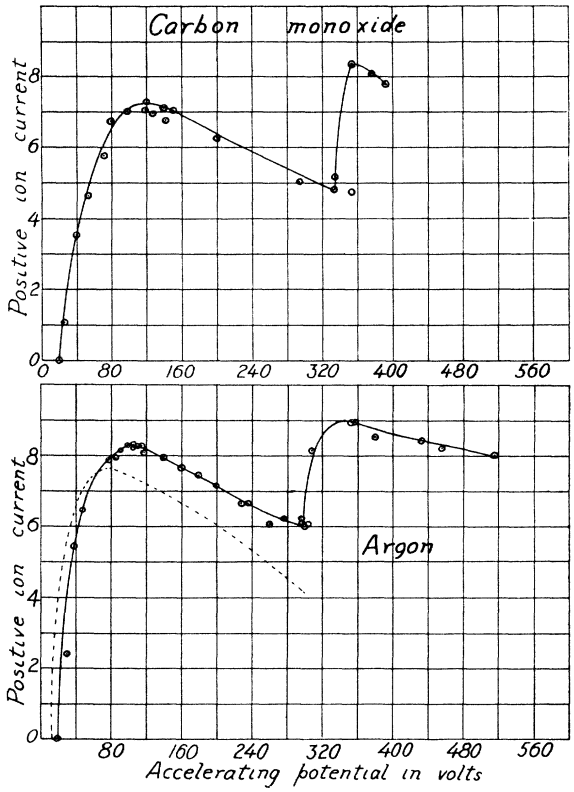

Fig. 5. Relation between positive ion current and electron energies in volts; pressure .001 mm.

ionization at 200 volts readings were obtained which leave no doubt as to the order of magnitude of the results (Fig. 3). Since the galvanometer sensitivity was quite different in this case, a neon curve is shown for reference. It may be noted that the ionization is not far different for the two gases. It was not possible to keep the pressure constant long enough to make a run with variable voltage.

Methane was prepared by a gentle heating of a mixture of sodium acetate and barium oxide. The resultant gas was passed over phosphorus pentoxide, potassium hydroxide, and through a trap immersed in liquid air. The ionization curve for 200 volts for this gas was almost coincident with that for carbon monoxide. The ionization relative to neon was found to be 3.50. An accidental contamination of the supply of gas prevented any trial being taken with varying electron energies.

Nitrogen was prepared by the action of bromine water on ammonium hydroxide according to a method devised by Waran.[3] The ionization at 200 volts was found to be 3.19 times that with neon under similar conditions. The "clean-up" effect in nitrogen, though smaller than in hydrogen, prevented the taking of as accurate a variable voltage curve as could be desired. However a maximum ionization was indicated at about 100 volts. Constant potential curves with varying pressures, similar to those taken at 200 volts, were also taken for this gas at 100 volts and 250 volts. The values obtained are given in the last column of Table I.

Discussion of Results

It will be seen that all the variable voltage curves have the same general shape. The formation of ions begins when the accelerating potential for the electrons is equivalent to the ionization potential of the gas in question. It may be noted that these threshold values are in good agreement with more accurately determined values when we consider that no attempt was made to obtain extreme accuracy at this part of the curve.

The electron energies, expressed in equivalent volts, for maximum ionization in the different gases are as follows:

Helium	Neon	Argon	CO	N_2
140	220	100	120	100

After the maximum is reached in each case, the ionization decreases as the energy of the ionizing electron increases, according to an almost linear relation. This decrease is not strange when we consider that there are two factors which play an important rôle in the process of removing an electron from an atom. The first of these factors is the energy of the impinging particle; the second is the time during which the particle is in the neighborhood of the electron to be removed. In the early part of the curve the first of these factors seems the predominant one and the ionization rises to a maximum as the energy of the particle increases.

[3] Waran, Phil. Mag. **42**, 246 (1921).

After this the chance of ionization seems more dependent upon the time factor, being smaller as the time of proximity between electron and atom decreases.

The sudden rise in the curves in the region of 300 volts is somewhat perplexing. It cannot be attributed to the beginning of ionization in another ring of electrons, since the position of the break may vary by twenty or thirty volts in different trials with the same gas and, moreover, occurs in helium which has no second ring of electrons. The ionization is therefore due most probably to some secondary emission in the tube itself.

If secondary electrons were emitted from the plate P (Fig. 1) under the bombardment of the primary electrons, they would give no effect until they had arrived at the energy required for ionizing the particular gas in the tube. As their energies further increased the ionization due to them would rapidly mount, and with still further increase in energy we should get a repetition of the primary ionization curve on a smaller scale. If a similar smaller curve were superimposed upon each of the main curves in Figs. 4 and 5, we should obtain approximately the results found experimentally. The varying position of the break for the same gas might, on this hypothesis, be attributed to changes in the surface of the plate produced by occluded gases, heat treatment and similar causes, which might affect the velocities of the emitted secondary electrons. In fact, it was observed that a prolonged glowing of the plate at a red heat had the effect of causing the break to move toward higher potentials.

The above explanation is not wholly satisfactory. It neglects the distribution in velocities of the secondary electrons and has other weak points. However, after carefully examining other possible causes, the writer is firmly convinced that the effect is due to ionization produced by secondary electrons from the plate, though perhaps not by precisely the process described above.

An attempt was made to estimate the amount of secondary emission from the plate by making the collecting ring positive with respect to it in a gas-free tube. For an accelerating potential of 280 volts a secondary electron current was obtained of about 12 percent of the primary electron current. Fully half of these electrons could be stopped by a retarding potential of 10 volts. No very satisfactory results could be obtained on account of the complication of tertiary electrons from the collector itself. Hence it is somewhat difficult to estimate the effect of secondary emission upon the measured ionization but it is believed to be small up to 300 volts.

The Relation between the Relative Ionization and the Number of Electrons in the Molecule

In Table I are collected the various values for the ionization relative to neon. Under each gas is given the ratio of its ionization to that of neon under similar conditions for the acceleration potential given in the first column of the table.

Table I

Ionization relative to neon

Accelerating potential	Neon	Helium	Argon	CO	H_2	CH_4	N_2
200	1	0.487	4.15	3.45	0.91	3.50	3.19
200	1	0.472	3.93	3.46			....
50	1	0.661	9.18	6.23			....
100	1	0.563	5.47	4.60			3.93
250	1	0.447	3.54	3.12			3.02
300	1	0.437	3.34	2.86			....

In the first horizontal line of the table are given the ratios derived from the slopes of the linear ionization-pressure graphs, which were taken throughout at 200 volts only. These results are the most accurate of the whole investigation since they represent the average of quite a number of trials taken at this one voltage, and each trial gives the average of some six or eight plotted points. The trials checked among themselves within three or four percent.

In the second and succeeding lines of the table are recorded ratios obtained from the ionization-voltage curves (with the exception of those for nitrogen where on account of the troublesome clean-up effect ionization-pressure curves were taken for the voltages indicated). A strict proportionality between ionization and pressure has been shown to exist at 200 volts, and similar results were obtained for 100 and 250 volts. The values of the ratios given in the second and succeeding lines were taken from the curves shown in Figs. 4 and 5 and have been verified by other trials. Although this method does not yield results quite so accurate as

Table II

Relative ionization divided by the number of electrons in molecule

Accelerating potential	Neon (10)	Helium (2)	Argon (18)	CO (14)	H_2 (2)	CH_4 (10)	N_2 (14)
200	0.10	0.243	0.230	0.246	0.455	0.350	0.228
200	0.10	0.236	0.218	0.247			
50	0.10	0.331	0.510	0.445			
100	0.10	0.281	0.304	0.329	.....	.....	0.280
250	0.10	0.224	0.196	0.223	.....	.....	0.216
300	0.10	0.218	0.185	0.204			

those obtained from the slopes of the lines, nevertheless the agreement between the values in line two and line one is very good, the maximum variation being 5 percent.

In Table II are given the results of dividing the relative ionization values for each gas in Table I by the number of electrons in its molecule. If the ionization is proportional to the number of electrons, the ratio indicated should be a constant in each horizontal line. It is evident that such is not the case, the widest variations occurring in the cases of neon, hydrogen and methane. The values of ionization for hydrogen and helium have been observed by Dushman and Found with the ionization gauge to be approximately twice as great as the relation predicts. This is true for the writer's value of hydrogen but helium gives values quite in accord with the relation. The value for methane might perhaps be expected to be large since it contains four hydrogen atoms. However, Dushman and Found cite water vapor as giving values quite in accord with the relation, the number of electrons per molecule being taken as 10.

A glance at the curves of Figs. 4 and 5 shows that no constant ratio between the ionization in two different gases can exist which shall be independent of the accelerating voltages, for in such an event each curve must be the exact duplicate of the other save for the scale of the ordinates. On the contrary, the shapes of the curves are quite different. The maxima do not occur at the same points, neither are the rates of decline of ionization beyond the maximum the same in the various cases. Hence, it seems impossible that the direct proportionality between ionization and the number of electrons per molecule can be a general law.

Due to some uncertainty as to the exact length of path from which ions were collected the absolute values of the number of ions per electron per centimeter path are not considered very accurate. However, these values may be obtained for a pressure of 1 mm by multiplying the ordinates of the curves shown in Figs. 4 and 5 by the factor 1.75.

The writers results are on the whole in fairly good agreement with the results of Hughes and Klein.[2] For 200 volts the following comparison is found between the relative ionizations with respect to neon.

	Ne	He	H_2	CH_4	A	N_2
Hughes and Klein:	1	.472	1.016	3.53	3.44	3.47
Writer:	1	.487	.91	3.50	4.15	3.19

The maxima for ionization are obtained at the following voltages:

	He	Ne	A	N_2
Hughes and Klein:	147	158	80	101
Writer:	140	220	100	100

The dotted curves in Figs. 4 and 5 are those of Hughes and Klein reduced to the same arbitrary scale as the writer's. Their neon curve was given the same maximum ordinate as the writer's and the ordinates

for the helium and argon curves were then plotted in the proper ratio to those of neon. This gives a comparison of the relative ionizations in the three gases rather than of the absolute values of the ionization.

It will be seen that the greatest difference between the results is in the case of argon. The table above gives for the relative ionization for argon at 200 volts a discrepancy of 17 percent. Although some values slightly lower than 4.0 were obtained by the writer for argon, none were obtained approaching 3.44. In this case, the writer would be inclined to favor his own value, since his argon (presumably derived from the same source) was further purified by means of a calcium arc. It seems very doubtful, however, whether the small impurity of 0.2 percent mentioned by Hughes and Klein would give the above difference, unless in the gas-flow method used by them the lighter impurity diffused into the ionization tube much more rapidly than the argon and thus gave effects greater than would be indicated by the original percentage of the impurity. The values for the relative ionization in helium, methane, nitrogen and hydrogen are in excellent agreement, especially considering the difficulties of working with hydrogen.

In comparing the values of Hughes and Klein with the writer's it may be seen that in the position of the maxima for ionization the values for neon are quite different. The greatest difference might be expected in this gas, since in both the investigations the curve for neon was found to be the most nearly horizontal, and hence the true position of the maximum the hardest to determine. No value was obtained by Hughes and Klein for the electron energy for maximum ionization in carbon monoxide. Here the writer's value of 120 volts compares favorably with the value of 125 volts given in an earlier paper by Mayer.[4]

In conclusion the writer wishes to express his thanks to Professor R. A. Millikan who suggested the problem and under whose direction the preliminary work was done, to Professor John Zeleny for aid and encouragement during the progress of the work, and to Dr. H. C. Rentschler of the Westinghouse Lamp Company for most generous help in the construction of the experimental tube and of the inductive heating system.

YALE UNIVERSITY,
August 12, 1924.

[4] Mayer, Ann. der Phys. **45**, 1 (1914).