The Conductivity Produced in Neon and Helium by Irradiation with Their Own Resonance Radiations and the Effect of Foreign Gases on This Conductivity

R. W. SMITH AND O. S. DUFFENDACK, *University of Michigan*

(Received February 1, 1935)

The conductivity observed ten tube diameters or more beyond the end of a discharge in Ne or in He is investigated at pressures of from 0.25 mm to 14 mm. Great care is taken to insure rigorously pure gas. The conductivity is deduced from the characteristic of a rotatable pair of parallel plane collectors and guard rings completely shielded with glass. At pressures above about 0.25 mm no current is observed when the collectors are perpendicular to the tube axis so that the space between them is shielded from the direct radiation. The total current (to collectors and guard rings) is considerable. When the collectors are turned so that the primary radiation illuminates the space between them, considerable currents are obtained and the much larger total current is of the same order of magnitude as in the perpendicular position. These results show that the ions which give rise to the conductivity must be formed in the space between the collectors and also that any metastable atoms which may produce these ions must also be formed in this space. It is difficult to reconcile these results with the propagation of resonance radiation through the gas by diffusion for they indicate an abnormally long free path for the resonance radiation of He and Ne. The large conductivity observed in the pure gas under conditions such that the photoelectric action of the primary beam is very small suggests that electron emission by impacts of metastable atoms is of major importance. Argon and krypton in small admixtures increase the conductivity of neon or of helium due to the action of the metastable atoms of the main gas in ionizing the argon or krypton. Neon greatly decreases the conductivity of helium while helium has no measurable effect in neon. In these cases ionizing collisions are not possible but the metastable atoms of helium readily transfer their energy to the nearby excited levels of neon.

INTRODUCTION AND PURPOSE

INVESTIGATIONS of the nature and properties of resonance radiations were for many years limited to those which could be pursued by the usual photographic methods. This restriction was severe in that it eliminated from consideration all of the interesting rare gases whose resonance radiations are much too short in wavelength to be transmitted by any known window material. These gases, particularly He, possess metastable states whose population under ordinary discharge conditions may be very large and whose lifetime is very long compared with that of the unstable states. It would be very significant to study quantitatively the part played by metastable atoms in the propagation of resonance radiation through a gas.

A few years ago a possible line of attack was suggested by Langmuir and Found[1] who discovered that the conductivity existing in a discharge tube at a considerable distance beyond the end of a discharge in Ne was much too large to be accounted for by any agent moving away from the discharge by diffusion. They ascribed this conductivity to electrons emitted from the glass walls and metal surfaces, and caused by metastable atoms. These metastable atoms, they suggested, were produced by resonance light of slightly different frequency from that of the core of the resonance line. As the primary light source produced a rather broad resonance line, such light would be present in considerable intensity. Kenty[2] repeated and extended these experiments and confirmed that many metastable atoms are produced at large distances (10 tube diameters or more) from the discharge, probably by the method suggested by Langmuir and Found. However, Kenty concluded that while these metastable atoms are of relatively great importance in causing conductivity in cases where there is present a small amount of impurity ionizable by metastable atoms, their effects in pure gases are very small compared with the photoelectric effect of the extreme ultraviolet radiations. Penning[3] made some important studies of this conductivity and the effect of small amounts of added impurities and agreed that the large increases in conductivity which result when argon is added to neon are caused by the ionization of A atoms by metastable Ne atoms in impacts of the second kind.

[1] Langmuir and Found, Phys. Rev. **36**, 604 (1930).

[2] Kenty, Phys. Rev. **38**, 377, 2079 (1931); **40**, 633 (1932); **43**, 181 (1933).

[3] Penning, Zeits. f. Physik **78**, 454 (1932).

Evidently the observed conductivity may be explained on at least three quite different bases: (1) The extraction of electrons from the discharge tube walls and electrode surfaces by metastable atoms; (2) photoelectric emission from the tube walls and electrode surfaces; (3) the ionization of traces of impurities present in the gas. However, all of these explanations are compatible with the conclusion that considerable concentrations of metastable atoms may be built up in a neutral rare gas which is irradiated by its own resonance radiation; and, further, that these metastable atoms may give evidence of their presence by their effectiveness in ionizing small traces of impurities. The investigations mentioned thus far do not permit a definite distinction to be made between the effects of the direct primary resonance radiation from the source, those of secondary resonance radiation produced by the absorption and reemission of resonance radiation in the gas and the effects of primary ultraviolet radiation multiply reflected from the tube walls. Collectors whose orientation with respect to the primary beam can be varied allow measurements to be made with the radiation directly incident on the collecting surface, just grazing it or not striking it at all. Plane parallel plates give more easily interpretable characteristics but only if they are fitted with guard rings of ample width. The use of unguarded collectors makes it difficult to interpret data taken in the presence of volume ionization. Especially would this be true in gas which was not rigorously purified as the conductivity is extremely sensitive to traces of impurities.

The present experiments, already briefly reported,[4] were begun with a threefold purpose: (1) To obtain gas as rigorously pure as possible; (2) to investigate quantitatively the effect of small admixtures of foreign gases on the conductivity produced in Ne and in He by irradiation with their own resonance radiations; (3) to study the various agencies contributing to the conductivity and the mechanism of the propagation of resonance radiation away from a source. Ordinary experience has shown that only the most elaborate precautions for long continued purification and complete degassing of the intimate apparatus will suffice to maintain rigorously pure gas. It was therefore felt that considerable effort could profitably be expended in an attempt to ascertain first what effects would be most important in a pure gas.

Apparatus

The vacuum system was rather elaborate and combined an efficient and flexible circulating and purifying system capable of purifying relatively large quantities of Ne and He together with a rapid and reliable means of adding very small amounts of foreign gases. The gases could be circulated through the purifying agents alone or also through the discharge tube during runs. In this way the gas could be purified continually while the tube was being baked and pumped dry. It was then very pure when admitted to the tube and could be maintained so by regulated circulation during the experimental runs.

The discharge tube used is shown in Fig. 1. It was 80 cm long and arranged so that a hot cathode arc could be maintained at the opposite ends. This made possible a fairly uniform illumination near the center of the tube. Midway between the two anodes, which were about 16 tube diameters apart, were supported two parallel plane nickel electrodes 1 cm in diameter fitted with guard rings 1 cm wide. These were completely shielded with glass except on their adjacent faces, the lead wires were also shielded, and the whole assembly was rotatable about a vertical axis perpendicular to the tube axis.

Great care was taken in procuring and maintaining pure gas. The rare gases used, Ne, He, A and Kr were obtained commercially spectroscopically pure. The Ne and A were further purified by prolonged circulation over charcoal in liquid air, chabazite in liquid air and over hot copper oxide. As a further precaution for the removal of H_2 the method of Paschen[5] was used. No waxed joints were used in the vacuum system and the few stopcocks were lubricated with a special low vapor pressure grease. Two liquid-air traps containing glass beads in series on each side of the discharge tube and wads of gold foil in the pumping leads served to exclude Hg vapor from the tube.

[4] Duffendack and Smith, Phys. Rev. **43**, 586 (1933).

[5] Paschen, Ann. d. Physik **45**, 625 (1914).

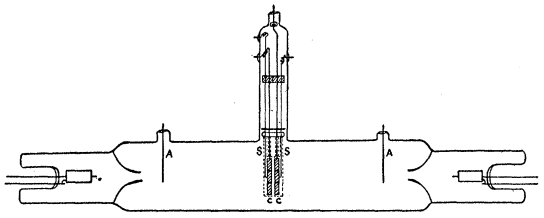

FIG. 1. Diagram of experimental tube.

Since the A and Kr were obtained already spectroscopically pure and in any case were to be used only as small admixtures it did not seem necessary to subject them to such exhaustive purification. As a precautionary measure, however, a low voltage arc was maintained in the A reservoir between Ca electrodes for about a month after which time the A was found to be very pure. The Kr was used directly from the original container.

Spectroscopic analysis of the various gases as received from the vendor revealed no trace of any impurities, except a trace of Ne in the He. Yet the experimental results revealed that impurities were certainly present and that these results were themselves probably the most sensitive test for such subspectroscopic traces of foreign gases. Throughout the investigation the actual behavior of the conductivity itself was taken as an indication of the gas purity.

PROCEDURE

The primary gas was circulated for two or three days through the purifying system until greatly overexposed spectrograms showed no trace of impurity. The gas was then pumped into a reservoir containing well-degassed charcoal immersed in liquid air where it was allowed to stand for 12 to 24 hours while the experimental tube was being baked at 400°C. After this the gas was slowly admitted to the tubes. Then the arcs were struck and maintained at a high current density while the gas was circulated through the tube and entire purifying system for 4 to 6 hours. This flushed out the tube and cleaned up residual impurities. The rate of circulation was then slowed down, the arcs adjusted to the proper current density and the run made.

When foreign gases were used, the charcoal and chabazite were shunted out of the circulating system as they readily absorb A and Kr. By means of a calibrated bulb and suitable cut-offs small amounts of the gas to be admixed could be accurately and rapidly added to the main gas and mixed by circulation. At low primary gas pressures equilibrium could be established in a minute or two while at pressures above about 6 mm it was necessary to wait about 15 minutes. This proved to be a convenient and accurate way of adding small amounts of foreign gases where large numbers of such additions were to be made. In the case of the addition of A or of Kr to He or to Ne, after the completion of a run, the gas was circulated for several hours through the charcoal and chabazite traps to remove the added gas. After it had been absorbed out the conductivity was compared with that observed before the addition of the foreign gas in order to ascertain that no unexpected contamination had occurred during the run.

The conductivity or ion concentration was determined from the volt-ampere characteristics of the collectors. The potential difference across the collectors was varied in small steps by means of a potentiometer arrangement and the corresponding current between them read on a current galvanometer having an overall sensitivity of 1.5×10^{-10} amp./mm. When plotted, these readings constitute the collector characteristic.

RESULTS

When the collecting disks are placed at right angles to the tube axis so that the space between them was shielded from the direct radiation, then, except at the lowest pressures (<0.25 mm Hg), no measurable current ($<10^{-10}$ ampere) flowed between the guarded collectors. The total current (to collectors and guard rings), however, was the same as that previously observed between unguarded collectors.[4] Fig. 2 shows that when the collectors were turned so that the primary radiation illuminated the space between them, appreciable currents were obtained and the much larger total current was of the same order of magnitude as before. All of the data were taken therefore with the space between the

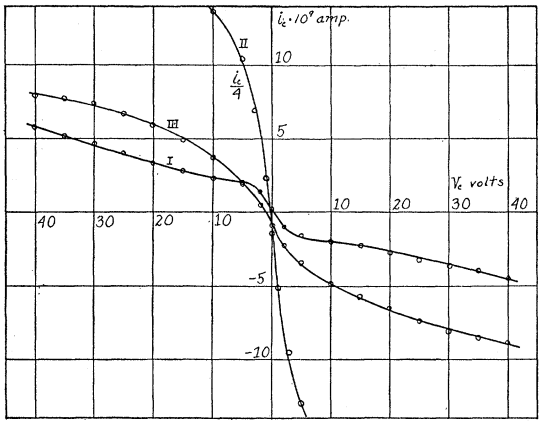

FIG. 2. Current to collectors as a function of potential difference between them. Collectors floating with respect to the discharge. I, current to guarded collector, parallel position; II, current to collector and guard rings, parallel position; III, current to collector and guard rings, perpendicular position.

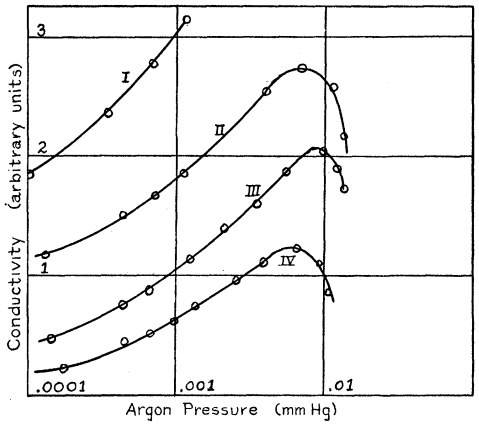

FIG. 3. Variation of the slope of the current voltage characteristic curve in neon with various argon admixtures. I, 2.6 mm Ne; II, 4.3 mm Ne; III, 7.0 mm Ne; IV, 11.5 mm Ne.

collectors irradiated by the primary beam. In no case were the collector surfaces exposed to the primary beams. All the characteristics of the guarded collectors are strictly linear through the voltage axis, and the slope at the voltage axis is taken as a measure of the conductivity of the gas. Figs. 3 to 5 inclusive show how this slope (in arbitrary units) varies with the pressure of the admixed gas. The variations are similar to those obtained with the unguarded collectors. For A added to Ne or to He the curve attains a maximum and then slowly decreases to a very low value. In agreement with Penning,[3] it has been found that if the percentage of A is greater than about one percent the curve again rises slowly, indicating the entrance of primary effects due to the A in addition to its secondary destroying effects. Kr is similar to A in its effects but is less efficient than A in increasing the conductivity of He or Ne. It is also seen that while A and Kr both increase the conductivity of Ne and of He, Ne effectively decreases the conductivity of He. He added to Ne causes no measurable effect even with large admixtures. In the case of pure He and pure Ne the residual conductivity decreases rapidly with increasing pressure and apparently reaches a constant limiting value at about 8 mm Hg. No further decrease was observed up to 14 mm pressure.

DISCUSSION

These results lead to two conclusions: First, that the ions which give rise to the observed conductivity must be formed in the space between the collectors; and second, that any metastable atoms which may produce these ions must also be formed in this space. In these experiments the photoelectric effect of the direct radiation from the source must be very small as the glass shields protect the collector surfaces in any position. The inference is that the agency giving rise to the conductivity is produced in or near the primary beam and cannot diffuse far from it at the pressures used (2–12 mm). Only at pressures below about 0.1 mm was any appreciable current collected when the collectors were perpendicular to the direct radiation. An accidental confirmation of these conclusions was obtained when one of the glass shields cracked in such a way as to leave a small opening behind the collecting electrode oriented so that no direct radiation could enter. Appreciable currents were then collected through the crack in the shield with the electrodes in the perpendicular position but were not collected after the shield had been replaced. Thus the surrounding gas must have been ionized.

The curves of Fig. 2 exhibit the same general form although the total current is very much larger than could be accounted for by any

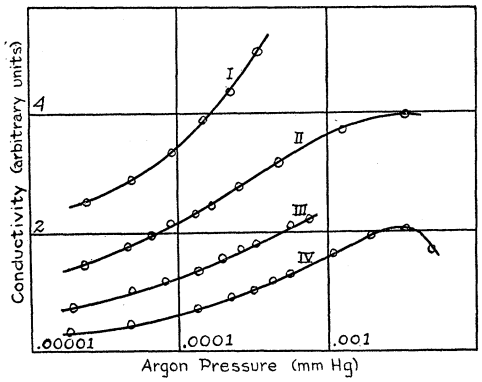

Fig. 4

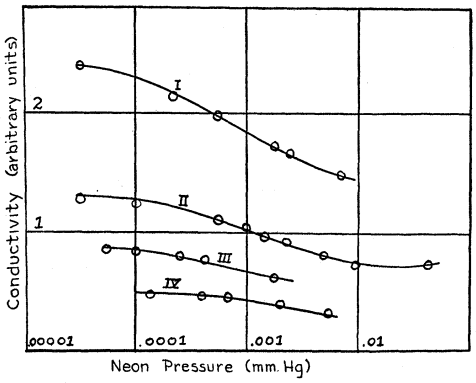

Fig. 5

FIG. 4. Variation of the slope of the current voltage characteristic curve in helium with various argon admixtures. I, 1.4 mm He; II, 3.2 mm He; III, 5.7 mm He; IV, 8.5 mm He.

FIG. 5. Variation of the slope of the current voltage characteristic curve in helium with various neon admixtures. I, 1.6 mm He; II, 2.2 mm He; III, 2.7 mm He; IV, 4.6 mm He.

difference in area between the collecting surfaces in the two cases. This discrepancy must be due to edge effects and indicates that when an unguarded collector is placed in an ionized gas a considerable portion of the ion current observed is due to edge effects so that such a collector, even if shielded on one side, would exhibit little difference in current collected regardless of its orientation.[2] Hence scattered short mean free path resonance radiation probably plays no important role in such experiments.

Further evidence for the existence of volume ionization arises from the fact that while at high pressures no current is collected by the guarded collectors in the perpendicular position, appreciable currents may be measured below about 0.25 mm. Moreover, the collector characteristics in He exhibit decided peaks at about 6 volts on either side of the voltage axis which become relatively more prominent as ionizable foreign gases are added. Penning[3] first observed these and showed that they were probably due to ions diffusing in from the surrounding volume when the field between the collectors was so small that the ions were not trapped by the guard rings.

It seems probable that the collector characteristics and the directional effect of the collectors as shown in Fig. 2 are mainly characteristic of the pure gas, as an apparent limiting value of conductivity was reached which could not be diminished by further purification or increase of gas pressure. Furthermore, this residual conductivity was remarkably reproducible. If this is true, the residual conductivity is surprisingly large in view of the amount of ionization that has been ascribed to the several processes suggested by previous investigators to account for this conductivity. However, abnormally large wall reflections and photoelectric efficiencies have been reported by Kenty[6] which might account for the ion concentrations ($\sim 10^8$ cm^{-3}) observed at these large distances from the source.

These experiments show definitely that, in gas which may be reasonably termed pure, short mean free path scattered resonance radiation contributes negligibly to the observed conductivity. Moreover, since while there is considerable volume ionization no ions are collected by a guarded collector except when it is adjacent to the primary beam from the source, the agencies giving rise to the observed conductivity must act in the path of the primary beam or, at most, only a few mean free paths from it.

FOREIGN GASES

The experimental results exhibit one outstanding regularity in that all of the foreign gases which effectively increase the conductivity of the gas to which they are added have ioniza-

[6] Kenty, Phys. Rev. **44**, 891 (1933).

tion potentials below the energy of excitation of the metastable states of the primary gas. Ne, the only gas to decrease the conductivity of He, is the only one whose ionization potential is higher than the energy of the He metastable states. This is also true of He when added to Ne. This confirms the conclusion that the conductivity in the presence of a foreign gas arises largely from ionization of ionizable impurities by metastable atoms. It should be noted in this connection that both A and Kr exhibit similar behavior in Ne and in He. While He appears more sensitive to impurities than Ne and while A is more effective than Kr in increasing the conductivity of the Ne or the He to which it is added, the differences are not in order of magnitude.

One interesting effect which was observed is the decided maximum which the conductivity attains as larger admixtures of ionizable impurity are introduced. The maxima occur at larger and larger percentages of foreign gas as the pressure of the main gas is decreased, due probably to the relative decrease in the number of collisions of metastable atoms with the admixture. These maxima may be accounted for briefly as follows.[3] If, as in ordinary quenching experiments, the resonance radiation is constant in intensity then the curves rise to a saturation value and remain constant; for this saturation occurs when all the metastable atoms are being destroyed as fast as formed and further addition of the destroying agency has no effect. However, in these experiments two factors may operate to decrease the intensity of the radiation: (1) Direct excitation of the radiation by electron impact in the arcs may be influenced by the foreign gas; and (2) if the resonance radiation which finally reaches the vicinity of the collectors is absorbed and reemitted at least once on the way, the intensity of this scattered radiation would be affected by the presence of any agency which could destroy the excited atoms giving rise to it. The maximum is thus a point of balance where the forces acting to destroy the metastable atoms are equal to those forming them.

Some interesting results have been obtained with Ne-He and He-Ne mixtures in which cases ionizing collisions are not possible between the metastable atoms of the main gas and the foreign gas atoms. Addition of an extremely small amount of Ne to He causes a marked decrease in conductivity which is difficult to explain if one attributes the action of the Ne to the weakening of the resonance lines of He which are excited entirely by direct electron impact. However, if one allows metastable He atoms largely to account for the conductivity in pure He[7] then the results are easier to interpret as there is very close resonance between the metastable levels of He and a large number of excited states of Ne. This reaction therefore should have quite a high probability of occurrence in He containing a small amount of Ne.

In the He-Ne mixtures the observed decrease is exceedingly small, being just detectable at about 30 percent He in the Ne. This should perhaps be expected in view of the fact that no collisions of the second kind can take place between excited Ne and neutral He because the excited states of He are all above the metastable levels of Ne. The slight decrease at the high percentages of He is probably due to considerable excitation by electron impact of the large number of He atoms present.

Because of the difficulties inherent in the inclusion, as here, of the source and of the measuring device all in the same vessel and the same gas, these experiments are probably not sufficiently accurate for any significant evaluation of action cross sections. The various effects mentioned limit any valid analysis of the variation of the conductivity with the foreign gas pressure to the range of very small admixtures. However, if one assumes the statistical processes occurring to be those discussed above, one can obtain a relation between conductivity and the pressure of the added foreign gas which fits the experimental results exceedingly well. The uncertainties in the interpretation of the collector characteristics and in the conceptions of the processes contributing to the conductivity do not justify a more detailed quantitative analysis of the experimental data.

[7] Reichrudel and Spiwak, Phys. Rev. **42**, 580 (1932); Ann. d. Physik **17**, 65 (1933).