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Photoelectric and Metastable Atom Emission of Electrons from Surfaces in the Rare Gases

CARL KENTY, *General Electric Vapor Lamp Company, Hoboken, N. J.*

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The causes of conductivity observed at considerable distances beyond the end of a rare gas discharge are investigated at pressures of 0.5–2 mm. In pure gases, currents from negatively charged electrodes are found to be mainly caused by photoelectric action thereon of the resonance or other extreme ultraviolet radiations. For similar discharge conditions, currents are roughly 10-fold greater in Ne than in He and 20-fold greater in Ne than in A. When traces of impurities (ionizable by metastable atoms) are added, the currents are increased because of the ionization of the former by metastable atoms (volume effect). Under these circumstances strong irradiation with light of the gas in question (which is found to destroy more than half the metastable atoms formed) causes marked decreases in the currents; but the currents in pure gases are only negligibly so reduced. Electron currents from a thin metal disk are several times greater when the plane of the disk is perpendicular to the direction of the radiation than when it is parallel thereto. The fraction of the currents in Ne which may be caused by the emission of electrons from surfaces by metastable atoms is <10 percent for the parallel position of the above disk and <3 percent for the perpendicular position. This fraction is still smaller in A but may be considerably higher in He. The fraction of the scattered resonance quanta which are converted into metastable atoms before reaching the walls may be as high as 50 percent in He but is probably <5 percent in Ne. The small value of this fraction in Ne is in accord with other evidence for the abnormally long free paths of resonance radiation in this gas. The efficiency of metastable atom emission of electrons from surfaces under the present conditions is found to be $<<1$ and is probably not much greater in order of magnitude than the photoelectric efficiency of the radiations concerned. The effective cross section for the ionization of A by metastable Ne atoms is estimated. A convenient method of detecting and measuring small traces of impurities in Ne and He is described. Evidence is given that, on account of wall reflections, visible radiation, and probably also (but for gaseous absorption) extreme ultraviolet radiation, passing down a glass tube will, over a considerable range, decrease approximately with the inverse first power of the distance.

I. INTRODUCTION

THE present paper is an account of a study of the conductivity existing in a tube at a considerable distance beyond the end of a discharge in Ne, He or A, at 0.5–2 mm pressure. Langmuir and Found[1] showed that such conductivity in Ne cannot be accounted for by any agent moving away from the discharge by diffusion; they ascribed this conductivity to the emission of electrons from the glass walls and metal surfaces by metastable atoms[2] which they concluded were produced as a result of the absorption of the penetrating edges of the resonance lines.

The present experiments, already briefly reported,[3] confirm directly that many metastable atoms are produced at large distances (10 tube diameters or more) from the discharge, evidently by the method suggested by Langmuir and Found. The experiments show, however, that while these metastable atoms are of relatively great importance in causing conductivity in cases where a small amount of impurity ionizable by metastable atoms is present, their effects in pure gases are very small compared with the photoelectric effect of the extreme ultraviolet radiations.[4]

Penning[5] describes important studies of conductivity at higher pressures (40 mm) and confirms that large increases in conductivity which result when traces of A are added to Ne

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[1] Irving Langmuir and Clifton G. Found, Phys. Rev. **36**, 604 (1930), and **40**, 129A (1932); Found and Langmuir, Phys. Rev. **39**, 237 (1932).

[2] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929) and others.

[3] Carl Kenty, Phys. Rev. **38**, 377L (1931).

[4] Preliminary, briefly reported, measurements (Carl Kenty, Phys. Rev. **38**, 2079L (1931)) indicate photoelectric efficiencies for these radiations which are quite high—of the order of 1–5 electrons per hundred quanta for a clean Ni surface depending on the gas (whether He, Ne, or A) and the cleanliness of the surface.

[5] F. M. Penning, Zeits. f. Physik **78**, 454 (1932).

are caused by the ionization of A by metastable Ne. Duffendack and Smith[6] report recent studies of the conductivity in Ne and draw conclusions in accord with the present ones insofar as these overlap. Spiwak and Reichrudel[7] on the other hand, conclude that currents from a negatively charged probe in Ne are caused mainly by the emission of electrons therefrom by metastable atoms; their work will be referred to below.

II. APPARATUS

In Fig. 1, *K* is a W filament serving as a cathode and *A* is a Mo anode. p_0-p_4 are W probes, 0.1 cm in diameter, and projecting 0.9 cm inside the tube. *D* is a W disk 1.88 cm in diameter and 0.025 cm thick; this is mounted on a glass float as shown, containing a piece of Fe, so that it can be rotated by means of a magnet or moved back into the side tube for degassing purposes or for coating with Mg from a Mg gun *M* (for a study, to be reported later, of the variation of the emitted currents with the work function). *P* is a Mo disk, 2.5 cm in diameter, mounted with its axis in line with the axis of rotation of *D*. In the measurements to be discussed, *D* was adjusted in every case to a central position in the main tube where its edge was about 0.3 cm from *P*. *G* is a Ni gauze which can be moved magnetically to a position where it fills the main tube reducing the intensity of the radiation passing down the latter by a known amount (36 percent). *H* is a positive ion detector, of the type originated by Lawrence and Edlefson.[8] The use of this detector as well as the use of the gauze *G*, will be discussed below.

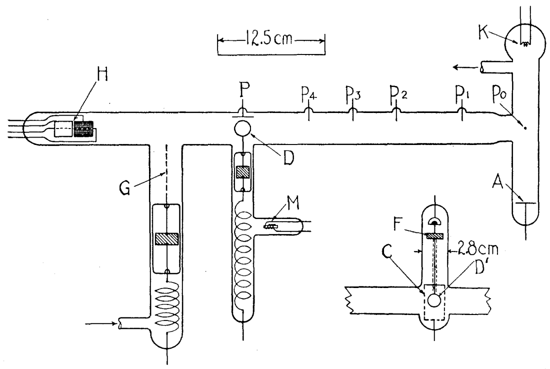

FIG. 1. Diagram of apparatus.

Another tube used is essentially similar to the one just described except that the disk is covered with mica on one side. In still another tube used, of the same general character, a thin Ni disk *D′* is suspended from a swivel joint so that it can be rotated inside a Ni gauze cylinder *C*, Fig. 1, by means of a magnet acting on the Fe strip *F*. The cylinder *C*, 2.5 cm in diameter, is made of Ni gauze having ten 0.022 cm wires per cm; it is closed at the top with a Ni disk, having a hole in its center. A quartz tube passes through this hole serving to insulate and center the disk inside the cylinder.

The tubes were of Pyrex and were degassed under exhaust for 2 hours at 450°C. The metal parts were degassed by heating inductively to incandescence. The Ne was purified by continuous circulation, in the direction of the arrows, over charcoal in liquid air; the He by circulation over chabazite in liquid air; and the *A* by the action (before the admission of the gas to the experimental tube) of a misch metal arc. Means were provided to prevent Hg from entering the tube. The presence of impurities in the gas (especially in the cases of Ne and He) was found to be of great importance. A method for conveniently measuring the purity of Ne and He was developed and used throughout the experiments; this method will be described in appendix *A* at the end of this paper.

III. RESULTS IN PURE NE

a. Characteristics with disk perpendicular and parallel to axis of tube

In Fig. 2 curve 1 is the current between *D* and *P* (Fig. 1) in quite pure Ne at 1.5 mm pressure, as a function of the voltage applied between them when *D* is perpendicular $(\perp)$ to the axis of the tube and a positive column discharge of 120 m.a. is maintained between *K* and p_2. Curve 2 is the current under the same circumstances when *D* is parallel $(\|)$ to the axis

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[6] O. S. Duffendack and R. W. Smith, Bull. Am. Phys. Soc. **7** [7] 8 (1932).

[7] G. Spiwak and E. Reichrudel, Phys. Rev. **42**, 580L (1930). See also F. Ludi, Zeits. f. Physik **76**, 319 (1932).

[8] E. O. Lawrence and N. E. Edlefson, Phys. Rev. **34**, 233 (1929).

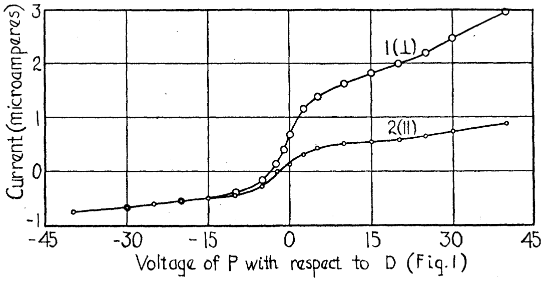

FIG. 2. Current voltage characteristics of electrode system $D-P$, Fig. 1.

of the tube. The electrode system is floating with respect to the discharge, here and in what follows.

Fig. 3 shows similar characteristics for the system D'—C of Fig. 1 for two different pressures. The discharge is 120 m.a. between the cathode and a probe situated 10 cm from D'.

b. Interpretation of characteristics

Assuming that the currents in the preceding section are caused by an electron emission from the electrodes, the curves of Figs. 2 and 3 can roughly be broken up into three regions: (1) a region from 0 to say 7 volts (to take first the right-hand parts of the curves) where the currents are probably limited by the back diffusion of electrons;[9] (2) a relatively flat region, say from 7 to 20 volts, which may be taken to represent the saturation electron emission from D or D'; and (3) a region above 20 volts where the currents are increasing by cumulative ionization in the space. The same divisions presumably hold for the left-hand parts of the curves.

The approximate saturation currents in the region (2) above, measured with D or D' at the arbitrarily chosen potential of -15 volts with respect to P or C, respectively, and with conditions of pressure and discharge as in Fig. 2 unless otherwise specified, will be referred to below as I_s and I_p for the ⊥ and || cases, respectively; the ratio I_s/I_p will be called R.

That I_s and I_p are actually the approximate saturation currents perhaps requires further justification. We note first that curves 1 and 2 of Fig. 3 show considerably more evidence of saturation than the other curves. This is to be expected since because of the relatively low pressure, both the back diffusion of electrons (at the lower voltages) and cumulative ionization (at the higher voltages) will be less important in this case. Also the higher electric field at D', due to the fact that the gauze cylinder totally surrounds it, will tend to decrease the effect of back diffusion in this case. Rough calculations, made on the basis of Langmuir's theory, indicate that even at the higher pressures (1.5–2 mm) back diffusion will not be of major importance in the voltage region (2) here discussed.

The currents in the present experiments are presumably too small to be limited by space charge.[10] We note that I_s is several times greater than I_p; this could not be so if I_p were already limited by space charge. Further, when a discharge of 120 m.a. was run between K and A, Fig. 1, instead of between K and p_2 as in the case of Fig. 2, curves similar to those of Fig. 2 were obtained and R was practically unchanged although the currents themselves were tenfold smaller.

It is seen from Fig. 3 that for the curves 1 and 2 the value of R is about 4.3. Considerably

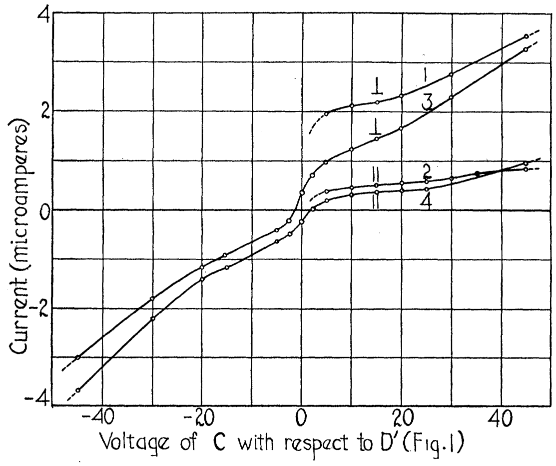

FIG. 3. Characteristics of electrode system $D'-C$ of Fig. 1. Curves 1 and 2 are for Ne at 0.5 mm pressure and curves 3 and 4 are for Ne at 2 mm pressure.

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[9] Irving Langmuir, Phys. Rev. **38**, 1656 (1931).

[10] Penning, see reference 5, has found a space charge effect in cases where the currents are mainly due to ions and electrons formed in the space (impure gas) but we believe this is to be associated with the relatively very low mobility of the ions (as compared with that of the electrons in our case) especially at the much higher pressures in Penning's experiments (40 mm).

larger values were found for the mica-backed disk.[11] (§ II.) Since the geometry of the space surrounding D' is identical[12] for all orientations of D' (and the similarity of the curves and the merging together of the left-hand parts of the curves of Fig. 2, indicate that this is also approximately true in the case of D), and since space charge and back diffusion have been eliminated as unimportant,[13] the difference between I_s and I_p must represent a real difference in the electron emission from the disk in the two cases. This difference is easily explained as being due to the photoelectric effect of the primary radiation beam passing down the tube.[3, 4] If the currents considered were wholly due to the emission of electrons from D' by metastable atoms, R should be somewhat less than 1, instead of 4.3, since on account of the shadow cast by D' in the $\perp$ case less radiation (for the production of metastable atoms) will fill the cylinder in this case than in the $||$ case.[14]

That the $\perp$ currents in the case of the *left-hand* branches of curves 3 and 4 of Fig. 3 should be less than the $||$ currents follows naturally on the present views since in the $\perp$ case the disk casts a shadow on the inner rear surface of C, lowering the photoelectric emission therefrom, and at the same time cutting off the production of scattered radiation in the space in the region of the shadow (which might otherwise partly act photoelectrically on C and partly produce metastable atoms which would cause electron emission from C).

Assume, for the $\perp$ position, that

$$I_s = I_s^0 + I_s' + I_s'', \tag{1}$$

where I_s^0 is that part of I_s which is produced by the photoelectric effect of the primary beam on the front face of D', and I_s' and I_s'' are the currents caused by the scattered energy (as radiation or metastable atoms) incident on the front and back surfaces of D', respectively. Call I_p' that part of I_p caused by the scattered energy incident on one side only of D' in the $||$ position. Further assume that the production of scattered energy in the space is uniform. Then if D' were small compared to the surrounding enclosure it would follow that

$$I_s'' = I_s' = I_p' \tag{2}$$

since the scattered energy reaching a given side of D' would not vary with the orientation of the latter. In the case of D of Fig. 1 this is fulfilled; for, on replacing D by another similar disk covered with a thin layer of mica on one side, I_p was found to be closely equal to I_s in the case where the uncovered face was turned away from the discharge. It is assumed that also in the case of D' and C, Eq. (2) will hold approximately. From Eqs. (1) and (2) it follows that

$$R = (I_s^0 + 2I_p')/2I_p', \tag{3}$$

from which, substituting $R = 4.3$ for the case of curves 1 and 2 of Fig. 3, it follows that $I_s^0 = 6.6I_p' = 6.6I_s'$. Thus the electron emission caused by the primary radiation flux incident on the front face of D in the $\perp$ case is 6.6 times as great as the emission caused by the random flux of scattered energy incident on the same surface. From this result and Eqs. (1) and (2) it follows about 77 percent of I_s is caused by the direct photoelectric action of the primary beam. Similarly in Fig. 2, R is about 3.3 and the corresponding percentage is 70. Results with the mica backed disk were entirely compatible with these results.

c. The effects of irradiation

If the region around the electrodes D and P (or D' and C) of Fig. 1 is strongly irradiated

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[11] Cf. Found and Langmuir, last paper of reference 1, Fig. 10.

[12] Spiwak and Reichrudel (reference 7) attribute somewhat similar results to differences in geometry. Their grounds for this are not entirely clear to the writer; but in any case it is evident, as discussed above, that there is no difference in geometry in the case of the arrangement D' and C of Fig. 1.

[13] Even if back diffusion were important here the theory of this effect (reference 9) requires that the currents be proportional to the saturation emission.

[14] R at pressures of 1–2 mm in A and He (see § V) is found to be 25–50 percent less than the corresponding values in Ne. At pressures $< 1/2$ mm R is about the same in A as in Ne although still relatively small in He (the case of He is of special interest—see remarks in § V). R increases slowly with discharge current in Ne and relatively rapidly in A (e.g., from 1.4 to 3.5 as the discharge current, otherwise similar to that in Fig. 2, is increased from 20 to 200 m.a.). Now if the currents in the present experiments were mainly due to metastable atom emission, R should be roughly the same in all cases, and equal to or slightly less than unity.

with light from another Ne discharge tube,[15] the currents are only slightly affected, provided the gas is very pure, being decreased by small amounts[16] (2.5 percent in the case of I_p and <1 percent in the case of I_s). In impure gas, however, irradiation produced very considerable decreases in the currents (which had already been considerably increased by the added argon. See below).

Now Meissner and Graffunder[17] and Penning[18] have shown that metastable atoms are strongly destroyed by such irradiation. Experiments to be described below show that also in the present studies metastable atoms are so destroyed. The near absence of effect of irradiation on the currents (in particular I_p) leads us to conclude either (1) that metastable atom emission causes only a small fraction of I_p or (2) that if this process causes an appreciable fraction of I_p, its efficiency is nearly the same as the photoelectric efficiency of the scattered radiations. (2) follows since when metastable atoms are destroyed by irradiation, resonance quanta result[18] which we assume will follow the same laws of diffusion as the metastable atoms and hence have equally good chances of reaching a given electrode. Further experiments, now to be described, give (in effect) an estimate of the actual number of metastable atoms formed and help us to judge concerning (1) and (2).

IV. Study of the Rôle of Metastable Atoms

a. Ionization of impurities by metastable atoms

The effects on the currents I_s and I_p (as defined in § IIIb) of adding A to Ne are shown in Fig. 4.

Penning[19] showed that starting potentials in Ne are markedly decreased by adding small traces of A, and he ascribed this effect to the ionization of A by metastable Ne atoms. It is reasonable to attribute the increases of current in Fig. 4 to the same cause.

Fig. 4 shows that although I_s is about 3.4 times as great as I_p at zero A percentage, the increments ΔI_s and ΔI_p, respectively, by which these currents are increased by a given A percentage are closely equal to each other. This indicates that the effect is caused simply by the sweeping out to the electrodes of the ions and electrons formed in the surrounding space by the process above discussed; for D is small enough, with respect to the surrounding space, that a roughly uniform concentration of metastable atoms would be expected to exist for both orientations of D.

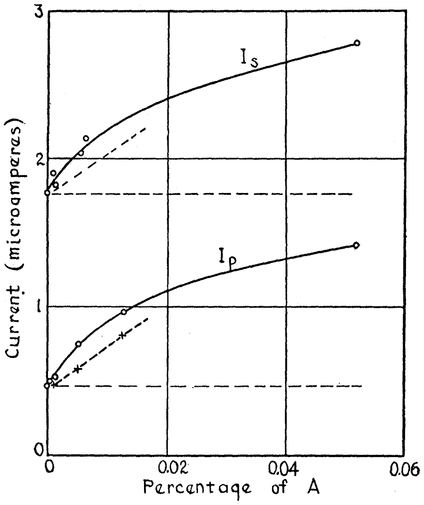

FIG. 4. The effect of A in increasing I_s and I_p. The broken lines show these currents as reduced by irradiation.

The rate of production of ions, and hence $\Delta I_p(=\Delta I_s=\Delta I)$ should be proportional to the product of the concentration (N_{A}) and the metastable atom concentration (N_m). Thus, for A concentrations sufficiently small so that they

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[15] Positive column discharge tubes 2 cm in diameter were used for this purpose containing Ne at about 1 mm pressure and carrying currents of about 3 amp. Only the region around the electrodes was irradiated, the remainder of the tube being shielded from the light. Photoelectric currents due to this external light itself were undetectable.

[16] It is probably significant that in the case of A (see below), where there are no common impurities ionizable by metastable atoms (except possibly O_2, see E. W. Pike, Phys. Rev. **39**, 534L (1932)), irradiation with strong A light produced no detectable effect on the currents whatever.

[17] K. W. Meissner and W. Graffunder, Ann. d. Physik **84**, 1009 (1927).

[18] F. M. Penning, Phil. Mag. **11**, 961 (1931) and a number of preceding papers.

[19] F. M. Penning, see reference 18. Penning also studied mixtures of other rare gases and impurities ionizable by metastable atoms and found similar results.

do not appreciably affect N_m, ΔI should be proportional to N_A; Fig. 4 indicates that this is experimentally the case. With higher A concentrations N_m will begin to be strongly reduced by the A and there will be no longer proportionality between ΔI and N_A. We would expect the curves to bend over with increasing A concentration, finally becoming horizontal when practically all the metastable atoms are being destroyed by the A; this the curves appear to do. It is assumed here, of course, that the rate of production of metastable atoms (which is dependent on the primary radiation reaching the region of the electrodes) is not appreciably altered by such A percentages as are here used. Evidence for this is the approximate constancy of $I_s - I_p$ which according to § IIIb represents the photoelectric action of the primary beam on D in the perpendicular position.[20]

It is well known that metastable atoms of Ne (and other gases) are strongly destroyed by even small traces of certain impurities. T. E. Foulke in unpublished work in this laboratory, has recently carried out experiments similar to earlier ones of De Groot[21] which show that under the circumstances of the present experiments, metastable Ne atoms were present in considerable numbers and that these were strongly destroyed by A. Foulke focussed, by means of a lens, a strong narrow beam of Ne light (from a special discharge tube furnishing an intense point source of light) on the region just beyond the end of a 100–200 m.a. positive column discharge in Ne (pressure 2–3 mm). Provided the gas were pure, the beam was strongly visible by light scattered by the metastable atoms. Under the best conditions the beam could be detected many tube diameters away from the end of the discharge. If, however, as much as 0.2 percent A was added to the Ne, the beam could no longer be detected even quite close to the discharge.[21]

Based on the assumption that N_m is reduced to half its value in pure gas by that amount of A which in Fig. 4 causes a ΔI_p which is half the apparent saturation ΔI_p approximate calculations indicate that the cross section for the ionization of A by metastable Ne is of the order of 0.4 times the normal cross section* (see remarks in Appendix A regarding H_2 and N_2).

b. Effects of irradiation in impure gas

In Fig. 4, the broken lines show the effects of irradiation on the currents I_s and I_p. It is seen that, for low A percentages, irradiation nullifies more than half of the increases in current (ΔI) which were caused by the addition of A. Since according to the views of the preceding section $\Delta I \propto N_A N_m$ it follows that N_m has been reduced by more than 50 percent by irradiation in these cases.

These conclusions have been confirmed by experiments in which ion concentrations were measured with the detector H of Fig. 1, and the effects of irradiation on these concentrations studied. The front cylinder of H was made of fine mesh Ni gauze so that radiation could pass through it. By use of the gauze G (described in

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[20] Recent unpublished experiments carried out at the General Electric Research Laboratory, Schenectady, show that, for positive column discharges at such gas pressures and discharge currents as are here dealt with, the only effect on the visible lines of Ne of adding a small quantity (e.g., 0.1 percent) of A to pure Ne is to decrease the intensities of these lines by a few percent, the decrease being roughly the same for all lines; it seems reasonable to assume that also the intensities of the extreme ultraviolet lines here involved will not be altered by more than a few percent. See also Penning, reference 5.

[21] W. De Groot, Physica 6, 53, 158 (1926).

* Briefly, solving the equation

$$D(d^2N/dr^2+(1/r)dN/dr)+K-RN=0$$

where N is the concentration of metastable atoms at a point distant r from the tube axis ($N=0$ at walls), D is the diffusion coefficient for metastable atoms and K and RN are the rates of production from resonance quanta and destruction by A, respectively, of metastable atoms per cm^3, for $R=0$ and $R=1.76D\ \mathrm{cm}^{-2}$ we find values of N at the axis in the ratio of $1 : \frac{1}{2}$. (Tube radius $a=1.7$ cm. For the solution of a similar equation see M. W. Zemansky, Phys. Rev. **34**, 213 (1929).) We assume from Fig. 4 that the latter situation occurs with about 0.02 percent A. Then employing the usual kinetic theory expressions for D (diffusion cross section assumed normal) and R (see E. W. Samson, Phys. Rev. **40**, 940 (1932)), we find $\sigma_i^2 = 0.37\sigma_0^2$ where σ_i^2 is the cross section for ionization in question and σ_0^2 is the normal cross section $(1.17\times10^{-8}\ \mathrm{cm} + 1.43\times10^{-8}\ \mathrm{cm})^2$. More correctly, half the metastable atoms will be used up by the A (say 0.02 percent) when the gradient of N at the wall is reduced by half. For such a reduction $R=2.7D\ \mathrm{cm}^{-2}$ and we find $\sigma_i^2=0.57\sigma_0^2$. This estimate will be raised somewhat when the destruction of metastable Ne atoms in pure Ne by collisions with normal Ne atoms (${}^3P_2 \rightarrow {}^3P_1$) and the reduction of the effective values of a by the electrodes are taken into account.

§ II) the response of H to positive ions was found to be roughly linear for the range of ion concentration dealt with.

The percentage reduction in I_p caused by irradiation as a function of A percentage, is shown in Fig. 5, which is drawn from the data used in constructing the curve I_p and the corresponding broken curve of Fig. 4. Fig. 5 shows the effect to pass through a maximum at about 0.0075 percent A, and to decrease with higher A percentages. Experiments have shown the effect to be very small at 0.2 percent A; here the destroying effect of irradiation will be small compared with that of the A. Under such circumstances two irradiation tubes gave roughly twice as much decrease as a single tube as would be expected if irradiation is here a small effect compared with other effects. At the lower A percentages (e.g., 0.005 percent) the second tube gave a much smaller decrease than the first; this is in agreement with the view, already arrived at by other means, that N_m is reduced markedly (50 percent or more) by irradiation under these circumstances.

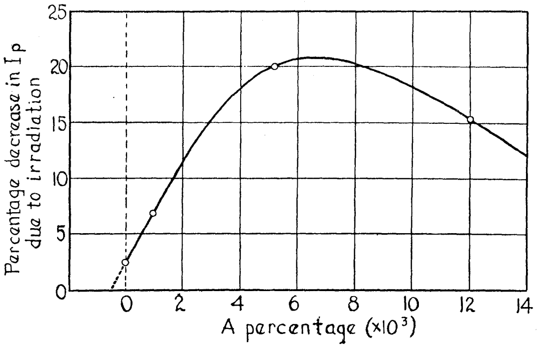

FIG. 5. Curve showing the effect of irradiation in decreasing I_p at different A percentages.

Since at the point denoting zero A percentage in Fig. 5, the gas could scarcely have been entirely free from traces of impurities ionizable by metastable Ne atoms it would be interesting to know how closely the curve would approach zero in absolutely pure gas. If we knew (see § IIIc) that irradiation produced zero effect in absolutely pure gas, we could extrapolate the curve backward as indicated till it cut the horizontal axis and call this intercept the A percentage equivalent to the actual percentage of impurity in the tube.[22] Since we do not know this, all we can say is that this intercept probably represents the *maximum* impurity present, in terms of equivalent A percentage (in this case about 0.0005 percent).

c. Analysis of results

Suppose that Q resonance quanta are absorbed uniformly from the primary beam per cm³ per sec. in the region around D and P (Fig. 1), and that a fraction f of these are converted into metastable atoms before they reach the wall (see reference 26). Further suppose that a volume V surrounding D can be specified which will include all the absorbed quanta which diffuse to D. Such a surface, surrounding D, would be described by the locus of points of maximum radiation quantum (or excited atom) concentration. We shall assume as a first approximation that this same volume includes roughly also all the metastable atoms formed which diffuse to D. Then it follows that the saturation electron emission from D in the || position (I_p in pure gas) will be given by

$$I_p{}^0 = VQe[\alpha f + \beta(1-f)], \tag{4}$$

where e is the electronic charge. Now suppose that a sufficient concentration of A atoms is added so that all the metastable atoms are used up in ionizing them (we shall assume that this is the only important process by which the A destroys the metastable Ne atoms); and further suppose that all the ions and electrons so formed in a new volume, which we shall assume is M times as great as V, are swept out to the electrodes by the field. It follows that the current will be given in this case by

$$I_p{}^{\mathrm{A}} = VQe[Mf + \beta(1-f)]. \tag{5}$$

In the case of Fig. 4 the current I_p appears to increase with added A to a saturation value 3 or 4 times as great as the original current; let us assume the value 4 as an upper limit. Then $I_p{}^{\mathrm{A}}/I_p{}^0 = 4$ for this case from which by division

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[22] F. M. Penning, Zeits. f. Physik **57**, 723 (1929), Fig. 4. Penning has pointed out (see reference 18, pp. 964, 965) how curves, somewhat similar to Fig. 5 above, which he obtained in studies of starting potentials, could be used as a method of detecting and measuring very minute traces of impurities in the rare gases. See also reference 5.

of Eq. (5) by Eq. (4) it is found, solving for f, that

$$f = 3\beta/(M - 4\alpha + 3\beta). \tag{6}$$

In this equation β may be taken[4] to be of the order of 0.02–0.04. We do not know the value of M but we note that it will have the value 2 in the ideal case of plane parallel electrodes large enough so that edge effects can be neglected and provided the field is great enough to overcome the ionic space charge effect described by Penning.[10] In the actual case of electrodes D and P of Fig. 1, M will probably be considerably greater than 2: we shall assume that it lies somewhere between 2 and 6. Assuming a number of different combinations of M and β, f in Eq. (6) has been calculated for various values of α and the results are shown in Fig. 6.

Consider for example, the point $f=1$, on the curve ($M=4$, $\beta=0.02$), Fig. 6. At this point, $\alpha=1$, which by Eq. (4) means that $I_p{}^0$ would be wholly due to metastable atom emission; this would conflict very seriously with the irradiation experiments; for, if it were true, irradiation should have decreased the current by 50 percent or more instead of the actual 2.5 percent (§ IIIc). At the point $f=0.0164$, $\alpha=0.1$, Eq. (4) shows that about 8 percent of $I_p{}^0$ would be due to metastable atom emission. Now if half the energy of the metastable atoms is converted into radiation by irradiation (as follows from § IVb) the effect will be to reduce f in Eq. (4) by half; hence, by substituting first ($\alpha=0.1, f=0.0164$) in Eq. (4) and then ($\alpha=0.1$, $f=0.0082$) it is found that we would expect $I_p{}^0$ to be decreased by 3.5 percent by irradiation instead of the observed 2.5 percent. Thus this point would appear to be eliminated. However, this elimination process cannot justifiably be continued much further along this curve until experiments can be carried out, with gas of still greater purity than was obtainable in the present experiments, to ascertain just how nearly the effects of irradiation in such gas will approach zero.

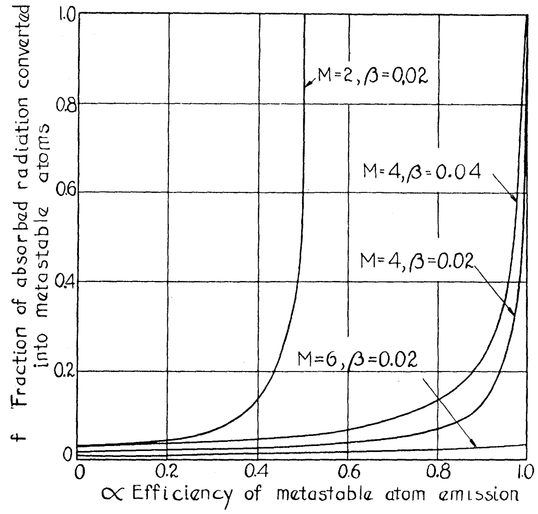

FIG. 6. Plots of Eq. (6) for a number of assumed sets of values for M and β.

Similarly, all the parts of all the curves can be eliminated except small regions to the extreme left. The conclusion has been drawn that f probably lies somewhere between 0.01 and 0.04, that α lies somewhere between 0 and 0.20,[23] and that the fraction of $I_p{}^0$ caused by metastable atom emission lies somewhere between 0 and 0.1.

It has been assumed above that all the metastable atoms formed in pure Ne reach the walls and electrodes and that none are destroyed by collisions of the first kind with normal Ne atoms. Now according to Penning[24] about 1 collision in 10^5 between a metastable atom and a normal atom will raise the former to the nearby resonance state (only the lower metastable level is here considered as it will probably be of preponderating importance). If λ_m is the mean free path of the metastable atom, the number of collisions made before such an atom reaches the walls will be $(a/\lambda_m)^2$ in order of magnitude[25] where a is the radius of the tube. In the

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[23] E. W. Pike, Phys. Rev. **40**, 314L (1932) and private communication, has deduced from experimental results of Penning that α (Pike's λ) for Ne and for an Fe surface is probably not very different from β. As Pike, Phys. Zeits. **33**, 457 (1932) has pointed out, such a low value of α in the case of slow (room temperature) metastable atoms is not incompatible with the apparently high value of α for high-speed (800–1200 volt) He metastable atoms found by Oliphant (reference 2), in view of the high reflection coefficient for slow metastable atoms indicated by Oliphant's results.

[24] F. M. Penning, Zeits. f. Physik **46**, 335 (1928) see particularly pp. 342, 343. Also see some remarks in this connection by Carl Kenty, Phys. Rev. **40**, 633L (1932).

[25] W. Harries and G. Hertz, Zeits. f. Physik **46**, 185 (1927).

present case $\lambda = 0.0081$ cm ($p = 1.5$ mm, $T = 18°\text{C}$) on the basis of a normal radius for the metastable Ne atom, and $a = 1.7$ cm, and it is found that on the average some 5×10^4 collisions will be made by a metastable atom before reaching the wall. Thus a metastable atom will be somewhat more likely to reach the wall (or electrodes) and there be destroyed than to be destroyed in the gas. This probability will be increased by the presence of the electrodes which in effect decreases a above. Let us take as an extreme case that in which the chances of being destroyed at the wall (or electrodes) and in the gas are equal. Then half the metastable atoms formed will be raised to the resonance state before reaching the walls, or electrodes and the energy of these will reach the walls or electrodes as resonance radiation. This can be taken account of by replacing f in Eq. (4) by $f/2$, Eq. (5) remaining as before. Corresponding to Eq. (6) there is then obtained $f = 3\beta/(M - 2\alpha + \beta)$. By substituting $\beta = 0.02$ and $M = 4$, for example, in this expression, it is found by the previous methods that the upper limits for α and f allowed by the irradiation experiments are about 0.2 and 0.0166, respectively, as against the limits previously found for this case of 0.1 and 0.0164. Thus the effect of collisions of the first kind will be mainly to raise the upper limit for α.

It can be also readily verified that if the true saturation current in pure gas is somewhat greater than $I_p{}^0$ (see § IIIb) the effect will be mainly to increase the allowable value of α; and that if an appreciable fraction of $I_p{}^0$ is caused by the photoelectric action of light reflected from walls (see Appendix B) as appears probable from recent experiments in which light from a quartz Hg lamp were admitted to the tube through a quartz window, the effect will be mainly to increase the allowable value of f. However, it can be verified that none of these possibilities increase appreciably the maximum fractions of about 10 percent of $I_p{}^0$ and about 3 percent of $I_s{}^0$ attributable to metastable atom emission.

By choosing an experimental arrangement of simpler geometry (calculable M value), eliminating wall reflections, attaining higher gas purity and by taking other precautions it should be possible, by the present method, to improve considerably the estimates of α and f. Attempts in this direction are now in progress.

d. Some remarks concerning *f*

Based on the result of the preceding section that f is probably small (1–4 percent) rough calculations which have already been referred to[26] indicate that the mean free paths of the scattered radiations in Ne are much greater than are usually thought of for resonance lines[27]; for otherwise little scattered energy would reach the walls except as excited or metastable atoms. This result is in accord with thermopile measurements to be reported in a later paper which show that in Ne the extreme ultraviolet radiations penetrating large distances in a tube comprise a considerable fraction[4] of the total radient energy reaching the same distance. Heating experiments showed that the breadth of the lines is not governed, in these experiments, by the Doppler effect; further, the ion concentration in the discharges used are probably much too small to give broadening by the Stark effect; hence it is inferred[28] that coupling or some other form of pressure broadening,[29] present every-

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[26] Carl Kenty, Phys. Rev. **40**, 633L (1932). In this calculation it was assumed that $f = (a/\lambda)^2 b\tau(v/\lambda_m)$ where a is the tube radius (1.7 cm), λ is the average free path (see paper, reference 27) of the scattered quantum, b is the efficiency of collisions changing resonance atoms into metastable atoms, τ is the mean life of the resonance state, v is the mean thermal speed of the atoms and λ_m is the mean free path of the atoms (assumed to be the same for resonance atoms as for normal atoms). The quantity $(a/\lambda)^2$ represents (see reference 25) roughly the number of free paths made by a quantum before reaching the wall, and (v/λ_m) is the collision frequency; it will be evident that f as represented by the expression is the chance of a quenching collision taking place before the quantum reaches the wall. The values tentatively assumed for τ and b were, respectively, 10^{-7} sec. and $10^{-2} - 10^{-3}$ (see paper, reference 27 for some remarks on b) from which, taking f as between 1 and 3 percent, λ came out to be of the order of 0.2–2 cm. This calculation may be taken to apply to the ${}^1S_0 - {}^3P_1$ resonance line and the lower (${}^3P_2$) metastable state.

[27] The discrepancy appears to be too great to be accounted for by a consideration of the effect of Doppler broadening on the radiation diffusion process—see Carl Kenty, Phys. Rev. **42**, 823 (1932).

[28] Carl Kenty, Phys. Rev. **42**, 823 (1932) and **40**, 633L (1932).

[29] J. Holtsmark, Zeits. f. Physik **34**, 722 (1925). For other references see footnotes 22 and 23 of first-mentioned paper of reference 28.

where in the tube, is the cause of the long mean free paths.[30] Direct evidence that the extreme ultraviolet Ne lines scattered in a side tube have abnormally long free paths (probably comparable with the tube diameter or larger) have recently been obtained, in unpublished work, by Langmuir and Found.

V. Argon and Helium

A and He at pressures of 1–2 mm give values of R (see § IIIb above) 25–50 percent less than those obtained in Ne, indicating that the radiations involved are more highly absorbed in these gases. In accord with this is the result that I_s is only about 0.05 times as great in A as in Ne, for similar discharge currents, and about 0.1 times as great in He as in Ne. It may also be, of course, that extreme ultraviolet radiations are developed with relatively less intensity in these gases than in Ne.

Preliminary experiments show that traces of Hg vapor added to A give the same kind of ionization effects as were noted in § IVa for the case of A added Ne. Irradiation (as in § IIIc, except using A discharge tubes) in pure A has no detectable effect on the currents I_s and I_p, although it decreases these currents provided a little Hg vapor is present. It is concluded by the methods of § IIIc that in this gas either (1) the current caused by metastable atom emission is entirely negligible or (2) α is closely equal to β and therefore of the order of 0.01 or 0.02.[4] The data were not complete enough to permit the application of the analysis of § IVc to be applied.

When A is added to He, the currents I_s and I_p increase relatively much more than in Ne. Preliminary curves (including those for irradiation) similar to the curves of Fig. 4 were taken for this gas at 1.5 mm pressure and the results when analyzed by the methods of § IVc indicate that (1) f may be as high as 50 percent,[31] (2) α may be as high as 0.1 or 0.2 and that (3) 20 or 30 percent of I_p^0 (i.e., 15–20 percent of I_s^0—see reference 14 regarding the relatively low value of R of about 1.5 in He) may be caused by metastable atom emission. Metastable atoms thus appear to be of considerably more importance in He than in Ne or A. Their presence at considerable distances beyond the discharge, and their destruction by A, were verified by scattering tests similar to those described in § IVa for Ne. (The scattered beam appeared greenish in color, evidently due to the absorption and reemission of λ5016A by singlet metastable atoms.)

VI. Discussion

Large values of R (§ IIIa) in Ne were obtained with the electrode system (like that of D and P, Fig. 1) only about $1\frac{1}{2}$ tube diameters from the end of the discharge where the metastable atom concentration was high enough to give a beam strongly visible by scattering. This suggests that some of the abnormality of size and lack of saturation, which has been observed[32] of currents to negatively charged collectors placed *in* discharges in the rare gases may be caused by the photoelectric effect. In any case the relative importance of metastable atom emission[32] in causing these effects seems likely to have been frequently overestimated.[3, 23] Oliphant[33] has recently reported experiments which seem to show that the greater part of these effects can be accounted for by the secondary emission of electrons by positive ions; it is perhaps significant that he found some evidence for an emission of electrons by some other agency than positive ions in Ne but not in the other gases (He or A) whereas by far the strongest photoelectric cur-

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[30] It has been pointed out to the writer that we might expect the longer wave-length resonance line ($^1S_0-{}^3P_1$) being an intercombination line, to have an abnormally long free path inasmuch as intercombination lines have generally been found relatively weak in absorption in elements of low atomic number.

[31] This result is in accord with the fact that in He metastable atoms can be produced spontaneously from singlet resonance atoms by radiation of the strong line λ20,582A whereas in Ne and A no such process is possible, transitions between resonance and metastable states being accomplished in these gases only by means of collisions of the first or second kinds (with probable small cross sections, see first-mentioned paper of reference 28).

[32] For bibliography see footnote 4 of reference 3. See also M. C. Harrington, Phys. Rev. **38**, 1312 (1931). Harrington points out that the method used by himself and Uyterhoeven does not distinguish between photoelectric and metastable atom emission. See also Found and Langmuir, reference 1.

[33] M. L. E. Oliphant, Proc. Roy. Soc. **A132**, 631 (1931).

rents were found in Ne in the present experiments.

Insofar as the resonance or other extreme ultraviolet radiations, like the visible radiations, may be strongly produced in the region of the negative glow, the results of the present experiments suggest that the photoelectric effect may play a rôle of more importance than has usually been recognized in contributing to the liberation of electrons from the cathode in the glow discharge in the rare gases.

It is a pleasure to record my indebtedness to Dr. Irving Langmuir, Mr. Clifton G. Found and Mr. T. E. Foulke for a number of stimulating conversations during the course of this work.

Appendix A

Method of detecting and measuring small quantities of impurities in Ne and He

The effect, discovered by Foulke (see footnote 2 of reference 3), that the conductivity in a side arm to a tube carrying a discharge in a rare gas is greatly increased by small quantities of impurities ionizable by metastable atoms, has been used to provide a convenient method of detecting and measuring small percentages of such impurities. In this method, the current to a probe situated several tube diameters from the discharge is measured under standard conditions of probe voltage, discharge current and total gas pressure, for different percentages of A or other impurity. The magnitude of this standard probe current (i_s) is then plotted against the known A percentage. Having once obtained such a calibration curve the percentage of A can then easily be obtained from i_s on any subsequent occasion. An example of such a calibration curve is shown in Fig. 7. Here the standard conditions adopted were:—Gas pressure: 1.5 mm discharge: 120 m.a. positive column type discharge between *K* and *A* (Fig. 1), probe (p_2) potential: -25 volts with respect to *A*. Small current differences (to the left of the curve) not representable on the scale of Fig. 7 were easily readable on the galvanometer used (sensitivity 10^{-8} amp. per mm). Such calibration curves were obtained by admitting small measured doses of A to carefully purified Ne by means of a dosing system employing only small Hg cut-offs and running the discharge only long enough to obtain the necessary readings (on account of a gradual clean-up of the A by the discharge).

At the standard probe potential the current varies only relatively slowly with the potential. This is shown in Fig. 8 where curve A represents a complete voltage-current characteristic for p_2 for the case of 0.0125 percent A. As the A percentage is decreased the positive currents decrease much faster than the negative currents until with the purest gas obtainable the two branches of the curve become nearly symmetrical.

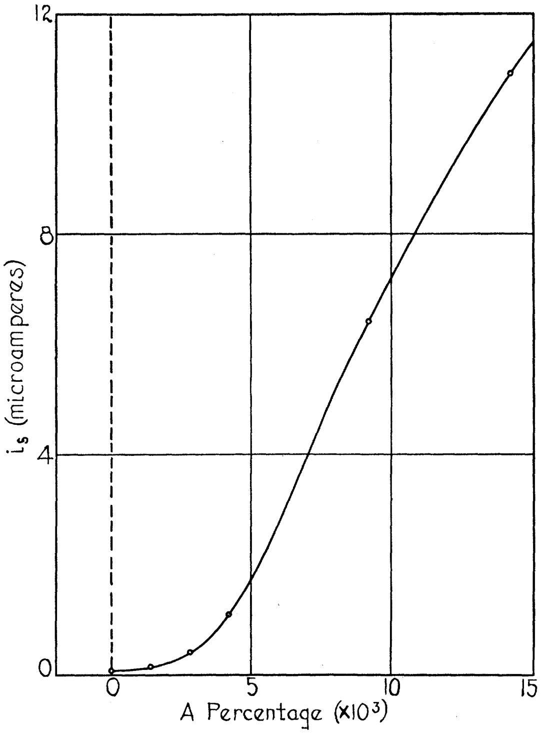

FIG. 7. Standard probe current as a function of A percentage.

Fig. 8 also shows the effect on the currents of strong irradiation on the space between the probe and the discharge (including the space around the probe).[34] The positive currents are decreased about 37 percent and the negative currents about 18 percent (effect not shown). If this percentage decrease in i_s is plotted

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[34] Cf. C. G. Found and I. Langmuir, last-mentioned paper of reference 1, Fig. 9.

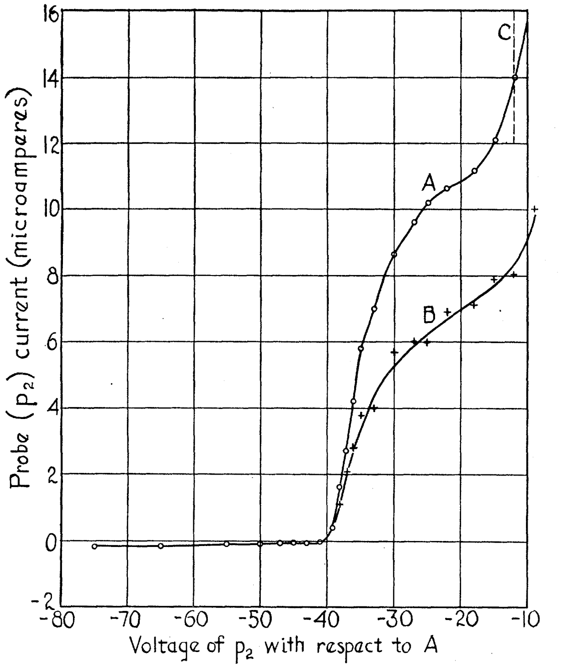

FIG. 8. Current voltage characteristics of probe p_2; *A*, without irradiation; *B*, with irradiation. A percentage 0.0125.

against A percentage a curve like Fig. 5 is obtained, which when extrapolated backward as in Fig. 5, indicates a maximum residual impurity at zero A percentage equivalent to less than 0.00025 percent A (compare § IVb).

The method has been used advantageously in the present experiments in keeping a check on the gas purity and in measuring A content; the state of gas purity could practically be read at all times from a dial. Such a rapid means of measuring impurity (e.g., A) content is especially desirable on account of the gradual (and sometimes fairly rapid) clean-up of the impurity by the discharge.

The upper limit of pressure at which the method is useful has not been determined but it has been found to lose its sensitivity rapidly at pressures much below 1 mm. The method has been used with He with success comparable to that obtained with Ne. With A as the main gas the method is of practical use only in detecting and measuring very small percentages of Hg. Small measured doses of H_2 and N_2 added to Ne gave i_s readings of the same order of magnitude as those obtained with similar doses of A, indicating cross sections for ionization of the same general order of magnitude in all these cases.

APPENDIX B

The effect of wall reflections on the transmission of radiation down a glass tube

Fig. 9 shows an example of the results obtained in an experimental study of the law of decrease of light intensity with distance inside a nonex glass tube of 2.5 cm internal diameter. In this study a thermopile was mounted at one end of the tube, the receivers of which substantially filled the whole field. A plane source of light filling the tube was approximated by mounting a small automobile headlight lamp 3 cm behind a white paper diffusing disk and movable with it. Distances were measured from the paper disk to the thermopile receivers.

It is seen from Fig. 9, curve A, that inside the glass tube the total intensity falls off quite closely according to the inverse first power of the distance (slope of curve 0.97 over the range 10–60 cm, which was as far as the measurements were carried out. Curve 2 shows that, without

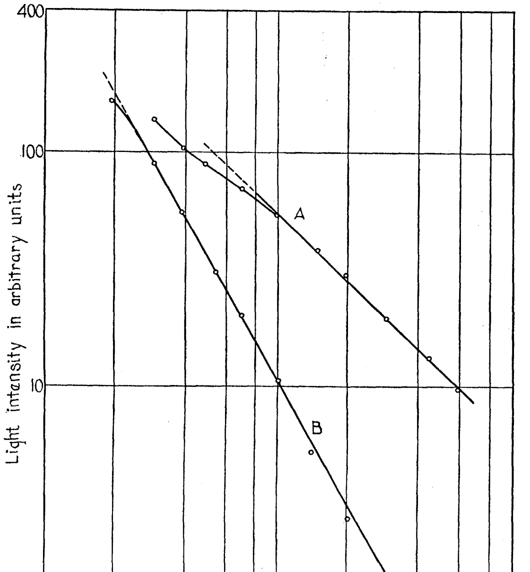

FIG. 9. Curve A: the rate of decrease of light intensity, with distance from the source, inside a glass tube. Curve B: the same without the glass tube.

the glass tube, the expected inverse square law was practically obtained; the line has the slope 1.9 over the range 4–20 cm which was as far as these measurements were carried out. On account of the finite size of the source the inverse square law would not be expected to hold at distances smaller than 4 cm. That the line has a slope 1.9 instead of 2 may be explained in that the apparatus was not completely removed from reflecting objects.

By comparison of curves A and B of Fig. 9 it is found that at 40 cm distance the effect of the glass tube is to increase the intensity more than 20-fold.

By placing a sheet of white paper over the end of the glass tube instead of the thermopile the intensity of illumination appeared quite uniform.

By comparison of the reflection coefficients for glass at small grazing angles of λ770A as found by O'Bryan[35] and similar reflection coefficients (somewhat less) for the radiations used here as calculated for unpolarized light by use of Fresnel's equations, it is concluded that, but for absorption in the gas, the resonance radiations in the present experiments would fall off with the distance even more slowly than according to the inverse first power. This helps to account for the unexpectedly large effects at considerable distances from the discharge.

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[35] H. M. O'Bryan, Phys. Rev. **38**, 32 (1931).