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THEORY OF IONIZATION BY CUMULATIVE ACTION AND THE LOW VOLTAGE ARC.

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Synopsis.

Theory of Ionization by Cumulative Action of Successive Impacts by Electrons and by Quanta of Resonance Radiation.—The phenomena of the low-voltage arc seem to require, for their explanation, ionization of the gas molecules in two (or more) successive stages. In the theory here developed it is supposed that each electron from the cathode after falling through a minimum potential difference reaches an active zone in which it collides either with a neutral molecule and partially ionizes it or with a partially ionized molecule which thereby becomes completely ionized. Each molecule when partially ionized emits a quantum of resonance radiation and this may go off in any direction and will in a short distance be absorbed by a neutral molecule which thereby becomes partially ionized and emits another quantum of radiation. So the passage through the gas of the quanta of resonance radiation initially set free by electronic impacts is analogous to the diffusion of foreign gas molecules. *Equations for the case of coaxial cylindrical electrodes* are derived for the proportion of molecules partially ionized (1) by direct impact and (2) by resonance radiation in terms of quantities which can all be readily measured except τ the mean life of the ionized molecules and $1/\rho$ the scattering coefficient for the radiation, for which (except ρ for mercury) only upper and lower limits can be estimated. The substitution of experimentally determined values leads to the conclusion that, under normal circumstances, partial ionization by photo-impact is many times as great as that by electronic impact alone and is necessary and sufficient to account for the observed ionization. The possibility of complete ionization by successive photo-impacts alone is also discussed.

Theory of Low-voltage Arc.—If n_0 is the number of electrons emitted and P_0 is the proportion of partially ionized molecules in the active zone, n_0P_0 is the number of molecules ionized per second. Since the positive ions move more slowly than electrons, each positive ion neutralizes the space charge due to $4\sqrt{(2 \times 1840M)}$ electrons; hence the electronic current increases to $1/(1 - 242P_0\sqrt{M})$ times the value it would have without ionization, provided the current is limited by the space charge around the cathode. As P_0 is increased by increasing the temperature of the filament or the applied potential, the current first increases to the saturation thermionic current, then the negative space charge is replaced by a positive space charge, the potential drop becomes concentrated near the cathode, the temperature of the cathode is raised by bombardment by positive ions, increasing n_0 and hence P_0; as a result the current increases at an accelerated rate, instability is usually soon reached and the arc strikes suddenly. The chief function of the gas is to give the

positive space charge around the cathode which is the distinguishing feature of the arc. If n is the saturation value of thermionic emission, the maximum current will be $3/2ne$ or $2ne$ depending on whether the voltage is below or above the minimum ionizing potential.

Low-voltage Arc in Mercury Vapor.—Recent experiments indicate that the *striking voltage* is about 5.6 instead of 4.9 volts, and that the arc may be dependent on either the 4.9 volt (2536 Å.) or the 6.7 volt (1849 Å.) radiation according to the age of the vapor. Thus there seem to be *two meta-stable states of the neutral mercury atom.*

Theory of Temperature of Ionization of Gases.—It is pointed out that resonance radiation must also be the chief factor in temperature ionization both in the electric furnace and in the sun and other stars.

1. INTRODUCTION.

IN two recent papers the writer emphasized the impossibility of explaining low voltage arcs by ionization of gas molecules by single electron impacts.[1] By a low voltage arc, is meant one which strikes and operates at a voltage less than the minimum ionizing potential of the gas. The phenomena seem to demand, for their explanation, ionization of gas molecules in successive stages by two or more separate agents. Hughes has suggested the name "cumulative ionization" to describe such effects and has given a survey of the subject in his recent Report on Photoelectricity.[2] Cumulative action is probably an important factor also in temperature ionization, but it is in the low voltage arc that it can be most easily investigated.

There are three possible processes of cumulative ionization which seem reasonable in the light of our present knowledge: (1) Ionization by Successive Impact; (2) Photo-Impact Ionization; (3) Ionization by Successive Photoelectric Action. In the first of the writer's earlier papers an attempt was made to test the first of these possibilities. The equations there derived, however, are not accurately applicable to actual experimental conditions, so that the conclusions reached in the former paper must be considered as quite tentative. In the present paper the first two of these processes are tested by comparing the amount of ionization observed experimentally with the amount predicted by each of the processes under the conditions of the experiment. While there is uncertainty regarding the magnitude of several quantities appearing in the equations, yet the argument leads to some important and fairly definite conclusions.

2. (*a*) TOTAL CURRENT IN ABSENCE OF ARC.

Let Fig. 1 represent a discharge tube, in which A is the anode and C is the incandescent cathode which emits the electrons whose impacts

[1] PHYS. REV., 15, p. 476, 1920; Phil. Mag., 43, p. 531, 1922.

[2] National Research Council Bull., Vol. 2, No. 10.

against gas molecules may result in their complete or partial ionization. If the applied accelerating potential difference V exceeds the minimum radiating potential V_r of the gas, there will be inelastic collisions, and partial ionization of some of the molecules, together with emission of resonance radiation, will occur. Let the shaded area represent the region in which, on the average, these effective impacts occur. As a result of these collisions, suppose a fraction P of the molecules in this shaded region to be in a partially ionized state, capable of being completely ionized by the impact of any electron which has not yet lost its energy. If n electrons leave the cathode, then Pn is the resulting amount of ionization.

Each molecule thus ionized adds to the total current in two ways: (1) by contributing two additional ions, and (2) by the effect of the relatively slowly moving positive ions in neutralizing some of the space charge around the filament and thus permitting the escape of more electrons from it. These additional electrons may also be effective in producing further ionization, which will liberate more electrons, and so on. The total resulting current can thus be expressed as the sum of an infinite number of terms, forming a converging series, which can readily be expressed in a simple form as follows.

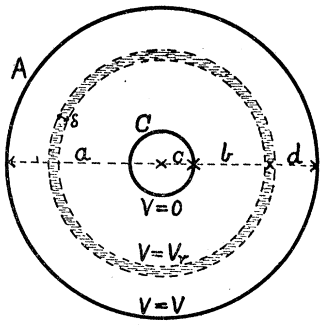

Fig. 1.

Each positive ion is drawn toward the cathode, through the outward stream of emitted electrons, and both make numerous collisions with molecules, since the phenomena in which we are interested are important only provided the mean free path is small in comparison with the distance between the electrodes. The average rate of motion of an ion through the gas is proportional to $\lambda\bar{c}$, where λ is its mean free path and $\bar{c}$ is its average velocity. The mean free path of the electrons is $4\sqrt{2}$ times greater than that of the ions and their average velocity is $\sqrt{1840M}$ times greater, where M is the molecular weight on the basis of 1 for the hydrogen atom. Thus each positive ion remains in the region of the negative space charge $4\sqrt{3680M}$ times as long as an escaping electron, neutralizes the space charge of that number of electrons and permits that number to escape from the cathode. Furthermore, as will be shown later, the probability P of partial ionization of a molecule in the shaded region is necessarily proportional to the number of bombarding electrons.

Let n_0 be the number of electrons which would leave the cathode if there were no ionization. Due to these, a fraction P_0 of the molecules in the shaded region are partially ionized and the resulting number of molecules completely ionized is n_0P_0. This number of positive ions liberates $4\sqrt{3680Mn_0P_0}$ additional electrons from the cathode. Thus

$$n' = n_0(1 + 4\sqrt{3680MP_0})$$

electrons would leave the cathode if only the original n_0 could ionize. Putting, for the present, $4\sqrt{3680MP_0} = Cn_0$, we have

$$n' = n_0(1 + Cn_0).$$

But, if we include the effect of ionization due to those electrons liberated by positive ions produced by the n_0 electrons, we have

$$n'' = n_0(1 + Cn') = n_0(1 + Cn_0 + C^2n_0^2).$$

Similarly

$$n''' = n_0(1 + Cn'') = n_0(1 + Cn_0 + C^2n_0^2 + C^3n_0^3)$$

is the number of emitted electrons if we include ionization due to all the n'' electrons. The actual total number of electrons leaving the cathode is seen to be

$$n = n_0(1 + Cn_0 + C^2n_0^2 + \cdots) = \frac{n_0}{1 - Cn_0}.$$

Thus we have

$$n = \frac{n_0}{1 - 4\sqrt{3680MP_0}}, \qquad (1)$$

provided the current is limited by the negative space charge around the cathode.

It is easily possible to measure n and to calculate n_0 by the relation[1] $n_0 \propto V^{3/2}$, determining the constant of proportionality by measurements of n at values of V less than V_r, where n and n_0 are identical. Thus equation (1) enables definite values of P to be determined under definite experimental conditions and permits a quantitative test of the values of P predicted by the theories of ionization by successive impact and photo-impact ionization to be outlined later.

Incidentally, this equation offers an explanation of the striking of an arc. As P_0 is increased, by increasing n_0 or the applied potential, n increases more and more rapidly and would become infinite when

$$P_0 = 1/4\sqrt{3680M}$$

[1] Langmuir, PHYS. REV., 2, p. 402, 1913.

were it not limited to the value corresponding to the saturation thermionic current at the temperature of the cathode. The number of available electrons being thus limited, the negative space charge becomes neutralized and is finally replaced by a positive space charge as the voltage is raised. As the space charge becomes positive, the potential drop becomes concentrated near the cathode, so that the electrons attain their critical speed within a short distance of the cathode. This concentration of the region of effective impacts tends further to increase the probability of cumulative ionization, measured by P. At the same time the temperature of the cathode is raised by the bombardment of the positive ions, which increases n_0 and P_0. Thus, after ionization sets in, the current increases at an accelerated rate as the voltage is raised. This increase may be slow or rapid, depending on the value of n_0, so that the setting in of the arc may be made gradual enough to be experimentally followed in all of its stages. Usually, however, the conditions near the arcing voltage are such that P_0 spontaneously increases as a result of the more favorable distribution of potential and the increase in the cathode temperature, so that a point of instability is reached at which the arc strikes suddenly,—the further increase of current occurring spontaneously. In any case the presence of a positive space charge around the cathode is the distinguishing feature of an arc.

2. (*b*) Total Current in Arc.

If the arc is operating at a voltage a little larger than the minimum ionizing potential V_i, the maximum current is obtained if each of the n electrons emitted from the cathode ionizes a molecule, so that the total current is $(n + n)e = 2ne$.

If the arc operates at a voltage between the minimum radiating potential V_r and the minimum ionizing potential V_i, the maximum possible current occurs when half of the n electrons collide to partially ionize molecules and the other half complete the process of ionization. Thus, in the low voltage arc, the maximum current is $(n + n/2)e = 3/2ne$. In both cases n is the saturation value of thermionic emission from the cathode at its temperature.

Recombinations would diminish the above values somewhat. Probably this decrease due to recombination is not large in the case of an intense arc, since each loss by recombination liberates radiant energy which may contribute to another ionization, and since the ionization occurs close to the cathode so that there is only a small region in which electrons and positive ions exist together.

Thus the chief function of the gas in a low voltage arc is to give a positive space charge around the cathode, causing sufficient potential

gradient to give a saturation current with low voltages, and to raise the cathode temperature by ionic bombardments and thus increase the saturation current.

The foregoing conclusions have received very satisfactory experimental support, which will be discussed in a later paper.

3. THEORY OF IONIZATION BY SUCCESSIVE IMPACTS.

The n electrons per second from the filament are drawn through the gas and attain a speed corresponding to the minimum radiating potential V_r. Each will lose its energy at some subsequent impact and partially or completely ionize the impacted molecule, according as the molecule was in the normal or partially ionized state before impact. Let τ be the average interval of time during which a molecule remains partially ionized, *i.e.*, the average interval between excitation and radiation. If δ is the thickness and f the length of the layer within which, on the average, these effective impacts occur, and if a fraction P of the molecules are partially ionized at any instant, then $n(1 - P)$ molecules are partially ionized each second. The aggregate time of activation of all molecules partially ionized in the layer δ per second is $n(1 - P)\tau$. This, divided by the number of molecules in the layer, gives the fraction of the molecules in the region of effective impacts which are, at any instant, in the partially ionized state as the result of a direct electron impact. Calling this P_i, we have

$$P_i = \frac{n(1 - P)\tau}{vNp},$$

where p is the gas pressure, N the number of gas molecules per unit volume at unit pressure and v the volume of the layer in which effective impacts occur. If the electrodes are coaxial cylinders, as in Fig. 1, $v = 2\pi(b + c)f\delta$.

Furthermore, P is always very small compared with unity unless the arc has already struck, as is evident from equation (1). Under these conditions

$$P_i = \frac{n\tau}{2\pi(b + c)f\delta Np}. \tag{2}$$

In order to apply this equation it is necessary to know $(b + c)$ and δ. Simple consideration of the distribution of potential (see Fig. 1) shows that

$$(b + c) = a\epsilon^{-\frac{V - Vr}{V}\log\frac{a}{c}}, \tag{3}$$

where a and c are the respective radii of anode and cathode.

The calculation of δ is more difficult, for it depends on the average distance which the electrons move beyond the point at which they have

acquired energy eV_r before making an effective impact, and also on the distribution of velocities of electrons which causes them to gain the critical energy at different distances from the cathode.

Suppose, first, that all n electrons are emitted from the cathode with

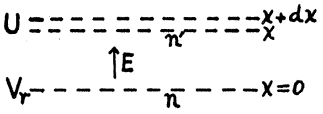

Fig. 2.

the same speed. Since all collisions at speeds less than the minimum radiating speed are perfectly elastic, they all attain this critical speed at the equipotential surface V_r whose position we shall specify by $x = 0$.

$$\nu = \frac{4rUp^2}{El^2} \tag{4}$$

is the number of collisions made by an electron, whose mean free path in the gas at unit pressure is l, in advancing unit distance.[1] E is the electric intensity and r is a numerical factor whose value lies between 0.87 and unity, and which may be neglected in our present work. If n' out of the n electrons reach the surface x, at potential U, without having lost their energy at an intervening impact, then $n'\nu dx$ of these will collide in the ensuing layer of thickness dx. The probability that any one of these impacts will be effective in activating a molecule is known to be, at least approximately, of the form $(U - V_r)/V_r = Ex/V_r$.[2] Thus the decrease in n' in passing through the layer dx is

$$dn' = -\frac{E}{V_r}\nu n' x dx,$$

whence

$$n' = n\epsilon^{-\frac{E\nu x^2}{2V_r}}.$$

The average distance which the electrons go beyond the surface V_r before colliding effectively is xdn'/n, integrated over all possible values of x, or

$$\bar{x} = \int_0^\infty \frac{E}{V_r}\nu x^2 \epsilon^{-\frac{E\nu x^2}{2V_r}} dx.$$

When this expression is integrated, and the value of ν substituted from equation (4), we find

$$\bar{x} = \sqrt{\frac{\pi}{8}}\frac{l}{p}, \tag{5}$$

which is about two thirds of the electronic mean free path.

[1] Benade and Compton, PHYS. REV., 11, p. 194, 1918.

[2] Compton, PHYS. REV., 15, p. 482, 1920.

This expression would give the appropriate value of δ (to at least the right order of magnitude) if all electrons left the cathode with equal speeds. Actually, however, they have initial speeds distributed approximately according to Maxwell's Law, and with an average energy $e\bar{V} = \alpha T$ characteristic of gas molecules at the temperature of the cathode.[1]

Thus the electrons, on the average, attain their critical energy eV_r within a layer whose thickness is $\delta' = \bar{V}/E$. Since this layer is distant $(b + c)$ from the axis,

$$E = \frac{V}{(b + c) \log a/c}.$$

Therefore,

$$\delta' = \frac{\alpha T}{eV}(b + c) \log \frac{a}{c}. \tag{6}$$

The value of δ, at least to a close approximation, is given by the sum of equations (5) and (6). An idea of the magnitude of $\bar{x}$ and δ' is obtained from the following calculations for mercury and helium, which have extremely small and large values, respectively, of the electronic mean free path.

TABLE I.

For Hg : $l = 0.0133$ cm.; $V_r = 4.9$ volts.
He : $l = 0.1175$ cm.; $V_r = 20.4$ volts.
Take $V = V_r + 1$, $a = 0.5$ cm., $c = 0.025$ cm.

p (mm.).	$\bar{x}$ (cm.).		$T°$ K.	δ' (cm.).	
	Hg.	He.		Hg.	He.
1	0.0083	0.0732	2000	0.0375	0.0150
2	0.0041	0.0366	2500	0.0470	0.0187
10	0.0008	0.0073	3000	0.0561	0.0225

It is seen that δ' is more important than $\bar{x}$ except at low pressures, particularly in the case of the heavier elements.

Returning to equation (2), we have for the final expression

$$P_i = \frac{n\tau}{2\pi(b + c)fNp\left\{\sqrt{\frac{\pi}{8}}\frac{l}{p} + \frac{\alpha T}{eV}(b + c) \log \frac{a}{c}\right\}}, \tag{7}$$

in which $(b + c)$ is given by equation (3). All quantities appearing here are known or can easily be measured except τ, which may tentatively be assigned a value of probably the right order of magnitude.

4. THEORY OF PHOTO-IMPACT IONIZATION.

On this theory, impacts in the shaded layer produce resonance radiation which is absorbed and reëmitted by atom after atom before escaping

[1] Sih Ling Ting, Roy. Soc. Proc. A., 98, p. 374, 1921.

from the gas, so that, as a result of each atom which is "activated" by a direct impact, many others are indirectly activated through absorption of radiation. Thus the probability P_r that an atom in the shaded region of effective impacts is in a partially ionized condition as a result of absorbed radiation is greater than the probability P_i of activation by direct impact. Our problem is to derive an expression for P_r.

It will be seen that the passage of radiation of the resonance type through the gas may be handled by expressions of the same type used to describe the diffusion of ions or of foreign molecules through a gas. A beam of light, passing through an absorbing or scattering medium falls off in intensity according to the law $I = I_0\epsilon^{-\alpha/x}$, where α is the absorption coefficient. A stream of particles passing through a gas is reduced by collisions, or scattering, according to the law $n = n_0\epsilon^{-x/l}$, where l is the mean free path. By analogy, let us call λ the mean free path of the radiation, defining it as the reciprocal of the absorption coefficient, or the distance in which the intensity of a beam falls to $1/\epsilon$ of its value as a result of resonance scattering. Then the average speed of the radiation $\bar{c}$ is this distance λ divided by the time of "activation" τ. We may then apply the diffusion equation

$$\int\int \frac{1}{3}\lambda\bar{c}\,\frac{\partial N'}{\partial n}\,dS = -\int\int\int R dx dy dz, \tag{8}$$

where N' is the number of activated atoms per unit volume at any point in the gas, R is the net rate at which atoms are becoming activated by direct electron impacts and n is the outward normal to the closed surface over which the surface integral and within which the volume integral are taken.

This equation may have a mere formal, and not a physical, similarity to the case of diffusion of particles. However, there are grounds for quantelizing the radiant energy in units of magnitude $h\nu$, since it is known that this amount of energy is absorbed by an atom in becoming "activated" and it must be emitted again when the atom radiates and returns to the normal state. In this case the mean free path λ may be physically similar to the mean free path of a gas molecule. However this may be, it seems safe to use equation (8) to calculate N', which is our purpose.

Referring to Fig. 1, $n(1 - P)$ quanta of resonance radiation are produced by electron impacts each second in the cylindrical layer of radius $(b + c)$, length f and thickness δ. Some of this radiation diffuses toward the anode and some toward the cathode. Let the corresponding numbers of quanta be $n_a(1 - P)$ and $n_c(1 - P)$, respectively. There will be one

cylindrical surface within the layer δ across which the net radiation flux will be zero and which we may call the neutral surface. If we apply equation (8) to the region bounded by this surface and a co-axial surface of radius r, lying outside the neutral surface, we have

$$\frac{1}{3}\lambda\bar{c}\frac{dN'}{dr}(2\pi rf) = -n_a(1-P);$$

whence

$$N_a' = -\frac{3n_a(1-P)}{2\pi f\lambda\bar{c}}\log r + C_a$$

is the value of N' at any point outside the neutral surface, distant r from the axis. If the reflecting power of the electrodes for resonance radiation is negligibly small, as is approximately the case for most substances, $N_a' = 0$ when $r = a$, so that

$$N_a' = \frac{3n_a(1-P)}{2\pi f\lambda\bar{c}}\log\frac{a}{r}.$$

Similarly, at points inside the neutral surface,

$$N_c' = \frac{3n_c(1-P)}{2\pi f\lambda\bar{c}}\log\frac{r}{c}.$$

We have $n_a + n_c = n$ and at the neutral surface $r = (b + c)$ we have $N_a' = N_c' = N'$. From these relations it is easily shown that, at the neutral surface,

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\frac{\log\frac{a}{b+c}\log\frac{b+c}{c}}{\log\frac{a}{c}}. \tag{9}$$

We implicitly assumed, in deriving this, that the thickness δ is negligible in comparison with the distance between the electrodes. This is nearly enough true in cases where low voltage arcs can be obtained. If the reflecting power of the electrodes for resonance radiation were considerable, equation (9) would take a more complicated form. It should, however, give results of the right order of magnitude in the cases to which we wish to apply it.

If the space charge around the cathode is negative, and if the voltage V is not much larger than V_r, then the critical layer δ is near the anode and we may replace a by $(b + c)$ in the denominator, so that

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\log\frac{a}{b+c}.$$

Substituting for $(b + c)$ from equation (3) we have

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\frac{V-V_r}{V}\log\frac{a}{c}. \tag{10}$$

If $1/\rho$ is the scattering coefficient of the gas at unit pressure for the resonance radiation, *i.e.*, ρ is the distance in which the intensity of a beam would fall to $1/\epsilon$ of its value, then p/ρ is the scattering coefficient at pressure p. If a fraction P of the atoms are partially ionized, and therefore unable to absorb resonance radiation, we have

$$\lambda = \frac{\rho}{p(1 - P)} \tag{11}$$

as the definition of the effective mean free path λ of the radiation. Putting $\bar{c} = \lambda/\tau$, we have

$$N' = \frac{3p^2 n\tau}{2\pi f\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}, \tag{12}$$

since the factor $(1 - P)^3$ may be neglected owing to the small value of P possible by equation (1).

We can now derive P_r, the fraction of atoms in an activated state because of absorbed resonance radiation, for $P_r = N'/Np$, where Np is the number of molecules per unit volume. Thus, finally,

$$P_r = \frac{3pn\tau}{2\pi fN\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}. \tag{13}$$

5. IMPORTANCE OF P_i AND P_r.

The total probability of partial ionization in the region of effective impacts is $P = P_i + P_r$. It is found that P_r is much larger than P_i under conditions in which low voltage arcs are obtained, for

$$\frac{P_r}{P_i} = \frac{3p^2(b + c)\delta}{\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}.$$

δ is the sum of $\bar{x}$ and δ' and is seen, in Table I., to be of the order of 0.01. $(b + c) \log a/c$ is of the order of unity in ordinary apparatus. If the arc strikes at about 0.1 volt above the minimum radiating potential, $(V - V_r)/V$ is of the order of 0.01. The pressures range from 0.5 to 10 mm. R. W. Wood [1] gives data from which ρ may be calculated to be 0.000675 cm. for the 2536 line of mercury vapor. Lamb [2] gives a very general law of resonance scattering, applicable if *every* molecule possesses an oscillator of proper frequency, from which it is readily shown that

$$\rho = \frac{1.54}{N\lambda_r^2}, \tag{14}$$

[1] Recent Researches in Physical Optics.

[2] Camb. Phil. Soc. Trans., 18, Stokes Commemoration, 1900.

where λ_r is the wave-length of the resonance radiation. This gives a minimum possible value of ρ which, in the case of the mercury 2536 line, is 10,200 times smaller than the experimental value, indicating that not all the molecules contain this type of oscillator or that their natural frequencies are distributed over a sufficient frequency range to account for the discrepancy. As far as the writer is aware, ρ has not been experimentally determined in any case except for the mercury 2536 radiation.

Using the experimental value of ρ for mercury, it is found that the ratio P_r/P_i is of the order of 10,000. Under any ordinary conditions, therefore, the direct effect of impacts is negligible in comparison with the indirect effect due to radiation in producing partially ionized atoms, capable of ionization by a low velocity impact.

The above comparison is possible without any knowledge of the time interval τ or the magnitude of the thermionic current. It is of interest, also, to see whether the probable *absolute* values of P_r or P_i are of the right order of magnitude to explain the size of the currents at which low voltage arcs are observed to strike.

Take the following reasonable values for the quantities involved. a = 0.5 cm., c = 0.025 cm. (20 mil wire), f = 1 cm. give the dimensions of the apparatus. V_r = 4.9 volts, l = 0.0133 cm. for mercury and V_r = 20.4 volts, l = 0.1175 cm. for helium are definite constants, as are also $N = 3.6(10)^{16}$ per c.c., $\alpha = 2(10)^{-16}$ ergs/degree and $e = 4.77(10)^{-10}$ e.s.u. $V = V_r + 1$ is a striking voltage for an arc in mercury or helium which is very easily realized with only moderate thermionic currents.

$\tau = 6(10)^{-7}$ sec. is the most favorable experimental value determined for any substance.[1] It was found for the D_3 line of helium. No determination of τ for a resonance line has ever been made. This is the most uncertain value entering into the calculations. $n = 1.84(10)^{14} V^{3/2}$, where V is in volts, gives the largest (hence most favorable) possible thermionic current. This is calculated from Langmuir's formula for the current limited by space charge in *vacuo*. Actually the current is less than this, since the presence of gas around the cathode reduces the rate of escape of electrons and thus increases the space charge for a given number of electrons. Furthermore, it is found experimentally that the currents need not be nearly so large as this to produce an arc at $V = V_r + 1$. Nevertheless, take this as the most favorable possible value.

ρ = 0.000675 cm. for mercury vapor, and is unknown, but probably smaller, for helium.

Substitution of these values in equation (7) for P_i gives the results in Table II.

[1] Stark, Ann. d. Phys., 49, p. 731, 1916.

TABLE II.

Values of P_i.

p (mm.).	$T°$ K.	Hg.	He.
1	2000	5.1 $(10)^{-7}$	12.6 $(10)^{-7}$
2		2.8	10.8
10		0.6	5.0
1	2500	4.7	12.1
2		2.6	10.0
10		0.55	4.2
1	3000	4.1	11.6
2		2.2	9.4
10		0.46	3.7

If these results are substituted in equation (1) we find n/n_0, or the ratio in which ionization has increased the total current just before the striking of the arc, as shown in Table III.

TABLE III.

Values of n/n_0.

p (mm.).	$T°$ K.	Hg.	He.
1	2000	1.00177	1.00061
2		1.00096	1.00052
10		1.00021	1.00024
1	2500	1.00161	1.00059
2		1.00089	1.00048
10		1.00019	1.00020
1	3000	1.00141	1.00056
2		1.00075	1.00045
10		1.00016	1.00018

These values are entirely inadequate to account for the experimentally observed values of n/n_0, which may range, roughly, from 2 to 100. Furthermore, they indicate variation both with pressure and temperature which is in a direction opposite to that observed.

R. W. Wood [1] has recently shown that, in the *excitation of fluorescence* of mercury vapor by light of wave-length 1850–2100 Å., there is a definite time interval of 1/15,000 second between the absorption of the light and the subsequent bursting into luminosity by the vapor. If this is the time interval which is effective in the present problem, we should put

[1] Roy. Soc. Proc. A., 99, p. 362, 1921.

$\tau = 6.7(10)^{-5}$ sec., which is about 110 times larger than the value assumed above. Substitution of this quantity gives values of P_i for mercury ranging between $5.6(10)^{-5}$ and $0.5(10)^{-5}$ and values of n/n_0 between 1.24 and 1.02 in the above tables. These values approach in magnitude the observed values of n/n_0, but are still too small. Furthermore, the assumed maximum value of n is about 200 times larger than actual values of n at which low voltage arcs can be obtained in mercury vapor. Taking this into account it seems as if the values of n/n_0 in Table III. represent the predictions of the Theory of Successive Impacts fairly accurately. In any case the indications are that successive impacts play a relatively insignificant part in cumulative ionization.

Turning now to photo-impact ionization and substituting the above values in equation (13) for P_r, we find $P_r = 0.055p$ in the case of mercury vapor. No calculation can be made for helium because of lack of knowledge of ρ. At pressures at which a low voltage arc will strike in mercury, *i.e.*, above about 0.15 mm., this value of P_r is more than sufficient to cause the arc to strike, as indicated by putting $n/n_0 = \infty$ in equation (1). For instance, at 1 mm. pressure, the calculated value is about 180 times as large as necessary to produce the arc. In other words, the theory would predict an arc at a thermionic current at least 180 times less than the maximum possible current which was assumed above. This is in good agreement with observations in an experiment, still in progress, by Mr. Y. T. Yao and the writer. 1/180 part of the value of n assumed above is $1.46(10)^{13}$, which corresponds to a thermionic current of 2.2 micro-amperes. In an apparatus of the dimensions assumed above, and under approximately the assumed conditions, the arcs strike at currents of a few micro-amperes.

Thus it appears probable that the ionization observed in gases at voltages less than their minimum ionizing voltages is due chiefly to photo-impact ionization. We cannot say more than this until the constant τ is measured for the resonance radiation of those gases in which low voltage arcs can be obtained, *i.e.*, monatomic gases and vapors.[1]

[1] *Note.*—Hughes has pointed out the fact that, in a gas whose minimum radiating potential is less than half the ionizing potential, no two cumulative effects at this voltage could contribute sufficient energy for ionization. The experiments of Mr. Yao and the writer indicate, however, that proper corrections for velocity distribution place the striking voltage of the low voltage arc in mercury at about 5.6 volts, instead of 4.9 volts. Thus the electron impact against the partially ionized atom must contribute an amount of energy sufficient to increase the total potential energy to the value required for ionization, as demanded by theory. Furthermore, experiments to be later described by Mr. Yao indicate that the low voltage arc in mercury may be dependent on either the 4.9 volt (2356) or the 6.7 volt (1849) radiation according to whether the vapor is in close or distant communication with its liquid surface. This and spectroscopic evidence suggests two meta-stable states of the neutral mercury atom. Thus the actual conditions are somewhat more complicated than those assumed in the theory.

6. IONIZATION BY SUCCESSIVE PHOTOELECTRIC ACTION.

F. Horton and Miss A. C. Davies have recently suggested that the second stage in the process of ionization may also be accomplished by the absorption of radiation from neighboring impacts.[1] Their experimental results with helium prove the diffusion of resonance radiation through the gas, the existence of photo-impact ionization and, apparently, the existence of ionization by photoelectric action on atoms which are already partially ionized by absorption of radiation. If there exists a second type of resonance radiation which is capable of ionizing atoms which have partially absorbed the first type, or if the resonance potential exceeds half the ionizing potential, we should expect this radiation to be more effective than electron impacts in completing ionization, for the same reason that radiation is more effective than impacts in producing the first stage of ionization. An attempt to reduce this type of ionization to quantitative form led to some suggestive results, but the equations become so complicated and the relation of the second photoelectric process to the first involves such uncertain hypotheses that it will not be discussed here. The importance of this type of ionization, which seems proved in the case of helium, can probably best be established in the case of metallic vapors by direct experiment or by a proven inadequacy of the two alternative processes discussed in this paper.

7. DISCUSSION.

The chief result which seems to emerge definitely from the above discussion is that resonance radiation plays a very important part in ionization at low voltages. At high voltages and low gas pressures, as in the Geissler tube discharge, there is good opportunity for ionization by direct single impacts. But if the potential drop in the distance of a mean free path is much less than the ionizing potential, conditions are unfavorable for direct ionization and the cumulative type of ionization preponderates.

If we carry conditions a step further in the same direction we have the case of purely temperature ionization, in which there is no potential drop at all. Here, presumably, cumulative ionization is practically the only type and resonance radiation is an essential agent in the process.

This concept has an interesting application to the case of ionization in the solar chromosphere, recently discussed by Saha.[2] He treats the chromosphere as an enclosure at constant temperature and uses Nernst's equation of the isobar to calculate the degree of ionization of any gas,

[1] Phil. Mag., 12, p. 746, 1921.

[2] Phil. Mag., 40, pp. 472, 809, 1920.

treating ionization as a dissociation. This theory has been remarkably successful in explaining and predicting features of the solar spectrum. The theory fails, however, to explain the fact that, although sodium and barium have equal ionizing potentials, barium is much more completely ionized than is sodium. This may be explained, as has been pointed out by Professor H. N. Russell and the writer,[1] by taking account of the effect of resonance radiation of these elements. For the chromosphere is not an enclosure, but a layer through which is passing an enormous flux of energy from the hotter interior. Observation shows, and there are reasonable explanations of it, that this flux is particularly deficient in radiation of the resonance type for sodium,—much more deficient than in the corresponding radiation for barium. Thus neutral barium atoms must exist largely in the partially ionized state. This is equivalent to a relative lowering of the ionizing potential for barium, permitting more complete ionization.

The spectral peculiarities of light excited in the low voltage arc (and also in the high temperature furnace) are necessary consequences of the mechanism of ionization here discussed. If the gas pressure is high and the electric field weak, so that the energy gained by an electron between collisions is small, there is little chance of exciting any radiation except that of the resonance type corresponding to the inelastic impact of lowest velocity. Thus we get the "single line" spectrum. If the pressure is less or the field greater, an appreciable number of electrons may attain speeds sufficient to excite a second type of resonance radiation of shorter wave-length. Such lines are the $1S - 1p$ and $1S - 1P$ lines of the alkaline earths. As a result of cumulative ionization, a complete spectrum will be present, but will be weak and will become, relatively to the resonance line or lines, of vanishingly small intensity as the voltage and current are diminished.

As soon as the arc strikes, conditions are at the other extreme. Owing to the positive space charge around the cathode, the electric intensity in this region is very large and the electrons are shot out into the gas with practically the maximum velocity attainable at the applied voltage. Then the resonance lines are not particularly "favored," and the entire arc spectrum appears. If the voltage is sufficiently large, the enhanced lines will appear. In fact, in this type of arc, there is realized somewhat the same distribution of potential which has been secured in a more manageable way by Foote, Meggers and Mohler[2] by the introduction of an additional gauze electrode near the cathode, and which has made possible their most interesting work on enhanced spectra.

[1] Astrophys. Jour. (in print).

[2] Phil. Mag., 42, p. 1002, 1921.

In conclusion, mention should be made of a method of experimentally testing the above theories. The most decisive test of photo-impact ionization would be to illuminate a gas with its resonance radiation from an external source and see whether ionization can then be observed with electron impacts of velocity less than the ordinary minimum ionizing velocity. Such an effect has been observed in iodine vapor,[1] but this is a case of fluorescence and not true resonance—though the mechanism of ionization is probably similar. Last year, Mr. Yao made careful attempts to prove photo-impact ionization in this way with mercury and sodium vapors, but with results which were indecisive because of peculiar difficulties in getting intense resonance radiation of exactly the effective wave-length into a gas from an external source. These experiments are now being repeated under more favorable conditions.

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Since this article was submitted, a very interesting paper by F. M. Kannenstine (Astrophys. Jour. 55, p. 345, 1922) has described a method of determining the time during which the metastable (partially ionized) helium atoms persist in a helium arc after the exciting voltage has been removed. The time is about $2.4\ (10)^{-3}$ second, which is much larger than the value of τ used above. If cumulative ionization is by successive impacts, then Kannenstine's value should be the value of τ for helium. If the ionization is of the photo-impact type, however, Kannenstine's measurements give the time required for the resonance radiation to escape from the region of effective impacts, which may include the time of many absorptions and reëmissions, and therefore τ would be much smaller than $2.4\ (10)^{-3}$. This point, and other recent evidence will be discussed briefly in another communication.

[1] Smyth and Compton, PHYS. REV., 16, p. 501, 1920.