Volume 2 *April, 1930* *Number 2*

REVIEWS
OF
MODERN PHYSICS

ELECTRICAL DISCHARGES IN GASES

PART I. SURVEY OF FUNDAMENTAL PROCESSES

By
KARL T. COMPTON, *Princeton University*
and
IRVING LANGMUIR, *Research Laboratory of the General Electric Company*

TABLE OF CONTENTS

A. PRODUCTION OF ELECTRONS AND IONS IN GASES

B. LIBERATION OF ELECTRONS AND IONS FROM ELECTRODES

C. DISAPPEARANCE OF ELECTRONS AND IONS

D. MOTIONS OF ELECTRONS AND IONS

AS A result of continuous intensive investigation of the properties and phenomena of ionized gases during the past thirty years, it is likely that most of the fundamental elementary processes occurring in gas discharges are now recognized. The great problem at present is to analyze the complex phenomena so that they can be quantitatively described in terms of these fundamental processes in every region of each one of the widely differing types of gas discharges. These fundamental processes are classified and described briefly in this article. Some of them will be discussed more in Part II, which will deal primarily with a study of gas discharges themselves. In the present discussion particular attention is given to those aspects of the subject which are still rather obscure, and some phenomena which are very important are not discussed in such detail because they are quite familiar and generally understood. In every case, however, an attempt is made to give such references to the literature of the subject as will enable an interested reader easily to make his own more intensive study.

A. PRODUCTION OF ELECTRONS AND IONS IN GASES

(1) **Ionization by electron impact,** originally suggested by Townsend,[1] appears to be of first importance in nearly all gas discharges. In order to

---

[1] Townsend, Phil. Mag. 1, 198 (1901); "Electricity in Gases," Chap. VIII (Oxford 1915).

ionize any normal gas molecule,* the impacting electron must possess kinetic energy in excess of a certain minimum amount which is characteristic of each particular type of gas molecule. This minimum energy is usually specified as the *Minimum Ionizing Potential*[2] of the gas, since it is usually measured in terms of the potential difference V_i through which an electron must move in order to acquire this minimum ionizing energy. There are also higher ionizing potentials corresponding to the removal of two electrons simultaneously, or to the removal of a second after the first had previously been removed, or to the removal of one of the more deep-seated electrons from the molecule. Since the minimum energy required to remove an electron from a molecule is the same, whether this energy be supplied by an impinging electron (impact ionization) or by absorption of radiation (photo-ionization), we can equate these energies giving

$$eV_i = h\nu_i,$$

where ν_i is the convergence frequency of the spectral absorption series. This relation, whose proof and applications were so actively pursued by physicists between five and ten years ago, is now so well understood that no further discussion of it need by given here.

The *probability of ionization of a gas molecule by an electron impact*[3] apparently increases from zero approximately linearly with increase in energy of the impacting electron from the minimum ionizing energy up to about twice this energy, and then more slowly.[4] The experimental determination of this probability involves measurement first of the number of new ions formed per unit path by an electron of given energy and second of the measurement of the total number of collisions made per unit path by the electron. As we shall see, this latter quantity is not easy to measure nor even to define accurately. Thus, while it is often convenient to know approximately the proba-

---

* The term "molecule" is here used in its original sense, including monatomic as well as polyatomic molecules.

[2] For methods of determining ionizing potentials and their values see Compton and Mohler, "Critical Potentials," National Research Council Bulletin No. 192; Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," (Springer, 1926); Geiger and Scheel, "Handbuch der Physik," Vol. XXIII (1927); Bloch, "Ionization et Resonance des Gas et des Vapeurs," (Société Francaise de Physique, 1925); Mohler, "Critical Potentials of Atoms and Molecules," International Critical Tables Vol. VI, pp. 69–74 (1929).

[3] Compton and Van Voorhis, Phys. Rev. **27**, 724 (1926) give values for a number of gases up to 400 volts. Jones, Phys. Rev. **29**, 822 (1927) and Bleakney, *ibid.*, **35**, 139 (1930) give values for Hg vapor. Buckmann, Ann. d. Physik **87**, 509 (1918) gives values for air up to electron energies of 25,000 volts. Penning, Physica **6**, 290 (1926) shows that, if actual experimental values of the numbers of electron collisions are used in computing the probability, then the probability of ionization *at a collision* is found for a number of gases to be about the same function of the electron energy, if the unit of energy for each gas is taken to be its minimum ionizing energy.

[4] This is contrary to conclusions drawn by von Hippel, Ann. d. Physik **87**, 1035 (1928) whose results seem impossible to reconcile with those of other observers and whose method of measurement seems to have allowed some unsuspected complicating factor to play an overwhelming role. See also, however, Funk, Ann. d. Physik **4**, 149 (1930).

bility of ionization at an impact, it is simpler for purposes of the theory of gas discharges to deal directly with the more accurately determined quantity, the number of new electrons produced by ionization per unit path at a specified gas pressure by an electron of given energy. This may be called the *probability of ionization per unit path at unit pressure.*[3]

If the energy of the impacting electron exceeds the amount necessary to disengage two or more electrons from the molecule, then it is necessary to consider the nature of these products of ionization, *i.e.* whether they are singly, doubly, triply, etc., ionized. This was first done by Smyth,[11] and very recently by Bleakney,[3] who has determined also the probability of production of each of the various types of Hg ions as a function of the energy of the impacting electrons. These results are shown in Fig. 1.

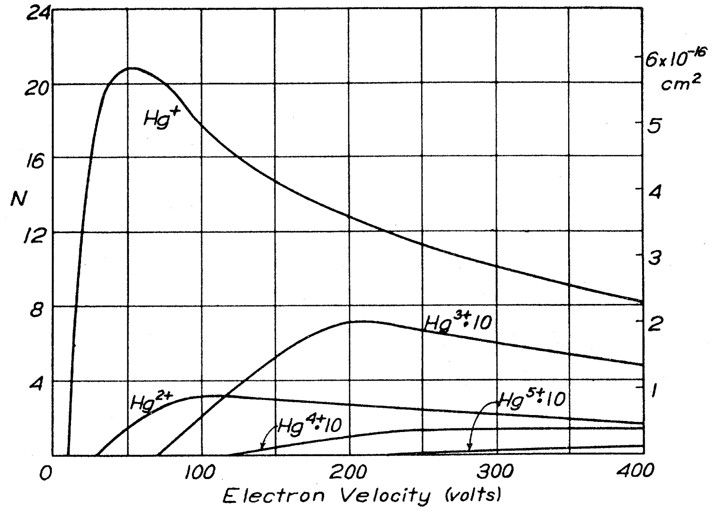


Fig. 1. Number of Hg^+, Hg^{2+}, Hg^{3+}, Hg^{4+} and Hg^{5+} ions per cm path per mm pressure at 0°C. To the right is the effective cross sectional area for ionization of a Hg atom.

The method by which the values of P in Table I were found is such that a doubly ionized molecule would be recorded as two single ions, a trebly charged molecule as three ions, etc. To the extent to which multiple ionization occurs by single electron impacts at the higher voltages, the values in Table I are in error *if considered in connection with any theory of ionization by impact.* For such considerations, separate measurements of single and multiple stages of ionization are desirable, as attempted by von Hippel, and achieved by Bleakney. But there is high probability that a multiply charged ion, at a collision with a neutral molecule, robs an electron from the molecule, so that very quickly the state is reached in which the multiply charged ions are replaced by singly charged ions of equivalent total charge. Furthermore, since the probability of forming original multiply charged ions appears always to be less than that of forming singly charged ions, it would seem justifiable to take values of P such as those in Table I to be correct *if considered in connection with theories of gas discharges,* for here it is the total rate of production of ions which is of interest.

TABLE I. *Ionization of gases by electron impact.*

V_i = minimum ionizing potential.

$P(V)$ = probability that an electron with V volts energy will ionize a gas molecule in 1 cm. path at 0.01 mm pressure at 28°C.[5]

C = constant in equation $P(V)=C(V-V_i)$, which holds rather accurately in the range V_i to $2V_i$. Most of the ionization by direct electron impact in gas discharges occurs within this range except in cases of very high voltage and low gas pressure.

Gas	V_i	$P(20)$	$P(30)$	$P(50)$	$P(100)$	$P(300)$	C
Cs	3.88 volts						
K	4.32						
Na	5.12						
Hg	10.39	0.067	0.146	0.195	0.213	0.193	0.00753
He	24.53	.000	.002	.009	.016	.018	.00039
Ne	21.47	.000	.003	.010	.026	.035	.00037
A	15.69	.017	.052	.093	.112	.094	.00365
*H_2	15.8 ±	.006	.021	.033	.038	.032	.00156
*N_2	16.3 ±	.004	.028	.072	.101	.101	.00223

* In the case of polyatomic gases the minimum ionizing potential is not as sharply defined as in monatomic gases, because there is a probability that the molecule will suffer a change in nuclear separation simultaneously with its ionization. This probability can be calculated by the quantum mechanics,[6] and the probability of a large change is found to be small. The experimental values given are therefore sufficiently accurate for ordinary purposes.

The impacting electron and the new electron formed in an ionizing collision may in subsequent collisions with gas molecules produce new ions. When the free paths of the electrons are small compared to the dimensions of the gas space, or where the boundaries are negatively charged so that the electrons continue to ionize until their energies fall below the ionizing potential, the total number of ions produced by each primary electron becomes independent of gas pressure.[7] Recently improved methods for measuring this total ionizing power of electrons of various energies have been developed

TABLE II. *Total ionizing power of electrons.*[7] *Ions per primary electron of V volts.*

Gas	$V=30$	50	75	100	150	— 0
He		1.2		2.9		
Ne			1.2	2.0		
Ar	0.45	0.9		1.6	2.2	
H_2				1.4		2.8
N_2			1.3	1.6		
Hg	1.1	1.4		2.7		5.3

---

[5] Compton and Van Voorhis, Phys. Rev. **27**, 724 (1926). Jones, *ibid.* **29**, 822 (1927), who used a method for the lower voltages superior to that of Compton and Van Voorhis in insuring more uniform energies of the ionizing electrons, obtained values of P for Hg similar to those of Compton and Van Voorhis, but approximately 25 percent larger at the lower values of V. This suggests that perhaps the constant "C" should be about 25 percent larger than shown in Table I for all the gases. The values above 100 volts are probably quite accurate.

[6] Condon, Phys. Rev. **32**, 858 (1928).

[7] Langmuir and Jones, Phys. Rev. **31**, 402–3 (1928).

which yield values somewhat larger for He and smaller for other gases than were given by earlier work.[8] Some of these values are given in Table II.

If the impacting electron has more than the minimum amount of energy required to ionize the molecule, the excess of energy must be retained by the impacting electron, or transferred to the ejected electron, or used in exciting or further ionizing the ion,—or to any combination of these. From the laws of momentum transfer it is obvious that the energy transformed into kinetic energy of the ion will be insignificant. There is evidence that the excess energy is not retained wholly by the impinging electron but may be shared in any proportion between the two electrons,[9] though there is some indication that its even distribution between them is considerably less probable than the retention of most of it by one or the other.[10]

The immediate *products of such ionization* are the ejected electron and a positive ion which is simply the original molecule minus an electron.[11] In many polyatomic molecules the internal energy of this "primary" ion is greater than that of its dissociated products, so that it may split up into a positively charged and one or more neutral "secondary" products of ionization. Generally this secondary transformation requires some external stimulus, such as a collision, even though it is energetically possible without external aid, but there are a few cases known where this dissociation, subsequent to ionization, follows spontaneously and perhaps instantaneously.[12] This behavior subsequent to ionization has been well explained[13] in terms of the relation between internal energy and nuclear separation of the atomic constituents of the neutral molecule and of the primary molecular ion, which relations can be found from a study of the band spectrum. In hydrogen, for example, the primary product of ionization is H_2^+. If the gas pressure is such that these ions collide with molecules, they tend to dissociate or to associate[14] into $H^+ + H$ or $H_3^+ + H$, the relative amount of H_3^+ being greater if the effective temperature (mean kinetic energy) of the ions is low.[15] It was formerly thought that polar molecules always dissociated into positive and negative atom-ions upon ionization, because the ionizing potentials of the halogen halides could be accurately calculated from a thermodynamic cycle based upon this hypothesis.[16] This is now known to have been a fortuitous agree-

---

[8] Johnson, Phys. Rev. **10**, 609 (1917); Lehmann and Osgood, Proc. Roy. Soc. **A115**, 609 (1927).

[9] Eldridge, Phys. Rev. **20**, 456 (1922); Langmuir and Jones, Phys. Rev. **31**, 385–7 (1928).

[10] Harnwell, Phys. Rev. **34**, 661 (1929).

[11] Smyth, Proc. Roy. Soc. **A102**, 283 (1922); **A104**, 121 (1923); Phys. Rev. **25**, 452 (1925); Hogness et al, Phys. Rev. **26**, 44, 284 (1925); **30**, 26 (1927); **32**, 784, 936, 942 (1928).

[12] Hogness *et al*, Phys. Rev. **32**, pp. 784, 936, 942 (1928); Kallmann and Rosen, Zeits. f. Physik **58**, 52 (1929).

[13] Franck, Trans. Far. Soc. **21**, part 3 (1925); Condon, Phys. Rev. **28**, 1182 (1926); **32**, 858 (1928); Winans and Stueckelberg, Proc. Nat. Acad. Sc. **14**, 867 (1928); Condon and Smyth, *ibid.* **14**, 871 (1928).

[14] Hogness and Lunn, *ibid.* **26**, 44 (1925).

[15] Brasefield, Phys. Rev. **31**, 52 (1928).

[16] Born, Verh. d. D. Phys. Ges. **21**, 13, 679 (1919); Grimm, Zeits. f. Physik Chem. **102**, 113, 141, 504 (1922); Foote and Mohler, "Origin of Spectra," Chap. VIII (Chem. Cat. 1922).

ment. In HCl, for example, the primary product of ionization is HCl^+, and there appear to be no secondary products.[17]

(2) **Photo-ionization** may occur if the normal molecule is exposed to radiation of frequency greater than the value of ν_i in the relation $h\nu_i = eV_i$. The probability of such ionization is proportional to the radiation density and varies with frequency. Quantitative experimental studies are extremely difficult because, except in the case of the alkali metal vapors, the effective radiation lies too far in the ultraviolet to permit easy estimation of radiation intensities. With light of this spectral region, moreover, photo-electric emission of electrons from the walls of the apparatus masks the gas ionization unless special precautions are taken.

The probability B_ν of photo-ionization may be defined as the probability that an atom, exposed to unit density of radiation of frequency ν, will be ionized within unit time. All theories agree in predicting that this probability is maximum for radiation at the arc series limit, of frequency ν_i, and decreases rapidly with increasing frequency. In general the experiments confirm this. For very high frequencies (X-rays) there is the well-known Owen's law, according to which the absorption coefficient of a substance is inversely proportional to the cube of the frequency. Since the energy absorbed in any absorption act is $h\nu$, we see that Owen's law may be stated in the form: "the probability of an absorption act varies inversely as the fourth power of the frequency." Since absorption produces photo-ionization, Owen's law is equivalent to

$$B_\nu = C\nu^{-4}.$$

By the statistical principle of detailed balancing, there is derived a relation[18]

$$\frac{B_\nu}{q_\nu} = \text{const}\,\frac{\nu - \nu_i}{\nu^3} \tag{1}$$

between B_ν and the effective cross section of the atom for recombination q_ν (which is equal to the electron velocity v times the coefficient of recombination α of an ion and an electron of velocity v to form the atom). But the effective recombining cross section q_ν is not known experimentally with accuracy (see section C2) and theories regarding it are not sufficiently developed to be strictly applicable. Milne[16] assumed that the probability that an electron wil be captured by an ion varies inversely as the square of their relative velocities, *i.e.* that $q_\nu \alpha$ "varies as" $1/v^2$, which led directly to

$$B_\nu = C'\nu^{-3}$$

since $\frac{1}{2}mv^2 = h(\nu - \nu_i)$ (see Eq. 65 in section C 2). This assumption is justifiable as an approximation, for Milne shows that it is the asymptotic form of q_ν as the relative velocity approaches zero. Morse and Stueckelberg[19] have recently proved this also by wave mechanics and have, moreover,

---

[17] Barton, Phys. Rev. **30**, 614 (1927).

[18] Becker, Zeits. f. Physik **18**, 325 (1923); Milne, Phil. Mag. **47**, 209 (1924).

[19] Morse and Stueckelberg, to appear in Phys. Rev.

shown how q_ν varies in general with velocity for various states of the hydrogen atom. These latter expressions, while exact, have thus far proved too complicated to permit of expression in form suitable for substitution in Eq. (1). Thus even the simplest case, that of hydrogen, has resisted exact solution. Kramers[20] derived Owen's law. Becker[18] assumed that q_ν varies with velocity in the same way that the probability that a canal ray robs an electron from a neutral molecule is found to vary with their relative velocity[21] and obtained from Eq. (1)

$$B_\nu = \frac{\text{const}}{(\nu - \nu_i)\nu^3}\left[1 - \frac{(\nu - \nu_i)^2}{4\nu_i^2}\right] \tag{2}$$

which is inapplicable for $\nu \gg \nu_i$ but reduces for ν close to ν_i to

$$B_\nu = \frac{\text{const}}{(\nu - \nu_i)\nu^3} \cdot \tag{3}$$

By methods of the recent quantum theories Suguira, Oppenheimer and Reiche have derived expressions[22] for the case of a hydrogenic atom in which B_ν varies as $1/\nu^5$, $1/\nu^{4.3}$, $1/\nu^5$ respectively. Obviously the situation on the theoretical side is far from solved with any degree of assurance.

On the expermental side, recent very careful work[23] shows conclusively that photo-ionization in vapors of calcium and rubidium agrees well with Eqs. (2 and 3), and not at all with any of the other equations. Even in these cases only relative values for different frequencies are known. In the case of potassium vapor[24] all results to date are in serious conflict with all the above theories, although this may be due to a complicating contribution of K_2 molecules to the observed ionization.

Thus, although it is observed in these vapors and some others,[25] we are as yet unable to estimate with confidence the role of photo-ionization in gas discharges. It is generally believed, however, that the absolute magnitude of photo-ionization is generally very inferior to that of ionization by electron impacts.

It should be stated that some photo-ionization has been found in mercury[26] and alkali metal vapors[23] for radiation of frequency less than the limit ν_i,—particularly for radiation belonging to the line absorption spectrum. This is undoubtedly due to cumulative effects involving two or more con-

---

[20] Kramers, Phil. Mag. **46,** 836 (1923).

[21] Rückhardt, Ann. d. Physik **71,** 377 (1923); Zeits. f. Physik **15,** 164 (1923).

[22] Suguira, Jour. de Phys. **8,** 113 (1927); Oppenheimer, Zeits. f. Physik **41,** 268 (1927); Reiche, *ibid.* **53,** 168 (1929).

[23] Kunz and Williams, Phys. Rev. **22,** 456 (1923); Foote, Mohler and Chenault, *ibid.* **27,** 37 (1926); Lawrence and Edlefsen, *ibid.* **34,** 233 (1929).

[24] Williamson, Proc. Nat. Acad. Sc. **14,** 793 (1928); Lawrence and Edlefsen, Phys. Rev. **34,** 1056 (1929).

[25] Mohler, Phys. Rev. **28,** 46 (1926).

[26] Rouss and Giddings, Proc. Nat. Acad. Sc. **11,** 514 (1925); **12,** 447 (1926); Houtermans, Zeits. f. Physik **41,** 619 (1927); Foote, Phys. Rev. **29,** 609 (1927).

tributions of energy. However, this effect seems to be larger than can be accounted for by any of the proposed theories.

A review of the subjects of Recombination and Photo-ionization has just been published by Mohler.[27]

(3) **Cumulative ionization** refers to ionization in two or more stages. This may be accomplished in a variety of ways. By electron impact or by light absorption a molecule may be excited to a state which falls short of complete ionization. It will then revert to a state of lower energy either spontaneously and with the emission of radiation, or as the result of a subsequent collision in which the energy may be radiated, or transferred to the impacting molecule. Experiments show that ordinarily an atom or molecule, if undisturbed by collisions, remains in the excited state for a time interval of the order of 10^{-8} sec.[28] If this state happens to be a "metastable" state, from which spontaneous escape by radiation is inhibited according to the "selection principles" of the quantum theory, the lifetime in this state is much longer. If the gas pressure is high so that molecular collisions are frequent, the life may be limited to the average interval before the next collision. But in any situation an excited molecule has a certain average period of existence denoted by τ. If, while in this excited state, it is struck by another electron or absorbs more radiant energy, or collides with another excited molecule, it may acquire enough additional energy to complete its ionization. *Successive impact*, *successive absorption*, or a combination of an absorption and an impact which may be termed *photo-impact* etc. denote the various ways in which this cumulative ionization may occur.

The rate of cumulative ionization is obviously jointly proportional to the intensities of the contributing ionizing factors, and to the average lifetime τ of the excited state. If the ionization is due entirely to current through the gas, the rate of two stage cumulative ionization should be proportional to the square of the current, other factors being assumed constant.

Except at the very lowest pressures, there are two phenomena which enhance the rate of cumulative ionization by increasing the concentration of excited molecules. The first of these is the strong absorption by the gas of the *"resonance" radiation* which arises when molecules revert from an excited state to the normal state. By this absorption other molecules are in turn excited,—and they in their turn will excite still others when they radiate their energy. In this way the energy is passed on from molecule to molecule, thus multiplying the chance that each quantum of energy may ultimately contribute to ionization. This passage of resonance radiation through a gas can be treated as a problem in diffusion[29] by the equation

---

[27] Mohler, Phys. Rev. Supp. **1**, 216 (1929).

[28] Wien, Ann. d. Physik **60**, 597 (1919); **73**, 483 (1924).

[29] Compton, Phil. Mag. **45**, 570 (1923); Milne, Jour. London Math. Soc. **1**, 1 (1926); Zemansky, Phys. Rev. **29**, 513 (1927). Milne's equation is more general than Compton's Eq. (4) in that it is not limited in application to cases in which the dimensions of the apparatus greatly exceed the effective "free path" of the radiation.

$$\int\int \frac{1}{3}\frac{1}{\alpha^2\tau}\frac{dN'}{dn}\,dS = -\int\int\int R\,dxdydz \tag{4}$$

where α is the absorption coefficient for the radiation, τ the average life of an excited state, N' the concentration of excited molecules, n the normal to a surface element dS and R the total rate of production of new quanta of resonance radiation within the closed surface. The second phenomenon is the tendency of molecules in excited states to go into *long lived metastable states* as the result of collisions with other molecules. It is still uncertain as to which of these phenomena is the more important in the cumulative ionization of mercury vapor and the noble gases. In the vapors of the alkali metals, which have no metastable states, the first process alone can be effective.

TABLE III. *Average life times τ of some excited molecules.*[30]

Molecule	Excited to emit:	Average life
H	H_α H_β or H_γ	$1.85(10)^{-8}$ sec.
Hg	$1s^1S_1-2p^3P_1(2536)$	9.7
Hg	$2p^3P_1-2s^3S_1(4358)$	1.81
Na	$1s^2S_1-2p^3P_{1,2}(NaD_{1,2})$	3.70
N	arc lines	9.33
N	spark lines	1.35

The experimental values of Wien's in Table III are not necessarily the true values of τ characteristic of the excited states in question, since the conditions of the experimental measurements permitted also higher states of excitation, from which the lower states in question could be replenished in one or more stages. For example hydrogen atoms excited to the fifth quantum state can emit H_γ by reversion directly to the second quantum state. But they may also revert successively to the fourth, third and second states, emitting H_α in the last transition. In this case the value of τ measured for H_α would be the sum of τ's for the three transitions. Wien's method gives a value of τ which is a weighted mean of all such processes. The probabilities of the transitions are such, however, that the experimental values are not greatly in error from such complications. Methods which are free from this complication can be used to determine the life times of some optically excited states.[31]

Maxwell[32] has measured τ for lines of mercury atoms in various states of ionization and found values ranging between 10^{-8} and $9(10)^{-7}$ sec. for lines of Hg II, Hg III, Hg IV, with a regular gradation of values which suggests that the mean life is longer for higher states of ionization. His calculation of the mean life τ of an excited state from the aggregate rate of its depopulation leads to

$$\tau = \left(\sum_{n',k'} A_{n,k}^{n',k'}\right)^{-1}$$

---

[30] Wien, Ann. d. Physik **60**, 597 (1919); **73**, 483 (1924); Kerschbaum, *ibid.* **79**, 465 (1926); Dempster, Astrophys. Jour. **57**, 193 (1923).

[31] Cario, Zeits. f. Physik **10**, 185 (1922); Turner, Phys. Rev. **23**, 464 (1924).

[32] Maxwell, Phys. Rev. **84**, 199 (1929).

where the summation is taken over all the states n', k' to which the state may change, $A^{n',k'}_{n,k}$ being the transition probability of such change. This expression, previously given by Tolman[33] and others, indicates that the same life should be found from measurements of all spectral lines originating from the same state. This expression also neglects the repopulation of the state in question from higher states.

The average "natural" life times of metastable states are of a larger order of magnitude than those of other excited states. Saha and Kothari[34] derived the theoretical expression

$$\tau=\frac{3c^5m^2}{\pi^2e^2h\nu^3}$$

for the natural lifetime of a metastable atom whose "forbidden" line has wave number ν. For $\lambda=10{,}000\,A$ this leads to $\tau=0.15$ sec.

In actual experimental discharge tubes the lives of the metastable atoms are limited by collisions with the walls of the apparatus or with other molecules, so that the actual lifetime is a characteristic of the apparatus rather than of the atom itself. Under such conditions it is given by a relation

$$\frac{1}{\tau}=\frac{A}{p}+Bp$$

where p is the pressure and A and B involve effective collision radii, dimensions of apparatus, etc. The term A/p gives the rate of disappearance of metastable atoms at the walls of the apparatus and the term Bp gives the rate of disappearance within the apparatus. Couliette[36] showed that metastable atoms of Hg diffuse through Hg according to the ordinary laws of gas diffusion, and as if the effective radius of a metastable atom is 1.5 times that of a normal atom. Much work has been done to discover the probability that a metastable atom will revert to the normal state as the result of collisions with other atoms or molecules. Apparently the most effective destroying collisions are those with molecules which can absorb the available energy by becoming themselves excited or dissociated,—such as dissociation of H_2 by metastable Hg. Dorgelo[35] found metastable atoms of neon in neon to persist as long as 0.10 sec. A critical survey of recent work in this field,[36] with an interesting theoretical analysis, has just been published by Zemansky.[37]

The *concentration of metastable atoms* in a discharge tube is very important to know, if they are active agents in ionization either of the gas or the electrodes. The only methods suitable for measuring this concentration are

---

[33] Tolman, Phys. Rev. **23,** 693 (1924).

[34] Saha and Kothari, Naturwiss. **17,** 271 (1929).

[35] Dorgelo, Physica, **5,** 429 (1925).

[36] Metastable neon in neon, Meissner and Graffunder, Ann. d. Physik **84,** 1009 (1927); in H_2, N_2, A, Eckstein, *ibid.* **87,** 1003 (1928). Metastable Hg in Hg, Zemansky, Phys. Rev. **29,** 513 (1927); Coulliette, *ibid.* **32,** 636 (1928); in N_2, Pool, Phys. Rev. **33,** 22(1929); Asada, Phys. Zeits. **29,** 708 (1928).

[37] Zemansky, Phys. Rev. **34,** 213 (1929).

optical ones, based on absorption or dispersion,[38] and these require extreme care in technique and interpretation. For neon in the positive column of glow discharges, Kopfermann and Ladenburg found the concentrations in the metastable states s_3, s_4 and s_5 to be given approximately by

$$N_s = \frac{aJ}{bJ+c} \tag{1.5}$$

where J is the current density and a, b, c are production and extinction factors which are independent of current but depend on pressure. For the state s_5 they give $a = 3.5(10)^{11}$, $b = 0.365$, $c = 1$ with J in milliamperes per cm^2. It is thus obvious that the concentration of metastable atoms may be as large as $(10)^{12}$, and therefore comparable with that of positive ions (as we shall see in Part II).

(4) **Ionization by positive ion impact** is well known in the cases of α particles and canal rays and has long been assumed[39] to occur to some extent with positive ions of much smaller velocity. Ions apparently begin to be very effective ionizing agents when their velocities are as large as those of electrons which have fallen through the minimum ionizing potential,[40] which means positive ions of energies corresponding to tens of thousands of volts. When their energies are much smaller, however, they become exceedingly ineffective, so that the ionization due to these impacts is masked by a variety of complicating secondary ionizing effects which are more or less inherent in any method of experimental investigation. As a result, our direct knowledge of this phenomenon is very meager and much of the evidence is contradictory.[41]

In apparatus which could have detected about one ionizing act for every thousand primary positive ions, no evidence of ionization of hydrogen by sodium or potassium ions was found for velocities of the ions up to about 1000 equivalent volts.[42] In the noble gases, ionization by potassium ions could be detected at velocities as low as 100 volts, and the trend of values in this region indicated that the probability of ionization would fall, if not strictly to zero, at least to very much less than 0.1 percent at velocities somewhat below 100 volts. The ionization of several gases by potassium ions at 750 volts, expressed as the number of ions formed per initial positive ion per cm path at 0.01 mm pressure, is:[43] argon 0.00288; neon 0.00112; nitrogen 0.00124; air, 0.00098; hydrogen 0.0000. Perhaps the most nearly direct evidence of ionization at velocities as low as 40 volts is found in the excitation of mercury arc lines in mercury vapor bombarded by sodium ions,[44] but quantitative

---

[38] De Groot, Zeits. f. Physik **55,** 52 (1929); Kopfermann and Ladenburg, *ibid.* **48,** 15, 26, 51 (1928); excellent discussion of the general theory of dispersion.

[39] Townsend, Electrician, April 3 (1903); "Electricity in Gases," Chap. IX (Oxford 1915).

[40] J. J. Thomson, "Rays of Positive Electricity," 1 ed. p. 36.

[41] Loeb, Science **66,** 627 (1927).

[42] Hooper, Jour. Frank. Inst. **201,** 311 (1926).

[43] Sutton, Phys. Rev. **33,** 364 (1929); Sutton and Mouzon, *ibid.* (in print).

[44] Tate, Phys. Rev. **23,** 293 (1924).

conclusions cannot be drawn from this. Experimental difficulties have thus far made it impossible to draw any definite conclusions regarding the efficiency of ionization of molecules of a gas *by ions of the same gas*, except for showing that this efficiency is of a smaller order of magnitude than that of ionization by electron impacts. Direct experiments designed to discover the ionizing efficiencies of positive ions of energies in the range of those to be expected in arcs, sparks and glow discharges are very much needed.

(5) **Ionization by collisions of the second kind** is ionization effected by a transfer of energy from an excited or ionized molecule to some other molecule. The prime requisite is that the energy available be adequate for the ionization. The probability of this process seems always to be maximum if the available energy is just sufficient, and to decrease with excess of energy. Thus, at contact, an ion of one gas may capture a neutralizing electron from a neutral molecule of another gas of lower ionizing potential,[45] thereby ionizing the latter, and at the same time the latter ion may also be raised to an excited state.[46] In these cases one type of ion is simply exchanged for another. But new ions also may be produced, as by the action of metastable helium atoms in the 2^3S or 2^1S states (of 19.77 or 20.55 volts energy) in ionizing atoms of impurities at contact (all requiring less energy).[47]

(6) **Thermal ionization** of a gas may be treated as a case of thermal dissociation in which the products are an electron and a positive ion, and the degree of ionization may be calculated as a function of the temperature T and pressure P of the gas by applying Nernst's heat theorem. This idea has been applied with striking success to problems of ionization in stellar atmospheres by use of the so-called "Saha" equation and its successive refinements.[48] There have been attempts to apply this equation to calculate the degree of ionization of gas in an enclosure,[49] but these are seriously wrong because of neglect of the very important part which may be played by emission of electrons from the walls of the enclosure. But a more general equation will apply equally well to a star or to a laboratory device, *viz.*

$$\log_{10}\frac{n_e n_p}{n_a} = -\frac{5040V_i}{T} + \frac{3}{2}\log_{10} T + 15.385 \qquad (5)$$

where n_e, n_p and n_a are the numbers of electrons, positive ions and atoms, respectively, per cm^3; V_i is the ionizing potential of the gas in volts and

---

[45] Harnwell, Phys. Rev. **29,** 683, 830 (1927); Hogness and Lunn, *ibid.* **30,** 26 (1927); Smyth and Stueckelberg, *ibid.* **32,** 777 (1928).

[46] Duffendack and Smith, Nature, May 21, 1927; Duffendack, Henshaw and Goyer, Phys. Rev. **34,** 1132 (1929).

[47] Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," p. 119 (Springer 1926). See also Penning, Zeits.f.Physik **57,**723 (1929, for the ionization of argon by metastable neon.

[48] Saha, Phil. Mag. **40,** 472 (1920); Proc. Roy. Soc. **99,** 135 (1921); Tolman, Jour. Am. Chem. Soc. **43,** 1630 (1921); Russell, Astrophys. Jour. **55,** 119 (1922); Fowler and Milne, Monthly Notices Roy. Astr. Soc. **83,** 403 (1923); Milne, *ibid.* **85,** 111 (1924); **86,** 8 (1925).

[49] Saha, Phil. Mag. **46,** 534 (1923).

T is the absolute temperature.[50] In particular, Langmuir and Kingdon showed that the proportional ionization of caesium atoms incident upon a hot metal surface is a thermal ionization which may accurately be calculated by this equation.

B. Liberation of Electrons and Ions from Electrodes

All processes of emission from electrodes are greatly dependent on their surface condition as regards surface films of foreign metals or adsorbed gases. For this reason it is not certain how accurately experimental data from special studies of these processes can be carried over to the actual conditions in gas discharges. It is likely that this can be done at least to a first approximation, though it is desirable, from the standpoint of the theory of gas discharges to investigate as many of these processes as possible under the conditions which obtain in the discharge.

(1) **Thermionic emission of electrons** is capable of yielding currents limited only by the temperatures to which the cathodes can be raised. At the melting point of tungsten, for example, the saturation emission is 480 amp./cm^2. The saturation current density j_s is a function only of the temperature T and the nature of the metal as defined by a certain constant ϕ_0 known as its *"work function"* and by another constant A:

$$j_s = AT^2\epsilon^{-e\phi_0/kT} = AT^2\epsilon^{-b/T}, \qquad (6)$$

where, by putting $e/k = 11{,}606$ degrees per volt, we can express ϕ_0 in equivalent volts. This equation was originally derived by a thermodynamical argument[51] based on the assumptions (1) that the potential energies of an electron inside and outside the metal surface differ by $e\phi$; (2) that $e\phi = e\phi_0 + (3/2)kT$, where ϕ_0 is independent of temperature; (3) that the electrons outside the metal follow the gas law $pv = nkT$; (4) that all electrons striking a surface are absorbed by it. Of these, (2) results as an approximation from a consideration of the Thomson coefficient based on assumptions (1) and (3), (3) is based on the experimental fact that the emitted electrons possess a Maxwellian distribution of velocities characteristic of the temperature of the emitting metal,[52] and (4) is known to be only approximately true, but the error thus introduced is probably nearly independent of temperature T(see ref. 57 below). Direct experimental confirmation of the relation

$$e\phi = e\phi_0 + (3/2)kT \qquad (7)$$

is very difficult. Such evidence as is available suggests a relation of this sort but with a somewhat larger temperature coefficient.[53]

---

[50] Langmuir and Kingdon, Proc. Roy. Soc. **107,** 61 (1925); Fowler, "Statistical Mechanics," p. 281 (Cambridge 1929).

[51] Richardson, "Emission of Electricity from Hot Bodies," Chap. II (1916); Phil. Mag. **23,** 601, 619 (1912); *ibid.* **24,** 740 (1912); *ibid.* **28,** 633 (1914).

[52] Richardson and Brown, Phil. Mag. **16,** 353 (1908); (see also ref. 57 below).

[53] Davisson and Germer, Phys. Rev. **20,** 300 (1922).

Subject to neglect of the contribution of electrons to the specific heat of a metal, to neglect of energy of surface charge, to acceptance of the Sakur-Tetrode chemical constant as the appropriate constant of integration for the Clapeyron equation and to assumption of zero reflecting power of all metals for electrons, it is predicted that A should be a universal constant[54] of value $A_0 = 60.2$ amp./cm^2 deg^2, and this seems to be the right value for a number of metals rather similar to tungsten. There is some evidence, however, that A is itself a function[55] of ϕ_0, such as $A = A_0 \exp(e\alpha/k)$, in which α is the negative temperature derivative of ϕ_0. For tungsten $\alpha = 0$, for platinum α is positive and for thoriated tungsten it is negative.

On the basis of Sommerfeld's recent theory of metals,[56] he and Fowler[57] have again derived Eq. (6), but with certain differences in interpretation. Fowler finds $A = 2A_0(1-r)$, where the factor 2 enters because of the two possible orientations of the electron spin vector, and r is the fraction of the electrons, incident on the metal surface from a surrounding electron atmosphere, which are reflected. On this theory, the variation in A for different metals is due to characteristic differences in this reflecting power r (a fact also recognized by Richardson). The experiments would support this theory if it could be shown that $r = 1/2$ for tungsten (for which $A = A_0$), $r < 1/2$ for platinum and $r > 1/2$ for thoriated tungsten. There is some little experimental suggestion that $r \sim 1/2$ for very slow electrons, but these experiments are subject to corrections which become very uncertain at low velocities. There are furthermore, convincing theoretical reasons against assuming an appreciable value of r for very slow electrons (see B 7). Thus Fowler's theory cannot be said definitely to be supported by experiments on this point. Sommerfeld shows that the work function $e\phi$ is the difference between the work required to take an electron out of the metal against the attractive forces at the surface and the contribution of the pressure of the conducting electrons within the metal toward overcoming these forces.

Despite these uncertainties in interpretation, Eq. (6) is one of the most accurately verified equations in the whole field of physics, since it holds within the degree of accuracy with which temperatures can be measured throughout a current range of about a million-million fold. Furthermore there is no doubt about the essential correctness of the interpretation of ϕ as the work necessary to remove a unit charge of electrons from a metal.

The more electropositive metals are characterized by smaller work functions and hence emit larger thermionic currents at any given temperature than do the electronegative metals. They are not, however, generally suitable for use as high temperature cathodes on account of their volatility. However, monatomic films of such substances on more electronegative metals adhere

---

[54] Dushman, Phys. Rev. **21**, 623 (1923); see also Richardson, "Emission of Electricity from Hot Bodies," p. 39.

[55] Du Bridge, Proc. Nat. Acad. Sc. **14**, 788 (1928); Bridgman, Phys. Rev. **31**, pp. 90, 862 (1928).

[56] Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

[57] Fowler, Proc. Roy. Soc. **A117**, 549 (1928); *ibid.* **122**, 36 (1929).

with remarkable tenacity and constitute convenient sources of low temperature emission. The best known of these are thorium[58] and caesium[59] on tungsten, which are typical of two methods of coating.

Thorium films are produced by diffusion of metallic thorium toward the surface. This diffusion is particularly rapid along crystal grain boundaries but must occur also from the interior of crystals to these boundaries and probably also through the surface layer of crystals. This diffusion occurs at a convenient rate at about 2100°K, and proceeds until the surface is covered by a monatomic layer of thorium. Such surfaces can be operated to give thermionic emission of about 1 amp. per cm^2 at the maximum temperature at which thorium is not lost by evaporation faster than it is replaced by diffusion.

Caesium films are produced by the deposit of caesium atoms from its vapor upon the tungsten surface. Its adherence up to temperatures as high as 900°K depends upon the fact that the ionizing potential of caesium atoms is less than the work function of tungsten, so that the tungsten robs the caesium atoms of their valence electrons when they strike the surface, and holds them on the surface as ions. If the temperature is raised high enough to evaporate them off the surface, they leave as ions so long as the work function of the surface exceeds the ionizing potential of the atom. If a metal of larger work function than tungsten is used, such as oxidized tungsten, the caesium adheres still more firmly and the maximum temperature at which emission can be obtained without loss of the film is raised. Similar effects are observed with vapors of rubidium and potassium.[60]

The degree of activation of such coated surfaces is conveniently expressed by a quantity θ, called by Langmuir "the fraction of the surface covered by adsorbed ions." This is approximately a linear function, of the work function so that

$$\theta=(\phi''-\phi)/(\phi''-\phi'), \tag{7.5}$$

where ϕ, ϕ' and ϕ'' are the work functions of the actual surface, of the most completely (effectively) coated surface, and of the clean surface, respectively.[58,59]

In gases at low pressures these activated surfaces, such as those of thorium, are easily destroyed (knocked off) by positive ion bombardment when the anode voltage is raised above certain critical values.[61]

The distribution of velocities of thermally emitted electrons is Maxwellian, and characteristic of the temperature of the emitting surface.[62] The mean kin-

---

[58] Langmuir, Phys. Rev. **22**, 357 (1923).

[59] Langmuir and Kingdon, Science **57**, 58 (1923); Proc. Roy. Soc. **107**, 61 (1925); Becker, Phys. Rev. **28**, 341 (1926); **29**, 364 (1927); Bell Telephone Laboratories Reprint No. B-412, August, 1929.

[60] Killian, Phys. Rev. **27**, 578 (1926).

[61] Kingdon and Langmuir, Phys. Rev. **22**, 148 (1923); A. W. Hull, Transaction Amer. Inst. of Electrical Engs. **49**, 753 (1928).

[62] Richardson and Brown, Phil. Mag. **16**, 353 (1908); Schottky, Ann. d. Physik **44**, 1101 (1914); Jones, Proc. Roy. Soc. **A102**, 734 (1923); Germer, Phys. Rev. **25**, 795 (1925).

TABLE IV. *Some thermionic work functions.*[63]

Metal	ϕ_0 (volts)	Metal	ϕ_0 (volts)
Hf	5.09	Th	3.35
*Pt	4.8 -6.35	**Th	2.63
W	4.52	**U	2.84
Mo	4.41	**Ce	2.72
Ta	4.07	**La	2.72
Zr	4.50	***BaO	1.68-3.44
**Zr	3.15	BaO+SrO	1.51-1.89
Cs	1.81	CaO	2.19
**Cs	0.72	MgO	1.02

* Pt, perhaps because of its electronegative character, is extremely hard to free from hydrogen and electropositive contaminants. It is only after the severest purification and degassing that the characteristic value 6.35 is reached.

** Monatomic layers on tungsten.

*** Values depend on treatment of the surface (flashing, bombardment, etc.).

etic energy of the electrons in equilibrium in a given volume is $(3/2)kT$, being $(1/2)kT$ for each of the three dimensions. For the electrons which cross or are emitted from a surface the mean kinetic energy is still $(1/2)kT$ for each of the two dimensions parallel to the surface, but the mean energy corresponding to the velocity component normal to the surface is kT, making a total of $2kT$ for the mean energy of the emitted electrons.

These energies may readily be expressed in equivalent volts defined by the relation

$$Ve = kT. \tag{8}$$

The value of e/k is conveniently expressed[64] as 11,606 degrees per volt $(10^8 \times 1.5911 \times 10^{-20}/1.3709 \times 10^{-16})$. Thus the mean energy $(2kT)$ of the electrons emitted at temperature T corresponds to $\overline{V}$ given by

$$\overline{V} = 2kT/e = 2T/11{,}606 \text{ volts}. \tag{9}$$

This mean energy corresponds to only 0.052 volt at room temperature 300°K, 0.41 volt at 2400°K and 0.63 volt at 3655°K, the melting point of tungsten.

The fraction n/n_0 of the emitted electrons which are capable of moving against a retarding field of V volts can be calculated from the Boltzmann equation[65]

$$n/n_0 = \epsilon^{-Ve/kT}. \tag{10}$$

Thus, for example, only one out of a thousand electrons from a hot cathode at 2400°K can move into regions which are more than 1.43 volts negative with respect to the cathode.

The heat of evaporation of electrons from a metal surface is the heat absorbed in the process of emitting an electron. It is analogous to the latent heat of evaporation of molecules from a liquid surface and is due to the fact

---

[63] Dushman, *ref.* 54; Dushman, Dennison and Reynolds, Phys. Rev. **29,** 903 (1927); Du Bridge, Phys. Rev. **31,** 236 (1928); Dushman, Int. Critical Tables VI, p. 53.

[64] Birge, Phys. Rev. Supp. **1,** 1 (1929).

[65] Langmuir and Mott-Smith,Jr., G. E. Rev. **27,** 449 (1929); Mott-Smith and Langmuir, Phys. Rev. **28,** 756 (1926).

that only the fastest electrons in the metal are able to escape. It and its converse, the heat of condensation, have been measured for electrodes in high vacuum,[66] and the latter also for electrons received by the anodes in gas discharges.[67] This heat of evaporation is found to be identical with the work function $e\phi$. The heat of condensation is perhaps the best way to determine the work function of an electrode in a neutral or ionized gas, since it may be measured without highly heating or otherwise influencing the electrode. With saturation emission the cooling effect due to loss of electrons increases exponentially with the temperature whereas the cooling due to conduction and radiation varies roughly as the first and fourth powers of the temperature, respectively. Hence at high temperatures the cooling effect due to thermionic emission may exceed that due to other causes.

(2) **Thermionic emission of positive ions** consists usually in the emission of charged atoms of electropositive substances such as the alkali or alkaline earth metals which are present, either purposely or accidentally as impurities on the surfaces of more electronegative metals.[68] Alkali atoms do not evaporate as ions from surfaces of their own metal. They do evaporate as ions from surfaces of platinum, iron oxide, etc. It seems likely that here, as in the case of alkali metal films on tungsten,[59,60] the criterion for evaporation as an ion is very nearly that the work function of the surface exceeds the ionizing potential of the atom. When the surface conditions remain constant, this positive ion emission varies with temperature according to an equation similar to Eq. (6).[69]

Quite recently another type of positive ion emission has been found, in which the ions are charged atoms of the heated metal itself, and not impurities. This is proved by measurement of their masses by a mass spectrograph. Wahlin[70] first reported this type of emission and has found that these characteristic ions are emitted by chromium, molybdenum, tungsten, rhodium, ruthenium, tantalum and columbium. They were not detected from iron, nickel, cobalt, copper, silver, gold, iridium, platinum, zirconium, palladium or antimony. Manganese is doubtful. All these metals gave the usual alkali impurities when first heated. The first group only gave the characteristic ion emission which persisted after the impurities had disappeared with continued heating.

L. P. Smith has investigated more extensively tungsten and molybdenum.[71] He finds these currents to vary with temperature according to an equation of the general type of Eq. (6), from which he calculates positive ion work functions of $\phi_{+0} = 6.55$ volts for tungsten and 6.09 volts for molybdenum.

---

[66] Richardson and Cooke, Phil. Mag. **20,** 173 (1910); *ibid.* **21,** 404 (1911); Cooke and Richardson, *ibid.* **25,** 624 (1913); Wehnelt and Jentzsch. Verh. d. D. Phys. Ges. **10,** 610 (1908)

[67] Schottky and Issendorff, Zeits. f. Physik **26,** 85 (1924); Van Voorhis, Phys. Rev. **30,** 318 (1927).

[68] Richardson, Phil. Mag. **16,** 740 (1908); Proc. Roy. Soc. **89,** 507 (1914); Davisson, Phil. Mag. **23,** 121 (1912); Barton, Harnwell and Kunsman, Phys. Rev. **27,** 739 (1926).

[69] Richardson, Phil. Mag. **4,** 98 (1902); Kunsman, Proc. Nat. Acad. Sc. **12,** 659 (1926).

[70] Wahlin, Phys. Rev. **34,** 164 (1929) and unpublished data.

[71] L. P. Smith, Phys. Rev. **34,** 1496 (1929); **35,** 381 (1930).

These values are much smaller than other estimates based on a simple thermodynamical energy cycle. Also the term corresponding to A in the equation corresponding to Eq. (6) does not agree with its theoretical value unless these positive ions are assumed to have a reflection probability of about 0.99999 if they strike the metal surface to condense upon it!! Hence it is obvious that the physical interpretation of this interesting type of emission is far from understood.

It should be emphasized that these "characteristic ion" currents are extremely small in comparison with other thermionic emission currents. For example measurements made in the Research Laboratory of the General Electric Company gave, from tungsten, about $5.4\ (10)^{-10}$ amp. per cm^2 at 2500°K and about $1.4\ (10)^{-8}$ amp. per cm^2 at 2800°K. These values indicate that the rate of emission of these ions is far less than the rate of evaporation of neutral atoms. Thus there is only about one ion for every 2000 atoms at 2500°K and about one for every 4200 atoms evaporating at 2800°K. One might suspect that this represents thermal ionization of the emitted metal vapor, but application of Eq. (5) shows that such thermal ionization would account for ionization of only about one in every million evaporated atoms, and is therefore quite inadequate as an explanation. Another suggestion is that such ion emission is causally related to the ionic nature of the metal lattice, but this is mere speculation at present.

For many purposes an extremely useful source of positive ions is obtained from a hot filament of electronegative metal in the presence of a vapor whose ionization potential is less than the work function of the filament.[59] For example, a tungsten filament at any temperature above 1200°K will send off as a positive ion *every* caesium atom which strikes it. In this way intense sources of positive ions can be obtained even though the vapor pressure of the source of these ions is so small that the vapor plays no detectable role in the discharge, except to supply these positive ions by contact with the filament. Such a source gives a current which is independent of the temperature of the filament, but is proportional to the pressure of the vapor.[72]

(3) **Photo-electric emission of electrons** occurs if a metal is illuminated by radiation of frequency ν greater than a threshold value ν_0 given by

$$h\nu_0 = e\phi \tag{11}$$

where h is Planck's constant and $e\phi$ is the work done in removing an electron from the metal. ϕ is generally called the "photo-electric work function" of the metal. The number of electrons emitted per second is directly proportional to the intensity of the incident radiation, but the velocities of emission are independent of the intensity.

Velocities of emission of photoelectrons are distributed between zero and a definite maximum which depends only upon the frequency of the radiation and the work function of the metal, as given by Einstein's well-known photoelectric equation[73]

---

[72] Bainbridge, Phys. Rev. **34,** 752 (1929).

[73] Einstein, Ann. d. Physik **17,** 145 (1905).

$$\tfrac{1}{2}mv_{\max}^2 = eV = h\nu - e\phi \tag{12}$$

which has been verified over the entire spectrum from near infrared to X-rays.[74] In it, V denotes the smallest retarding difference of potential which prevents the fastest electrons from going from the emitting to the receiving electrode. The ordinary interpretation of this equation is that the electron acquires energy $h\nu$ from the radiation and loses energy $e\phi$ in escaping.

Between zero and this maximum velocity there is a distribution of velocities such that the most probable energy is about half the maximum energy[75] in the case of ordinary or ultraviolet light acting on metal surfaces. When the photo-electric emission is caused by X-rays, the larger portion of emitted electrons have energies close to the theoretical maximum. The great generality of the $h\nu =$ energy relation suggests that those electrons which escape with less than the maximum energy must have lost the difference of energy at atomic encounters within the metal in the interval between acquiring the energy and escaping from the surface.[76]

Table V gives some typical data on initial energies of electrons, expressed in equivalent volts.

TABLE V. *Maximum emission energies of photoelectrons for various Metals and Wave-lengths.*

Metal	Threshold Å	V (volts)				
		4000	3000	2500	2000	1000
Pt[77] (outgassed)	1945	—	—	—	—	6.00
Pt[75] (ordinary)	2880	—	—	0.66	1.89	8.07
W[78] (outgassed)	2575	—	—	0.14	1.37	7.55
Hg[79] (liquid)	2735	—	—	0.42	1.65	7.83
Zn[75] (ordinary)	3760	—	0.83	1.65	2.88	9.06
K[80] (clean)	7000	1.32	2.35	3.17	4.40	10.58
K[80] (sensitized hydride)	10000	1.85	2.88	3.70	4.93	11.11

On the basis of apparent discrepancies between contact difference of potential and difference between work functions of two metals Millikan at one time held that thermionic electrons originate as *free* or conducting electrons in a metal and that photo-electrons are originally *bound* electrons in the metallic atoms.[81] This view was supported by the fact that temperature has very little effect on photo-electric emission[82] (unless the physical condition of the

---

[74] Richardson and Compton, Phil. Mag. **24,** 575 (1912); Millikan, Phys. Rev. **7,** 355 (1916); Duane and Hunt, *ibid.* **6**, 166 (1915); Webster *ibid.* **7**, 599 (1916).

[75] Richardson and Compton, Phil. Mag. **24,** 575 (1912).

[76] Richardson, Proc. Roy. Soc. **A94,** 269 (1918).

[77] Du Bridge, Phys. Rev. **31,** 236 (1928).

[78] Warner, Proc. Nat. Acad. Sc. **13,** 56 (1927).

[79] Kazda, Phys. Rev. **26,** 643 (1925).

[80] Richardson and Young, Proc. Roy. Soc. **A107,** 377 (1925).

[81] Millikan, Phys. Rev. **7,** 18 (1916); *ibid.* **18,** 236 (1921).

[82] Millikan and Winchester, Phys. Rev. **24,** 16 (1907); Burt, *ibid.* **24,** 207 (1924); Koppius, *ibid.* **18,** 443 (1921); Nielson, *ibid.* **25,** 30 (1925).

surface is affected by temperature changes[83]). Later the above discrepancies were found to be due to complications in the interpretation of the contact difference of potential measurements, and the original conclusion of Richardson and Compton,[75] in regard to the identity of contact difference of potential and difference of work functions of *pure* metals, has been well confirmed. (Complications, which are discussed later, cause departures from this identity in the case of metals with composite surfaces.) Furthermore, Sommerfeld's theory of metals[56] explains the independence of photo-electric effect with temperature. Thus there is no present reason for not supposing that the same group of electrons in the metal contribute to thermionic and photo-electric emission.

It it true that photoelectrons have been observed, which come from the deep interior of atoms as "bound" electrons under the influence of X-rays or γ-rays. For these the values of ϕ in Eq. (12) include the binding energies of the electrons in the various "shells" in the atoms, and indeed Eq. (12) gives a good method of measuring these energies.[84] It is doubtful, however, whether such energies play any appreciable role in the phenomena of gas discharge.

For a time it was thought that evidence had been found for "cumulative" photo-electric emission[85] in that, at frequencies less than the ordinary threshold ν_0, there was feeble emission in which the maximum velocity appeared to be given by Einstein's equation (12) with $2h\nu$ instead of $h\nu$, but this is now found to be due to the remarkable effect of even small accelerating fields in decreasing the apparent work function of activated surfaces, as will be discussed further in the following section (B 4).

The total photo-electric emission, besides being proportional to the light intensity, is a function of the metal and of the frequency. The more electropositive metals are the more sensitive. The sensitivity appears in general to increase, with increasing frequency of radiation, from zero at ν_0 to a maximum at $\nu = 3\nu_0/2$ after which it decreases, but rises to one or more maxima at still shorter wave-lengths.[86] Any maximum in the light absorption for a given frequency would give rise to a maximum in the photo-electric emission, but at least the first maximum seems not to be thus explained. The only theory of total emission as a function of frequency, which is by Richardson,[87] seems to be dimensionally correct and predicts the maximum of sensitivity at $3\nu_0/2$, but it has not been proved to be correct in detail.

The complete photo-electric emission under the influence of black body radiation has been shown theoretically[88] and experimentally[89] to vary with the

---

[83] Ives and Johnsrud, Jour. Opt. Soc. Am. and R. S. I. **11**, 565 (1925).

[84] De Broglie, Jour. d. Phys. et le Rad. **2**, 265 (1921); Robinson, Phil. Mag. **50**, 241 (1925); Ellis, Proc. Camb. Phil. Soc. **22**, 369 (1924).

[85] Nottingham, Phys. Rev. **33**, 633 (1929).

[86] Compton and Richardson, Phil. Mag. **26**, 549 (1913); Richardson and Rogers *ibid.* **29**, 618 (1915); Richardson and Young, Proc. Roy. Soc. **107**, 377 (1925); Ives, Jour. Opt. Soc. Am. and R. S. I. **8**, 551 (1924).

[87] Richardson, Phil. Mag. **23**, 619 (1912).

[88] Richardson, Phil. Mag. **23**, 619 (1912); **31**, 149 (1916); **47**, 975 (1924); Wilson, Ann. d. Physik **42**, 1154 (1913).

[89] Wilson, Proc. Roy. Soc. **A93**, 359 (1917); Roy. Soc. Proc. **A112**, 599 (1926).

black body temperature according to an equation similar to Eq. (6) for thermionic emission. This suggested the attractive hypothesis that thermionic emission is simply the photo-electric emission due to the radiation density within the hot metal, integrated over the complete spectrum and throughout the body of the metal. Quantitative test is very difficult, owing perhaps principally to uncertainty regarding the depth within the surface from which photoelectrons can emerge. The best estimates place the integrated photoelectric emission at about 5000 times less than the thermionic emission,[90]—this difference being attributed to the factor A of Eq. (6).

Experiments on the photo-electric effect from thin films of metal on quartz have shown that photo-electrons may escape from depths of several atomic diameters within the surface of the metal.[91] The average distance which an electron may move in the metal without losing its ability to escape appears to be about $2.7\ (10)^{-7}$ cm in platinum and $5.0\ (10)^{-7}$ cm in gold, and the probability of going a given distance without losing ability to escape falls off exponentially with the distance.

Finally, mention must be made of the *selective photo-electric effect*[92] which is found with electropositive metals and usually when the electric vector in the incident radiation has a component normal to the surface of the metal. It appears as an increased sensitivity reaching a maximum at the same frequency $\nu = 3\nu_0/2$ discussed above as the region of maximum photo-electric sensitivity. It was formerly thought to depend on some different mechanism from that of the *normal* photo-electric effect, but it is now believed to be identical in nature, and to exist in virtue of selective absorption in this spectral region and with light polarized so as to have its electric vector normal to the surface.[93] This theory has, however, not been entirely adequate to explain the observations.[94]

(4) **Relations of contact difference of potential** to thermionic and photoelectric emission are of a simple but most fundamental nature. These appear in the theoretical equation[95]

$$\phi_1 - \phi_2 = V_2 - V_1 + P_{12} \tag{13}$$

in which $V_2 - V_1$ is the contact difference of potential between metals 1 and 2, and P_{12} is the Peltier coefficient at their junction. P is negligible in comparison with the other terms. This expression has been verified within the limits of accuracy of experiments for ϕ measured photo-electrically,[96] thermionic-

---

[90] Richardson, Phil. Mag. **31**, 149 (1916).

[91] Ladenburg, Ann. d. Physik **12**, 558 (1903); Partzch and Hallwachs, Ber. d. D. Phys. Ges. p. 749 (1907); Robinson, Phil. Mag. **32**, 421 (1916); Compton and Ross, Phys. Rev. **31** 374 (1919).

[92] Pohl, and Pringsheim, Verh. d. D. Phys. Ges. **12**, 349 and 682 (1910); **13**, 474 (1911); **14**, 46 (1912); Ives and Johnsrud, Astrophys. Jour. **60**, 231 (1924).

[93] Millikan and Souder, Proc. Nat. Acad. Sc. **2**, 19 (1916); Hughes, Bull. Nat. Res. Council Vol. 2, Part 2, No. 10, p. 115; Ives and Briggs, Bull. Am. Phys. Soc. **5**, 18 (1930).

[94] Frehafer, Phys. Rev. **15**, 110 (1920).

[95] Richardson, Phil. Mag. **23**, 261 and 615 (1912).

[96] Richardson and Compton, Phil. Mag. **24**, 575 (1912); Millikan, Phys. Rev. **18**, 236 (1921).

ally,[97] and as a heat of condensation of electrons.[98] Of these, the thermionic test is least accurate because it is difficult to make a contact difference of potential measurement between metals which are suitable for simultaneous determination of the thermionic constants.

In the case of metals with surfaces which are not atomically homogeneous, such as metals with surface patches of adsorbed materials, the simple relation above cannot hold, for the following reasons. The contact potential property of a composite surface, as measured by any of the standard methods, is simply an average value to which patches of different character contribute simply in proportion to their areas. The photo-electric work function, if measured as usual by the long wave-length limit, is characteristic of the most electropositive region on the surface. The thermionic work function, as measured by emission as a function of temperature, is again an average value, but an average in which the electropositive areas are weighted much more heavily than the electronegative areas. These differences are strikingly illustrated if one considers, as a simple example, a square centimeter surface of platinum on which is a patch of potassium of one square millimeter. The latter area determines the thermionic and photo-electric work functions, but affects the measured value of contact potential by only about one-half percent. Such differences have frequently been observed in dealing with activated emitting surfaces, but only the start of a systematic study of them has been made.[99]

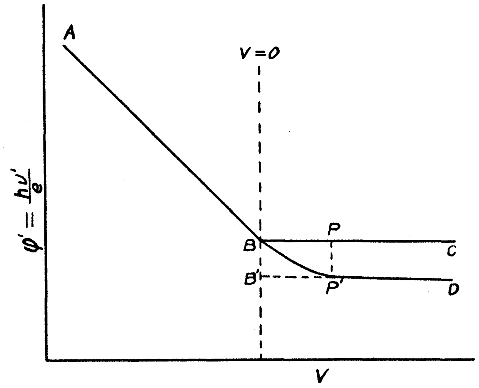


Fig. 1.5. Nottingham's curve of relation between "effective" low frequency threshold ν' and applied potential difference V. Curve ABC shows relation given by Einstein's equation and found for homogeneous metal surfaces. Curve ABD is found for activated surfaces. ϕ' is the "effective" work function.

Recent experiments and suggestions of Nottingham[99.5] appear to be very significant in this connection. He determined the maximum wave-length at

---

[97] Richardson and Robertson, Phil. Mag. **43,** 557 (1922).

[98] Van Voorhis, Phys. Rev. **30,** 318 (1928).

[99] Langmuir and Kingdon, Phys. Rev. **34,** 129 (1929).

[99.5] Nottingham, article soon to appear in Jour. Frank. Inst.; also Proc. Am. Phys. Soc. February (1930) meeting.

which photo-electric emission could be detected for each of a number of applied fields (both retarding and accelerating) between an emitting and a receiving electrode. The emitting electrode was of nickel, activated by a distilled film of an alkali metal. By Einstein's equation (12) the expected relationship would be as indicated by curve AB, Fig. 1.5. Here B is the point at which the field changes from retarding to accelerating and BC is the region of saturation current in which the threshold frequency is independent of field (except for the very slight Schottky effect described in the following section (B 5)). ν' is the lowest frequency at which photo-electric emission can be detected with applied potential difference V. The part AB of the curve has a slope of 45° if $h\nu'/e$ and V are expressed in the same units. Curve ABC actually represents the relationship as found with metals whose surfaces are homogeneous.

With activated surfaces, however, curve ABD describes the relations. The threshold frequency is changed by an accelerating field, PP' representing the reduction in "effective" work function due to an accelerating field BP. To illustrate the order of magnitude of this effect, an example is the following: A field BP of 4 volts caused a reduction $PP'=2$ volts in "effective" work function, but a further increase of 700 volts in the field caused only a few tenths of a volt further reduction.

A similar phenomenon is evident in the thermionic emission, at very small accelerating fields, from thoriated tungsten, as reported by Reynolds[105] (see Fig. 3 of Phys. Rev. **35**, 164 (1930)). There is every reason for believing that it is a general characteristic of emission from activated surfaces in weak accelerating fields.

There are several important consequences of this fact: (1) The values of work function of activated surfaces (Table IV) all refer to the "effective" work function as determined for accelerating fields greater than P' (Fig. 1.5) and extrapolated back to zero field (such as B'). Similarly photo-electric long wave-length limits are generally measured with considerable accelerating fields (see, for example, the work of Millikan). On the other hand, the long wave length limits calculated by Einstein's equation or extrapolated from the region AB of Fig. 1.5 give values characteristic of zero field, such as B. (2) There is a theory of change in effective work function produced by an accelerating field which accounts satisfactorily for experiments on emission from homogeneous surfaces. This theory, and all extensions of it which have thus far been proposed, fail signally in accounting for all the results obtained with activated surfaces. These theories are discussed in the following two sections (B 5, 6).

(5) **Electron emission in an accelerating electric field** never, strictly speaking, becomes completely saturated, for there is always an increase of current with field. For many purposes this effect is negligible, but in some cases it is very important. It gives rise to the necessity of examining just what we mean by the saturation electron emission, as defined for example by Eq. (6). It certainly plays an important role in phenomena at the cathode in some forms of gas discharges. It was first discussed by Lenard,[100] but was put into concrete

---

[100] Lenard, Ann. d. Physik **8**, 149 (1902).

and useful form by Schottky,[101] and is generally known as the *Schottky Effect*. Essentially the phenomenon is this:

Any escaping electron ($-e$) is attracted back toward the metal by a force $F(x)$ due to the induced positive charge on the metal surface, which is *approximately* equal to the attraction of the "mirror image" charge ($+e$). This force $F(x)$ is accurately $e^2/4x^2$ if the electron is at a distance x which is large compared with distances between consecutive atoms in the surface of the metal, for then the metal surface is effectively a conducting plane. Even at a distance of only four or five inter-atomic distances, this expression would hold to a rough approximation. On the other hand it would obviously fail completely at distances of the order of atomic diameters, being replaced, at the close distances, by a force function which depends on the discrete atomic structure of the metal surface and which must approach zero at the surface. The work function is given in terms of this force by

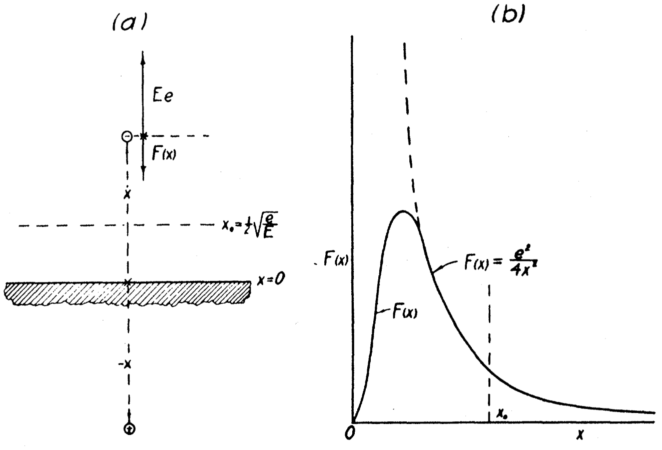


Fig. 2

$F(x)$ is the surface force which attracts an electron, distant x from the metal surface, toward the metal. x_0 is the distance at which this surface force is just equal and opposite to the force of the applied field.

$$e\phi = \int_0^\infty F(x)dx. \tag{14}$$

Obviously $F(x)$ cannot be simply the image force $e^2/4x^2$ in the entire range from 0 to ∞, for in that case this integral would be infinite. If we make the natural assumption that $F(x) = 0$ at $x = 0$ and, for small displacements, increases linearly with x, then the simplest graphical representation of $F(x)$ is a parabola rising from $F(x) = 0$ at the origin $x = 0$ to a maximum and then down-

---

[101] Schottky, Phys. Zeits. **15,** 872 (1914); **20,** 220 (1919); Ann. d. Physik **44,** 1011 (1914); Zeits. f. Physik **14,** 63 (1923).

ward merging into the curve of the image force at $x = x'$, as shown in Fig. 2 b. With such a law of force Langmuir[102] has shown that Eq. (14) leads to

$$\phi = \frac{e}{2x'}$$

and that x' is of the order of an atomic radius. Values of x' in Angstrom units are: W 1.58, Pt 1.12, Mo 1.62, Ta 1.75, Th 2.13, Cs 3.95. These values vary roughly as the cube roots of the atomic volumes and are approximately equal to the atomic radii.

Direct experimental evidence regarding the nature of $F(x)$ is obtained by investigating the effect of accelerating fields on the electron emission. In the presence of an accelerating field E, there is a critical distance x_0 from the surface at which the resultant force vanishes. Within it the intrinsic surface attractive force $F(x)$ predominates, while beyond it this force is inferior to the applied force Ee. The critical distance is defined by the relation

$$F(x)_{x=x_0} = Ee. \tag{15}$$

For all except the strongest attainable applied fields it turns out that this critical distance x_0 is sufficiently large that the approximation $F(x) = e^2/4x^2$ is valid, so that we can use $e^2/4x_0^2 = Ee$, giving

$$x_0 = \tfrac{1}{2}(e/E)^{1/2}. \tag{16}$$

The range in which this approximation is justifiable may be suggested by taking an extreme case of $E = 1{,}000{,}000$ volts/cm. Then $x_0 = 19\ (10)^{-8}$ cm. The closest distances between atoms in a metal are[103] Th. 3.54 $(10)^{-8}$ cm W 2.73 $(10)^{-8}$ cm, K 4.50 $(10)^{-8}$ cm, etc. Thus even in this extreme case x_0 is about six times the inter-atomic distance. For $E = 10{,}000$ volts/cm the approximation would be very close indeed, for x_0 would be about sixty times the inter-atomic distance.

The applied accelerating field reduces the work which must be done by an electron in order to escape in two ways: (1) the integral of Eq. (14) needs to be carried out only to a distance x_0 instead of to infinity since, once past x_0, its escape is assured; and (2) the force which must be overcome in the path from 0 to x_0 is not $F(x)$, but $F(x) - Ee$. Calling ϕ' the "effective" work function, *i.e.*, the actual work which must be done by an electron to get free from the metal, we have

$$e\phi' = \int_0^{x_0} (F(x) - Ee)dx = \int_0^{\infty} F(x)dx - \int_{x_0}^{\infty} F(x)dx - \int_0^{x_0} Eedx.$$

The first integral is simply $e\phi$, and in the second integral $F(x) = e^2/4x^2$ in the range x_0 to ∞. Thus, introducing the value of x_0 from Eq. (16) we have

$$\phi' = \phi - (Ee)^{1/2}. \tag{17}$$

---

[102] Langmuir, Trans. Am. Electrochem. Soc. **29**, 157 (1916).

[103] Compton, "X-rays" p. 116 (Van Nostrand 1926).

The actual emission, whether photo-electric or thermionic, is governed by the "effective" work function ϕ' rather than the true work function ϕ. Thermionic emission lends itself most readily to a test of this Schottky effect, because of the relative ease of securing a large field at the surface of a filament of small diameter. Eq. (6) then takes the form

$$j = AT^2\epsilon^{-(e/kT)[\phi_0-(Ee)^{1/2}]} = AT^2\epsilon^{-e\phi_0/kT}\cdot\epsilon^{e(Ee)^{1/2}/T} = j_s\epsilon^{e^{3/2}E^{1/2}/kT} \tag{18}$$

or, if E is expressed in volts/cm,

$$j = j_s\epsilon^{4.389(E^{1/2}/T}. \tag{19}$$

This equation may easily be tested if the current is small and gas ionization absent (so as to avoid distortion of the field by space charge, *see* Part II) for then E is directly proportional to the applied difference of potential V, the constant of proportionality being calculable by principles of electrostatics and depending only on the geometry of the electrodes. Grouping together this constant and the quantity $e^{3/2}/kT$ as a "shape factor" S, we have

$$j = j_s\epsilon^{SV^{1/2}}, \quad \text{whence} \quad \log j - \log j_s = SV^{1/2}. \tag{20}$$

The graph of $\log j$ against $V^{1/2}$ should therefore give a straight line, whose slope S is calculable from the geometry of the electrodes and whose intercept $\log j_s$ at $V=0$ serves to define the "saturation" current J_s.

Experimental tests of Eq. (20) are very illuminating in that they afford an insight into surface conditions which greatly affect electron emission. With clean metal filaments Eq. (20) is accurately verified in the entire range from 2 or 3 volts (below which initial velocities of emission and current limitation by space charge may cause a departure) up to the highest fields (10^6 volts/cm) which have been used in thermionic emission.[104] Generally the shape factor S is from 5 percent to 100 percent larger than the value calculated from the geometry, but this departure is found to be due to microscopic roughness of the surface which concentrates the field at protruding points. Abnormally large values of the slope S are found for wires which have been subjected to positive ion bombardment, indicating a "pitting" of the surface when struck by high speed ions. With clean tungsten wire of small crystal grain structure and flashed at a high temperature to smooth out surface inhomogeneities Eq. (20) is satisfied as accurately as the measurements can be made, with the theoretical value of the shape factor S. This proves that the surface force $F(x)$ is identical with the electrostatic image force $e^2/4x^2$ at distances greater than the minimum value of x_0 attained in these experiments.

Even if the surface force should, for any reason, not be the image force, the above method may still be applied to explore the surface force if it is permissible to assume that the force is uniform over a plane parallel to the surface. Writing Eq. (6) in the most general form suggested by Eqs. (14) and (17).

---

[104] Schottky, Ann. d. Physik **44,** 1011 (1914); Dushman et al, Phys. Rev. **25,** 338 (1925); Lauriston and Mackeown, *ibid.* **32,**326 (1928); Phorte, Zeits. f. Physik **49,** 46 (1928); de Bruyne, Proc. Roy. Soc. **A120,** 428 (1928); Reynolds, Phys. Rev. **35,** 158 (1930).

$$j=AT^2 \exp\left\{-\frac{1}{kT}\int_0^{x_0}[F(x)-Ee]dx\right\}$$

and differentiating by E, we obtain

$$\frac{d\log j}{dE}=\frac{ex_0}{kT}\,. \tag{21}$$

Thus the rate of change of the logarithm of the thermionic current with change in accelerating field gives the distance x_0 from the surface at which the surface force $F(x)$ equals the applied force. By using a wide range of fields, the surface force is thus found over a wide range of distances from the surface.

In general the emission from activated surfaces, such as caesium or thorium on tungsten or Wehnelt oxides, does not follow the simple Schottky equation (19), but shows wide departures especially at low fields. Furthermore these departures are greater for surfaces only partly covered with activating material than for surfaces which are either nearly bare or nearly completely covered. Eq. (21) has been used to investigate the peculiar surface force for such surfaces, as will be described later. It may be noted, further, that the degree of approximation to the Schottky Eq. (19) is largely affected by the previous history of the surface as regards method of activation, ion bombardment, etc.[105]

The only present theory of these departures from Schottky's equation is based on a suggestion by Langmuir[106] that the electropositive atoms on the activated surface give rise to electric force fields near the surface which vary from point to point and affect differently the escape of electrons from different regions, thus tending to produce imperfect saturation. The electropositive atoms thus behave as a sort of positively charged "grid" to affect the emission. These electropositive atoms may act in groups, or "patches" which are electropositive with respect to the surrounding bare metal, in which form the theory has been utilized by Richardson and Young[107] and by Reynolds.[105] Or they may act individually as charges situated just outside the surface giving rise, with their mirror images, to doublet fields, in the form of the theory developed by Becker.[108] We propose to discuss these theories somewhat at length, both because of the interest attaching to the phenomena and because the following analysis shows that *none* of the present theories appears to be capable of accounting for the observed departures from Schottky's equation.

The theory of patches was suggested by Langmuir[106] to explain the lack of definite saturation observed with filaments whose surfaces are only partly covered with adsorbed films, such as those of thorium. At 1500°K the electron emission from a tungsten surface completely covered with a layer of thorium atoms is about 126,000 times as great as that from pure tungsten.

[105] Reynolds, Phys. Rev. **35**, 158 (1930).

[106] Langmuir, Gen. Elec. Rev. **23**, 504 (1920).

[107] Richardson and Young, Proc. Roy. Soc. **107**, 377 (1925).

[108] Becker and Mueller, Phys. Rev. **31**, 431 (1928); Becker, Bell Tech. Lab. Reprint B-412, August (1929).

If half of a large tungsten surface were covered with such a thorium film while the other half were bare, the total emission would be about 63,000 times that of pure tungsten. If the thorium, however, is uniformly distributed over the filament, the work function is a linear function of the amount of thorium on the surface, and thus, according to Eq. (7.5), the electron emission from the surface would be 356 times that of pure tungsten $(126{,}000)^{1/2}$.

In the first case we have an emission which corresponds to an arithmetical average while in the second we have to deal with a geometrical mean. In either case the current should increase with the applied accelerating field in accord with Schottky's theory, Eq. (20). Thus with enough thorium to cover half the surface the line *AB* in Fig. 3(a) represents the emisson as a function of field for uniform distribution while a parallel line *CD* represents the 356 times larger currents when the thorium is gathered into large patches. If the linear dimensions b of a patch of active material on a cathode are sufficiently small compared to x_0, the distance to the critical surface as given by Eq. (16), the distribution will be effectively uniform and *AB* will give the current, but when $b \gg x_0$, *CD* will apply. As the field increases, x_0 decreases and thus the transition from *AB* to *CD* may be expected to occur as illustrated by *AGHD* so that in region *GH* the Schottky effect will be abnormally large.

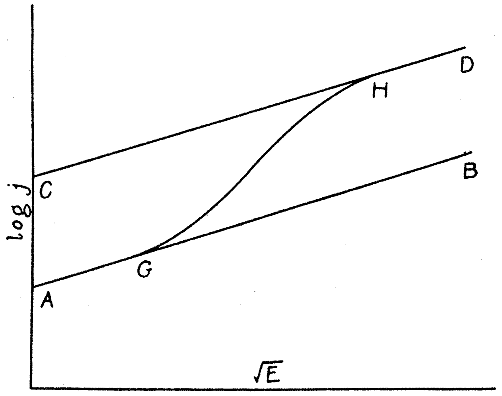


Fig. 3. Effect of patch size on electron emission.

A quantitative estimate of the field strength that is needed to cause the emission to depart appreciably from the Schottky line *AB*, for example at *G*, may be made by considering the following simplified case. Let a surface consist of patches of two kinds having a contact potential difference V_0 between them, and let them be arranged in alternate squares like a checkerboard, each square having sides of length b. If the potential of the more negative squares is 0, and there is no applied field, the distribution of potential in the space near the checkerboard is given by the following expression

$$V=\frac{1}{2}V_0+\frac{4V_0}{\pi^2}\sum_{n=1,3,5}\left[\frac{1}{n^2}\exp\left(-n(2)^{1/2}\pi z/b\right)\cos\frac{n\pi x}{b}\cos\frac{n\pi y}{b}\right]$$

where z is the distance from the surface while x and y are the distances measured from the center of one of the more electropositive squares in directions parallel to the edges of the squares.

To determine the motions of electrons we must add together this potential V, the potential due to the external field E, and the fictitious potential $e/4z$ due to the electric image force. The name "motive" has been proposed[109] for a scalar quantity whose gradient in any direction and at any point represents the force component per unit charge which *acts on an electron or ion.* The motive M is thus

$$M=M_\infty+\frac{e}{4z}+Ez+V$$

where M_∞ is a negative quantity numerically equal to the work function for 0 field and expressed in volts. Thus, for tungsten $M_\infty=-4.52$ volts.

By differentiating M with respect to z and equating to 0, an equation is obtained which, when solved for z, gives the distance z_M at which the motive is minimum; that is, it gives the location of the critical surface. This distance z_M is a function of x and y, but if V_0 is placed equal to 0, z_M then has the same value as x_0 given by Eq. (16). The value of z_M corresponding to $V_0=0$ we will call z_0 and we may then place

$$z_M=(1+\lambda)z_0 \tag{22}$$

where λ is a small quantity if $z_0 \gg b$. The equation $dM/dz=0$ can then be expressed in the folowing form,

$$1-(1+\lambda)^{-2}=\alpha \exp(-\beta\lambda)$$

where

$$\alpha=\alpha_0 \cos\left(\frac{\pi x}{b}\right)\cos\left(\frac{\pi y}{b}\right) \tag{23}$$

$$\alpha_0=\frac{4\,(2)^{1/2}V_0}{\pi E b}\exp(-\beta) \tag{24}$$

$$\beta=\frac{\pi}{b}\left(\frac{e}{2E}\right)^{1/2}=\frac{4.44z_0}{b}. \tag{25}$$

This expression can be expanded into a power series in λ, and then, by reversion, the following series is obtained for λ in terms of α,

$$\lambda=\frac{1}{2}\alpha+\frac{\alpha^2}{8}(3-2\beta)+\frac{\alpha^3}{16}(5-9\beta+3\beta^2).$$

This equation thus allows us to determine by Eq. (22) the distance z_M to the critical surface of minimum motive as a function of x, y and V_0. The motive M_M at the critical surface can also be expressed in terms of λ and therefore in

---

[109] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107,** 68 (1925).

terms of α. The final expression for the change in motive at the critical surface produced by making E different from 0 is given by,

$$\Delta M_M = (eE)^{1/2}\left[1+\frac{\alpha}{2\beta}-\frac{\alpha^2}{8}-\frac{\alpha^3}{16}(1-\beta)\right].$$

The total electron emission may then be calculated* from Eq. (6) by decreasing the value of b by an amount equal to $(e/kT)\Delta M$ and averaging the resulting current density over the whole surface of the cathode. The terms involving odd powers of α then drop out and the total current density from the surface is found to be,

$$j = j_n\left[1+\frac{\alpha_0{}^2}{32}\left(\frac{1}{\beta^2}-1\right)\right] \tag{26}$$

where j_n is the current density corresponding to the normal Schottky effect as given, for example by Eq. (19).

For convenience, the value of α_0 may be calculated by eliminating E between Eqs. (24, 25). Thus

$$\alpha_0 = 2.55\times 10^6 V_0 b\beta^2 \exp(-\beta) \tag{27}$$

where V_0 is expressed in volts.

As an example to illustrate the use of these equations we may take the case of a tungsten filament having a radius 0.01 cm inside of a cylinder having a radius of 1 cm.

With the cylinder at various positive voltages V_a with respect to the filament as given in line 1 of Table VI the accelerating field strengths E at the filament are given in line 2. Line 3 shows the normal increase in electron emission according to the Schottky theory as given by Eq. (19). The normal distance z_0 of the critical surface from the cathode is in line 4.

TABLE VI. *The effect of local fields due to checkerboard patches of thorium-covered tungsten in causing lack of saturation. Size of squares $b=10^{-6}$ cm; contact pot. diff. $V_0=1.9$ volts.*

1 V_a (volts)	0	100	250	500
2 E (volts cm^{-1})	0	2170	5430	10850
3 j_n/j_s	1.000	1.146	1.242	1.357
4 z_0 (10^{-6} cm)	∞	4.0	2.6	1.8
5 β	∞	18.0	11.4	8.0
6 α_0	0	2.10^{-5}	0.007	0.10
7 $(j-j_n)/j_n$	0	-10^{-10}	-10^{-6}	-3.10^{-4}
8 λ_M	0	10^{-5}	0.003	0.05

Let us now assume that the surface of the filament is one-half covered in checkerboard fashion by square patches of close-packed thorium atoms, the side of each square being $b=10^{-6}$ cm. Since a tungsten surface completely

---

* This assumes that the electrons which reach the critical surface from the cathode have a Maxwellian velocity distribution. This will be true regardless of the motive distribution near the cathode, if the critical surface is approximately plane, that is, if $\lambda \ll 1$. See Mott-Smith and Langmuir, Phys. Rev. **28,** 754–8 (1926) particularly the theorem on p. 756.

covered by thorium contains[110] about 7×10^{14} atoms of thorium per cm^2, each patch contains 700 atoms.

The values of β and α_0 given by Eqs. (25) and (27) are in lines 5 and 6 while line 7 gives the fractional change in current caused by the local fields of the patches as calculated by Eq. (26).

Thus even with such extremely non-uniform distribution of thorium atoms as we have assumed, with clusters of 700 atoms, the local fields cannot cause variations of emission which are at all comparable with those of the normal Schottky effect.

With patches of a little larger size, containing about 7000 atoms and about 3×10^{-6} cm square, the values of $(j-j_n)/j_n$ calculated by Eq. (26) become much larger and reverse in sign, so that the Schottky effect will increase rapidly as illustrated by GH in Fig. 3 but then $1/\beta$ and $\beta\lambda$ become so large that the approximations made in deriving these equations are no longer valid. However, it is very improbable that such large clusters of adsorbed atoms can exist on plane surfaces. Becker has shown,[108] for example, that a thorium layer at emission temperatures behaves like a 2-dimensional gas on the surface.

A random distribution of adsorbed atoms would also give considerable irregularities in emission even over rather large areas. For example, if the average number of atoms in equal square patches (each of area b^2) is q, then the average difference between the number of atoms in any two squares selected at random is $(2q)^{1/2}$ so that the average contact difference of potential between adjacent squares is $5.2\times10^{-8}\ V_0/b$ where V_0 corresponds to the difference between completely covered and uncovered surfaces. Thus if we take $b=4\times10^{-6}$ (about equal to z_0) and $V_0=1.9$ we get a potential difference of only 0.025 volt. With a filament at 1500° this would cause a 20 percent difference in the normal emissions of the two surfaces. In this case the arithmetic mean and the geometric mean (of 0.9 and 1.1) differ by only 0.5 percent so that no abnormally large Schottky effect can occur.

Finally, if there are attractions between the thorium atoms so that they form clusters of n atoms each, the clusters being distributed at random, then the average contact difference between adjacent squares of areas b^2 becomes $\Delta V=5.2\times10^{-8}\ V_0\ n^{1/2}/b$. Thus the difference between the arithmetic and geometric means which is proportional to $(\Delta V)^2$ becomes 50 instead of 0.5 percent if $n=100$.

Langmuir, Richardson and Becker have experimentally observed cases with filaments whose surfaces are partly covered by adsorbed films where the variation of emission with voltage is much greater than the variation observed with bare surfaces or completely covered surfaces.

K. H. Kingdon and Langmuir in some unpublished work in 1923 and more recently Reynolds[105] measured the emission as a function of voltage and temperature for thoriated filaments of various activities. They had unusually good vacuum conditions, the metal parts being thoroughly degassed and the

---

[110] I. Langmuir, Phys. Rev. **22,** 375 (1923).

bulbs excessively baked out and immersed in liquid air. The filaments were in the axis of a cylinder provided with end guards so that the field strengths were accurately known.

Reynolds, working with thoriated filaments which had been flashed to very high temperature and then activated, found a variation with voltage in excellent agreement with the Schottky theory for field strengths exceeding about 10,000 volts/cm, as shown by curves *A* and *B* of Fig. 4 for two different degrees of activation. If, however, the filament had been well activated and was then slightly deactivated by positive ion bombardment (which occurred slowly if the liquid air were removed while high voltage was applied), then the emission did not agree with the Schottky curve above 10,000 volts/cm, as shown by curve *C*, Fig. 4. This bombardment must have roughened the surface and there is evidence that it also fractured the surface layer of tungsten crystals. Subsequent flashing at high temperature followed by activation always brought the filament back to the condition giving curves *A* and *B*.

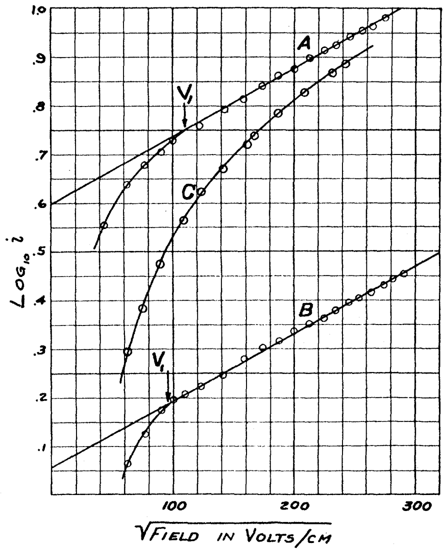


Fig. 4. Electron emission from a heated thoriated filament as a function of field, showing approach to Schottky's curve *A*, *B* above 10,000 volts/cm for a regularly activated filament, and the different relation *C* for a filament which had been subjected to positive ion bombardment. (Reynolds)

Kingdon's and Langmuir's results were the following. The thoriated filament was flashed 1 minute at 2740° and activated for 25 minutes at 2120°. It was free from carbon and thus could be completely deactivated by heating 10 seconds at 2600°K; partial deactivation was accomplished in 4 stages by heating 30 or 60 seconds at 2300 or 2400°. In each stage the emission was measured at 5 voltages and about 6 testing temperatures. Fig. 5 gives a few of the typical curves obtained by plotting $T \log_{10} j$ against $\sqrt{E}$ where E is in volts per cm. According to Eq. (19) the lines obtained should be straight and should all have a slope 1.906. At the highest field strengths (about 10,000 volts/cm) the curves are seen to approach the theoretical slope. In Fig. 5 they have been displaced in a vertical direction by various amounts Δ in order to show how they approach the Schottky line asymptotically.

These results indicate that with nearly complete thoriation of the surface ($\theta=0.91$) and with a bare surface ($\theta=0.00$) the approach to the Schottky curve is fairly close,* but relatively large departures occur with incomplete thoriation ($\theta=0.69$). In every case the departures from the Schottky line become greater as the temperature is lowered, thus proving that the deviatons are not due to space charge.

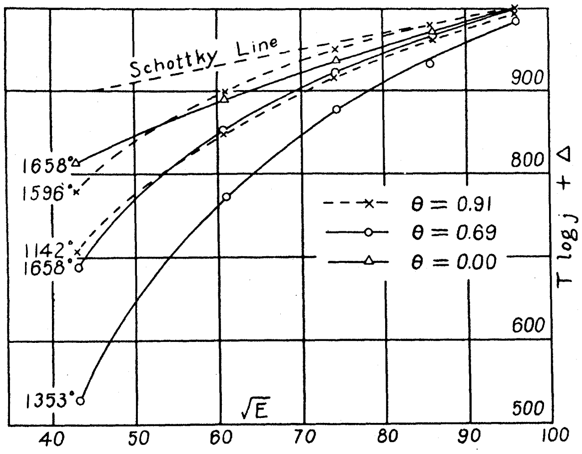


Fig. 5. Electron emission from thoriated filament as a function of activity θ and field, at various temperatures. (Kingdon and Langmuir)

Table VII gives η, the ratio of the observed emission at a field of 1840 volts/cm (50 volts on anode) to that calculated from the Schottky line by extrapolating down from $E=9200$ as shown in Fig. 5. It is seen that the maximum departure from the Schottky law occurs when the tungsten is about 70 per cent covered by thorium.

TABLE VII. *Departures* (η) *from Schottky's law with field of 1840 volts/cm.*

θ	$T=1500°$		η at a temp. giving $j=17\times10^{-6}$ amps cm^{-2}
	η	j(amps cm^{-2})	
0.91	0.81	9200×10^{-6}	0.69
0.76	0.64	1800 "	0.46
0.69	0.59	765 "	0.44
0.24	0.72	3.75 "	0.77
0.00	0.80	0.23 "	0.89

---

* Closer fits than this to the Schottky curve and over a much larger range of fields have been obtained by Reynolds with bare wires. The small departure here is believed to be due to the effect of slight surface roughness on the "shape factor" of Eq. (20).

When tungsten filments are heated to very high temperature so that evaporation occurs, the etching of the surface causes the development of the dodecahedral faces. These form angles of 120° with each other. Sometimes the resulting ridges are large enough to see under a microscope. The effect of such ridges and valleys on the variation of emission with voltage can be roughly calculated from the theory that we have developed for the case of patches. If we consider a plane surface level with tops of the ridges, then the potential at points on the surface over the centers of the valleys will be roughly Fh where h is the effective height of the ridges above the valleys. We may therefore use Eqs. (26, 27) by merely substituting $V_0 = Fh$. The increase of V_0 with F will then have the effect of causing departures from the normal Schottky effect which increase still more rapidly with increasing voltage than in the case of patches in a plane surface. The effect of such geometrical irregularities in the surface would thus seem also to give a curve of the type $AGHD$, Fig. 3.

The final result of this study is the conclusion that the "patch" theory predicts variations of emission with field which, while qualitatively in the right direction, are found on closer examination to be totally unlike the observed variations, such as shown in Figs. 4, 5. There are two outstanding difficulties. In the first place, to obtain departures from the Schottky curve comparable with those observed, the patches must be assumed to contain many thousands of atoms. In the second place, the patch theory predicts a departure from the Schottky curve which is small with small field and increases with large fields, whereas exactly the reverse is the actual case.

The reason for this failure is easy to see. By Eq. (21) it is seen that the rate of increase of current with field depends solely on the conditions at the critical x_0 (or later z_0) where the intrinsic surface force is just balanced by the applied field. For weak fields x_0 is large, approaching ∞ for zero field. Obviously local inhomogeneities in the field due to "patches" or to adsorbed ions, which may be important close to the surface, average out and become negligible at larger distances. Thus any theory based upon such surface inhomogeneities must fail to account for the observed relatively large deviations from the Schottky equation at small fields, and would predict large deviations at strong fields, which again is contrary to the facts. In order to obtain appreciable departures from the Schottky equation, these theories require that the scale of the surface inhomogeneity be comparable with the critical distance x_0, hence that the patches be large enough to contain thousands of atoms. Even if this were true, which is very unlikely, we would still be faced with the fundamental failure to account for the fact that it is at low rather than high fields that the deviation from the Schottky equation is most pronounced in this case of activated surfaces.

We now turn to that form of "grid" theory of activated surfaces which has been interestingly investigated and extended by Becker,[108] and which we may call "*the adion field theory*," borrowing from Becker the term "adion" to designate "adsorbed ion." The theory aims to account for the three peculiarities of activated surfaces, (1) low work function, (2) lack of saturation in emission, (3) electropositive character of surface, as follows:

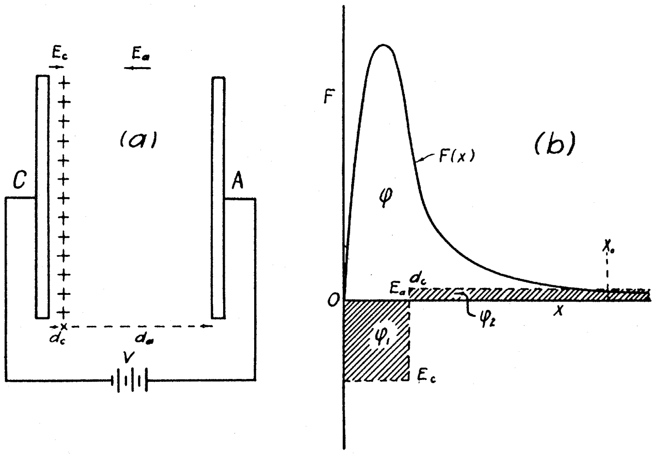


Fig. 6. Adion theory of activated surfaces.

Consider two similar electrodes C and A (Fig. 6(a)) distant d apart, and assume the cathode C to be more or less covered with a surface layer of positive ions distant d_c. We may suppose the electrodes to be of tungsten and the ions to be of some activating material such as Ba^+. The fact that the barium evaporates as ions is evidence of its existence in the form of ions on the surface, since the surface forces which tend to ionize it are presumably strongest at or very near the surface. The effect of this layer of "adions" on the field between the plates may be considered to *a first approximation* as that of a layer of positive charge of surface density $\sigma = Ne$, where N is the average number of adions per cm^2. The field due to this layer is uniform and is very nearly $E_c = 4\pi Ne$ on the cathode side and $4\pi Ne\, d_c/d_a$ on the anode side. The potential rise from cathode to layer is $4\pi Ne\, d_c$, and is equal to the potential drop from layer to anode.

If the electrodes C and A were connected by a wire ($V = 0$) then the adion layer would be without effect on the emission from the cathode C, since the total work done on an electron in escaping from C to A is the same as if the adion layer were absent. However the field E_a is interpreted by an observer as a contact difference of potential between C and A and he compensates it by an equal opposite field V applied externally in order to obtain what he considers to be the true saturation emission from C with zero field. (This is exactly in accordance with observation and procedure in any case of emission beween dissimilar electrodes.) Under these conditions the work which an electron must do to escape is less, by this apparent contact difference of potential $V = E_a d_a = E_c d_c$, than in the absence of the adion layer. The emission is therefore greater in accordance with this decrease in effective work function.

These considerations are shown graphically in Fig. 6(b), where $F(x)$ represents the surface force at various distances x from the cathode and the area under it equals the work function ϕ of the normal cathode surface. The adion layer produces an additional force E_c inside the distance d_c, and E_a in the reverse direction beyond this distance; these forces add an amount ϕ_1 to the energy of the escaping electron within the distance d_c and subtract an equal amount ϕ_2 beyond. The total work done in escaping is thus unchanged, being $\phi - \phi_1 + \phi_2 = \phi$. If however, the outer field E_a is compensated by applying an external field as in correcting for contact potential difference, the effective work function is reduced to the difference between the areas $\phi^1 = \phi - \phi_1$. This theory therefore gives a plausible interpretation of the effect of adions on the work function and the contact difference of potential.

Thus far the theory fails to account for departures of emission with accelerating field from Schottky's Eq. (19). In an attempt to do this, we go to a second approximation and treat the adion layer no longer as a uniform positive layer, but as discrete positive charges, each of which with its negative mirror image in the metal constitutes an electric doublet. Electrons escaping at various points pass through fields of various intensities and extending into the region outside the adion layer. Thus the effective work function varies over the surface and the nature of the force F varies with x differently than in the cases of bare or of uniformly covered surfaces. Qualitatively this is what is needed to account for the departure from the Schottky equation. Quantitative investigation, however, shows that this theory fails just as did the "patch" theoryin that it fails to account for the fact that the departure from Schottky's equation increases with decreasing fields. In Fig. 6(b), for example, such doublet fields may be important at distances of d_c or $2d_c$ from the surface, but not at the relatively large distances x_0 which, by Eq. (21) determine the variation of current with field for all ordinarily attainable fields.

Dr. Becker has kindly informed us of his intention soon to publish, in the Physical Review, an analysis of the "adion" theory extended to treat the case of an *activated rough* surface, rather than the ideal activated infinite plane discussed above, and has stated that this analysis will be found to be in much better agreement with the facts. The "rough" surface is conceived of as composed of the surface crystal facets, whose linear dimensions may be of the order of the critical distance x_0 for weak fields.

In connection with this theory there is the further interesting question as to what extent the specific emission properties of the adsorbed material are present in a monatomic layer. A layer ten, or five, atoms deep of caesium on tungsten almost certainly possesses the emission properties of caesium. To what extent do these specific properties completely vanish for a monatomic layer, being replaced only by an electrostatic effect of the charges of the ions?

In conclusion, it may be well to point out one assumption underlying both these forms of "grid" theory, *i.e.*, that the explanation of the departure from Schottky's theory in the case of activated substances is to be sought in the influence of adsorbed layers on the work function, neglecting a possible peculiarity in the constant A of the thermionic Eq. (6). For example Eq. (21)

which has been used by Becker and Mueller[108] to calculate the nature of the surface force $F(x)$ is based upon the assumption that A is constant. However Fowler[111] has recently shown that A is not, in general, a constant, and that particularly in the case of activated surfaces there may be a marked dependence of A upon temperature. We shall see in the next section that a strong electric field may affect electron emission (in addition to thermionic emission) in the same way in which high temperature affects thermionic emission. It may be, therefore, that activated surfaces have such a dependence of A upon the field as to account for the abnormally small emission in weak fields.

(6) **Field currents.** According to experimental evidence, the Schottky theory, Eq. (18), becomes more accurate with high field strengths. It is evident from Eq. (18) that if the field should increase until

$$Ee=\phi_0{}^2(\text{giving } E_M=\phi_0{}^2/e) \tag{28}$$

the work function and cooling effect should vanish and the current density should increase to a limiting value,

$$j(\text{max.})=AT^2. \tag{29}$$

We may measure rates of increase of the current j for given relative increases in T or E by exponents n_T and n_E defined as follows:

$$\left.\begin{aligned} &n_T=d(\log j)/d(\log T)\\ \text{and}\quad &n_E=d(\log j)/d(\log E).\end{aligned}\right. \tag{30}$$

By logarithmic differentiation by Eq. (18) with respect to T or E we then obtain

$$\begin{aligned} n_T&=2+(e/kT)[\phi_0-(Ee)^{1/2}]\\ &=2+(b-4.389E^{1/2})/T\end{aligned} \tag{31}$$

and

$$n_E=\tfrac{1}{2}(e/kT)(Ee)^{1/2}=2.20E^{1/2}/T. \tag{32}$$

For tungsten $b=52{,}600$. At $T=1500$, according to Eq. (31), n_T decreases from 37 when $E=0$ to $n_T=2$ when E approaches the limiting value, E_M, given by Eq. (28) which may for convenience be expressed

$$E_M=0.0519b^2. \tag{33}$$

For tungsten the limiting field is thus

$$E_M=1.44(10)^8 \text{ volts cm}^{-1}. \tag{34}$$

At this field the current density, by Eq. (29) with $A=60.2$, would be 1.36 $(10)^8$ amps. cm^{-2}.

According to Eq. (18) it should be possible even at room temperature ($T=300°$) to get a current of 5.4 $(10)^7$ amp cm^{-2} by raising the field strength to the same maximum value E_M.

---

[111] Fowler, Proc. Roy. Soc. **A122,** 36 (1929).

The temperature coefficient of the electron currents that could thus be pulled out of metals by intense fields becomes negligible compared to the temperature coefficients ordinarily characteristic of electron emission.[112]

Eq. (32) shows that the relative increase in current with field strength increases as the field becomes greater until finally, as E increases up to E_M, $n_E = b/2T$. Thus with tungsten at room temperature, the maximum value, n_E, is 88. As the field approaches the value E_M, a one percent increase in field causes a 2.4 fold increase in j. When E is 90 percent of its final value, that is, when $E = 0.9\ E_M$, the emission is only about 10^{-4} as great as when $E = E_M$.

If there are slight geometrical irregularities, such as ridges or crystal corners on the surface of the cathode, there will be much stronger fields at the summits of these elevations. In regions where the field is only 10 percent greater, the current density would be so much greater that practically the whole emission may well occur from such points.

With the strong fields necessary to pull electrons out of cold metals, the electrostatic pull exerted on the surface may become very great. This force amounts to $4.4\ (10)^{-7}\ E^2$ dynes cm^{-2} when E is in volts cm^{-1}. Thus, when $E = E_M$ for tungsten, the pull on the surface is equivalent to a negative pressure of about 9000 atomospheres. This, however, is a force far below the tensile strength of a material like tungsten and therefore should not be able to disrupt the surface unless the temperature is extremely high or there are projections only loosely held to the underlying metal.

Experimental phenomena which involve the pulling out of electrons from cold metals have been observed and studied in considerable detail in recent years. R. W. Wood[113] passed discharges from an induction coil between platinum spheres 1.5 millimeters in diameter placed 1 to 5 millimeters apart in relatively high vacuum. X-rays were produced at the anode sphere, showing that the voltage across the gap was very high. This is clearly an example of a cold cathode discharge. There was a considerable transfer of platinum from the anode to the cathode. This was probably caused by the mechanical disintegration of the anode resulting from the temperature fluctuations produced by the intermittent discharge, such as is produced at the anode of a Coolidge X-ray tube when operated on alternating current. The mechanical force due to the high local field would pull the disintegrated metal to the cathode. On reversing the polarity showers of minute sparks were shot out from the new anode, consisting of incandescent particles ripped off the anode.

F. Rother[114] has investigated the electron emission from a cathode in an intense field obtained by bringing the surfaces of the cathode and anode extremely close together, the distances ranging from 10^{-6} to 10^{-3} centimeter. In this way it is possible to obtain great field strengths with such low voltage differences that measurements can be conducted at atmospheric pressure.

---

[112] W. Schottky and H. Rothe, Handbuch d. Expl. Physik Vol. 13, Part 2, p. 261, Leipzig 1928.

[113] Wood, Phys. Rev. **5**, 1 (1897).

[114] Rother, Ann. d. Physik **81**, 317 (1926).

Lilienfeld, using high voltages and high vacuum, utilized electron currents drawn from pointed cathodes and produced X-ray tubes on this principle. Millikan and Eyring[115] have measured quantitatively the electron currents drawn from tungsten filaments with fields ranging from 0.4 to 1.1×10^6 volts per centimeter, and have studied the effect of the temperature of the filament and the condition of its surface.

The past history of the surface has a very great effect on the field strength needed to draw electron currents. A fresh surface generally shows large emission which may vary with time so that the results are at first not reproducible. If the surface is "conditioned" by drawing currents with a high field, then the emission at lower fields usually becomes reproducible. Glowing the filament to 2700°K changes the surface in such a way as greatly to increase the field required to obtain a given electron current with the filament at room temperature. These observers found not only that the temperature coefficient of the electron emission at high fields is much less than at low fields, but obtained the surprising result that the "field currents" were entirely independent of the filament temperature between 300°K and 900°K, within the experimental error of about 5 percent. At 1100°, however, the field needed to draw a given current (10^{-11} amperes) was as much as 30 percent less than the field needed at 300° when the condition of the filament was such that strong fields were needed. When, however, the condition was such as to give greater electron emission (fresh filament), the critical field even at 1100° was the same as at 300°.

In a later paper, Eyring, MacKeown, and Millikan[116] studied field currents in high vacuum from points of tungsten, platinum, nickel and steel. The points were made as nearly as possible in the form of hyperboloids of revolution and were brought close to a plane tungsten disk as anode. The field strength at the surface of the point was calculated according to a theory given. Within the experimental error (2 percent), the field at the surface required to draw a given current was independent of the distance between the point and plane, and thus was independent of the total voltage applied between these electrodes.

In all of these results as well as those published by the research staff of the General Electric Company, London,[117] the data agreed with the empirical equation[118]

$$j = A(T + cE)^2 \epsilon^{-b/(T+cE)} \tag{35}$$

according to which for strong fields and low temperatures the logarithm of the electron current is a linear function of the reciprocal of the field strength. This type of relation is in much better agreement with the experiments than that suggested by Schottky's theory according to which log I is a linear function of $E.^{1/2}$

---

[115] Millikan and Eyring, Phys. Rev. **27,** 51 (1926). This article contains references to the earlier investigators in this field such as Earhart, Kinsley, Hobbs, Hoffman and Lilienfeld.

[116] Millikan and Eyring, Phys. Rev. **31,** 900 (1928).

[117] Research Staff of the Gen. Elec. Co., London, Phil. Mag. (7) **1,** 609 (1926).

[118] Millikan and Lauritsen, Proc. Nat. Acad. of Sci., **13,** 45 (1928).

The fact that the temperature coefficient of the field current is practically zero and is thus negligible as compared with that given by the classical theory, Eq. (29), is proof that the electron energies do not increase in proportion to the absolute temperature as they should do according to the classical gas laws. This fact, however, seems to be consistent with the modern quantum theory of the degenerated electron gas as developed by Fermi, Dirac, Nordheim, and Sommerfeld.[119] On this basis there has been developed a theory[120] according to which the field currents from cold metals should be given by

$$j=aE^2\epsilon^{-D/E} \tag{36}$$

where a and D are constant for the metal. The data of Eyring, MacKeown and Millikan[116] obtained with a steel point give straight lines, when $\log j$ is plotted against $1/E$, whose slope gives for D the value $D=6.7\ (10)^6$ volts cm^{-1}. If we assume that the value of b for steel is 67000, this would give for the value of c in Eq. (35) the value 0.010 deg. cm volt^{-1}.

By logarithmic differentiation of Eq. (36) we find for the value of n_E, defined by Eq. (30), the value

$$n_E=2+D/E. \tag{37}$$

For the experiments with the steel points described just above, for which the average field strength was $E=0.33\ (10)^6$, $n_E=22$.

In some unpublished work by W. D. Coolidge and I. Langmuir in 1922 a V-shaped tungsten filament 0.0216 cm diameter was mounted in a small bulb opposite the center of a molybdenum disk 3 cm in diameter, the distance being adjustable by a micrometer through a Sylphon joint. The molybdenum disk was baked out at incandescence and the filament was aged at about 2700°K. One leg of the filament was then broken off by bringing the plate in contact with it so that there was then a straight piece of filament opposite the molybdenum disk.

The voltage difference between point and plane was adjusted until a field current of 10^{-5} amperes was obtained from the point at room temperature. The distance was varied and in each case the voltage was changed until the current rose to the same value. Fig. 7 gives the results obtained in this way, the voltages being plotted as abscissas and the logarithm of the distance between the end of the wire and the plane being given by the ordinates.

Maxwell[121] has calculated the potential distribution between two coaxial confocal paraboloids of revolution maintained at a given difference of potential. The potential at any point P is found to be a linear function of log $(r^{1/2}\cos\theta/2)$ where r is the distance of the point P from the focus O and θ is the angle POT where the line OT lies in the axis of the paraboloid. The electric

---

[119] E. Fermi, Zeits. f. Physik **36**, 902 (1926); P. A. Dirac, Proc. Roy. Soc. London, **112**, 661 (1926); L. Nordheim, Zeits. f. Physik **46**, 833 (1928); A. Sommerfeld, Zeits. f. Physik **47**, 33, 38, 43 (1927).

[120] Fowler and Nordheim, Proc. Roy. Soc. **119**, 173 (1928); Oppenheimer, Phys. Rev. **31**, 66 (1928).

[121] Maxwell, Collected papers, Vol. 1, page 242.

field normal to the surface of the inner paraboloid at its vertex is given by $E=V/(p.\,ln(c/p))$, where V is the difference of potential between the two paraboloids, p is the distance from focus to vertex for the inner paraboloid defined by $y^2=4px$, while c is the corresponding distance for the large one. If c is much larger than p so that the curvature of the outer paraboloid is negligible compared with that of the inner, the outer paraboloid may be replaced without appreciable error by a plane surface. We thus have a means of calculating the potential gradient at the surface of a rounded point brought opposite a plane surface. This theory should, in fact, be better applicable to the case of a point and plane than the theory of confocal hyperboloids. If a is the radius of curvature at the point (at the vertex of the inner paraboloid) and c is the distance between the point and plane, then the equation becomes

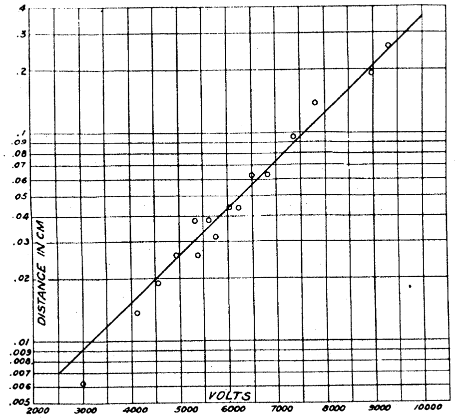


Fig. 7. Cold Cathode Emission. Relation of potential to distance between point and plane for constant current.

$$E=\frac{2V}{a\cdot ln(2c/a)}\cdot \tag{38}$$

If the currents from the tungsten point which gave the data of Fig. 7 depended primarily upon the electric field at the surface of the point, then, since the current is kept constant, the field E must have remained constant as the distance was increased. According to Eq. (38) the logarithm of the distance c should then be a linear function of the voltage V. It is seen, in fact, that the experimental points agree within the experimental error with a straight line.

Because of the fact that the wire was broken off square instead of having the surface like that of a paraboloid, the actual field strength at the end of the wire must vary greatly at different parts of the surface and will not be given by Eq. (38). However, this equation must give a close approximation to the *average* field strength over the end of the wire. Thus since the *ratio* between the fields at given points over the surface of the end of the wire will be approximately independent of the distance of the point from the plane, our conclusion that the voltage for a given field strength should vary linearly with the logarithm of the distance remains valid.

From the slope of the line in Fig. 7 we find that $dV/d(\ln c) = 1910$ volts and thus from Eq. (38), placing a equal to the radius of the wire (0.0108 cm) we find the *average* field strength E to be 350,000 volts cm^{-1}.

The foregoing results, together with those of Eyring, MacKeown and Millikan[116] prove that the field currents are actually a function of E only and not a function of the applied potential difference, V, and thus seem to disprove the conclusions of del Rosario[122] according to whom the current depended upon V and not E.

The following qualitative observations by Coolidge and Langmuir in connection with these experiments throw light on the nature of the field currents. When the currents exceed a few microamperes, spots of fluorescence appear on the glass and sometimes on the anode. These spots prove that the major part of the field currents emanate from minute spots on the cathode, for the fluorescence spots usually subtend angles of only a few degrees from their point of origin on the cathode, and sometimes less than 1°. In some experiments the cathode was a filament mounted on long leads. When the cathode was shaken the fluorescent spots always moved with it.

As the current and voltage are increased, the fluorescent spots become more brilliant and the walls of the tube become intensely heated at these points. This may lead even to the puncturing of the glass. These effects do not depend upon the presence of gas and the fluorescence spots are able to receive electrons continuously only because they become positively charged as a result of secondary electron emission.[123] As the field is increased, not only do the old spots become brighter but new ones continually appear. Thus experimental observations on the variation of field currents with field strengths should not agree accurately with the theory which led to Eq. (36) for this is deduced on the assumption that the current is uniformly distributed over the surface.

Field currents are obtained much more easily from surfaces covered with adsorbed films of electropositive materials. This effect was studied in some detail by Dushman, Langmuir and Hull in June and October, 1914.[124]

In the development of the high voltage kenetron, it was found necessary to degas the anodes by heating them to incandescence using voltages of 30,000 or 40,000 volts, the cathode temperature being reduced so that the current became limited by saturation emission, whereas in normal operation, the current is limited by space charge and the voltage drop from cathode to anode is relatively low. In 1915, kenetrons for 100,000 volts were manufactured. During exhaust the anode was made as much as 100,000 volts positive

---

[122] del Rosario, Jr. Frank. Inst. **203,** 243 (1927).

[123] Langmuir, Gen. Elec. Rev. **23,** 513 (1920).

[124] Unpublished work in Research Laboratory, Gen. Elec. Co., Schenectady; see also later work by Gossling, Phil. Mag. **1,** 609 (1926).

with respect to the cathode, while currents of 10 or 20 m.a. were drawn from the cathode. In this work the "cold cathode effect" became very noticeable at about 50,000 volts but by progressive degassing and heating of anode and cathode and baking the glass walls, it was finally possible to use 100,000 volts without appreciable "cold cathode effect". This effect when present, was evidenced by fluorescent spots on the glass, and by intense local heating at points on the anode which became white hot while the rest of the anode was below red heat. To avoid this effect entirely at 100,000 volts, it was found necessary to eliminate all sharp points from parts of the electrodes where the electric field was the strongest.

In 1914 some experiments were made to test the practicability of using thoriated tungsten filaments in kenetrons. At first it was not possible to obtain any higher electron emission than from a pure tungsten filament, but with continued degassing of the electrodes and the walls of the tube and by activating the filament by heating to 2100° it was possible to obtain the typical increased currents from the adsorbed film of thorium. Then, for the first time, it was found that at 30,000 volts, without any heating current through the filament, enough electron current was obtained from the thoriated filament to keep the anode red hot. At first the tube was not self-exciting, that is, if the anode was allowed to cool by removing the anode voltage for a couple of minutes, the tube would not start up again on applying the voltage. However ultimately, after further heat treatment, the tube was brought to the condition that it would start up as soon as 30,000 volts were applied to the anode, the currents being at first small but rising rapidly as the cathode became heated by the back radiation of the anode. These and many other similar experiences proved that the cold cathode effect occurred with an *activated* thoriated cathode at voltages of only one-third to one-half those needed to give a similar effect with pure tungsten. For this reason for many years much care was used to avoid all traces of thorium in both cathodes and anodes of kenetrons and Coolidge X-ray tubes.

In another experiment, a 5 mil V-shaped filament of tungsten containing 1.5 percent of ThO_2 was mounted in a tube with the tip of the V about 5 mm from a plate-shaped tungsten anode which had been degassed by heating white hot by electron bombardment. With the filament activated and giving currents of the order of 10^{-4} amp., the saturation current at 5000 volts was more than 10 times that obtained at 100 volts. A capsule containing metallic potassium was then broken in the tube in order to make it easier to maintain the thoriated filament in an active condition. With 7000 volts a magnificent blue fluorescence was then observed on the tungsten anode in spots and streaks and there was green fluorescence on the glass behind the anode. After the discharge had heated the anode red hot no further fluorescence on the anode was observed. With the filament heated to emit small currents at low voltages, the voltage was then raised to 10,000 and 20,000 volts. There were spots and streaks of green fluorescence on the glass which moved with the cathode when this was shaken. On a further rise of voltage sudden flashes or explosions seemed to occur within the bulb as though the charges on the glass readjusted themselves. After each flash the positions of all the fluorescent spots were shifted and the intensity usually much increased. Soon, however, the spots returned to their original places and the intensity decreased. Raising the voltage to 35,000 a sudden flash occurred accompanied by a crackling sound and there then appeared a dazzling bright minute spot on the anode which rapidly heated the whole anode to incandescence. This spot moved over the surface of the anode when the cathode was moved proving that it was due to a fine pencil of cathode rays emanating from a spot on the cathode. Turning off the filament heating current, field currents of 5 ma at 30,000 volts were obtained with cold cathode. There could have been no appreciable positive ion bombardment of the filament for there was never any heating observed at the cathode. Momentary heating of the filament to 1800°K made the filament inactive so that no cold cathode emission was obtained at 30,000 volts, but at 35,000 volts again a similar flash occurred which rendered the cathode active.

Coolidge in 1914 and Coolidge and Langmuir in 1922 observed that when the field currents from a point in high vacuum were raised to several m.a., incandescent sparks were shot out from the cathode in the general direction of the anode. These particles described sharply curved paths, the curvature being convex on the side towards the anode, so that most of the particles did not strike the anode. Many of these particles when they struck the bulb rebounded; some were also observed to strike the disk-shaped anode and to rebound from its surface. This effect is probably caused by local heating resulting from the enormous current densities at the spot from which the electrons are emitted. Such particles are strongly negatively charged when they leave the cathode and are attracted toward the anode. Because of their high temperature, however, they emit electrons and become positively charged and are then repelled from the anode. It is difficult to understand, however, how positive charges of sufficient magnitude can be acquired to cause such marked curvature as that which was frequently observed.

The temperature rise, ΔT, caused by a current, i, (amperes) flowing out of a small spot in which the current density is I (amp. cm^{-2}) can be calculated to be approximately

$$\Delta T = \rho I i / 8\pi\lambda \tag{39}$$

where ρ is the specific resistance of the material (ohms cm) and λ is the heat conductivity (watts cm^{-1} deg^{-1}). Thus, for tungsten at room temperature $\rho = 5\ (10)^{-6}$ and $\lambda = 1.5$ so that the temperature rise is $\Delta T = 1.3\ (10)^{-7}\ I\ i$. Thus, even if the current density were $I = 10^9$ amp cm^{-2}, the rise in temperature at the emitting spot would only be 1.3° with an emission of 10 ma. The incandescent particles pulled out from the tungsten cathode therefore probably originate only at points on the surface where the surface metal is not in good thermal and electrical contact with the underlying material.. Possibly also the Bridgman effect caused an increase in the heating.[125]

---

[125] Bridgman, Proc. Nat. Acad. Sci. **10,** 297 (1921); Proc. Amer. Acad. of Arts and Sci. **57,** 131 (1922). Bridgman found that the resistance of gold and silver increased about one percent when the current density was 4 $(10)^6$ amp cm^{-2} and this increase in resistance was roughly proportional to the square of the current density.

Schottky has calculated[126] that the field at any surface irregularity is proportional to the average field over the surface, but about 10 times greater in magnitude provided these surface irregularities are small in comparison with the linear dimensions of the surface. This is in agreement with the fact that the observed values of E giving field currents are 10 or even 100 times less than those calculated either by Schottky's theory or by the newer theories involving wave mechanics.

The distribution of potential near the summit of a ridge-like elevation upon a surface may be roughly calculated as follows. Consider first the potential distribution in the neighborhood of an infinite conducting solid body which is bounded by two intersecting planes forming a dihedral angle β, this angle being less than π. Let α be the external angle, $\alpha=2\pi-\beta$. Then it can be shown that the potential V at any point P in space outside the solid body is given by

$$V=Kr^n \sin n\theta \tag{40}$$

where

$$n=\pi/\alpha. \tag{41}$$

Here K is a constant, r is the distance of the point from the line of intersection O of the two planes and θ is the angle between the radius vector PO and its projection on one of the planes. The electric field E at the surface of either plane of the solid is given by

$$E=Knr^{n-1}. \tag{42}$$

We now consider a symmetrical ridge rising to a uniform height h above a horizontal plane and bounded by two plane surfaces forming an angle β, the bisecting plane being vertical. Let the line OC be a vertical line rising from any given point O at the summit of the ridge. At any given height c above O, the *field* due to the ridge (ignoring for the present the horizontal plane) is in a vertical direction and has the value

$$E=Knc^{n-1} \tag{43}$$

whereas the *field* due to the plane (ignoring that due to the ridge) is

$$E=E_0 \tag{44}$$

where E_0 is the field strength which would exist over the plane in the absence of the ridge. Similarly we may find the *potential* at a point at a distance c above O, first ignoring the plane and then ignoring the ridge, these potentials being respectively

$$V=Kc^n \tag{45}$$

and

$$V=E_0(h+c). \tag{46}$$

---

[126] Schottky, Zeits. f. Physik 14, 63 (1928).

We may now eliminate c and K by assuming that the fields given by Eqs. (43, 44) are equal and the potentials given by Eqs. (45, 46) are equal.* We thus find for the field strength E at the surface of the ridge at a distance r from the vertex the approximate value

$$E = E_0 \left[\frac{nh}{(1-n)r} \right]^{1-n} \tag{47}$$

or

$$\log\left(\frac{r}{h}\right) = \log\left(\frac{n}{1-n}\right) - \frac{1}{1-n} \log\left(\frac{E}{E_0}\right) \tag{48}$$

Table VIII gives the values of r/h calculated by Eq. (48) for ridges having various summit angles β. The values of r/h are calculated for two values of E, viz., 10 E_0 and 100 E_0. Thus for the 90° ridge (each side at 45° slope) a field E varies inversely with the cube root of r, the distance from the vertex, and the field is more than 100 times E_0 for a distance of 2 $(10)^{-6} \times h$ from the vertex and is greater than 10 E_0 for a distance of 2 $(10)^{-3} \times h$.

TABLE VIII. *Field E at distance r from summit of ridge of height h on plane; β = angle at ridge, E_0 field at large distance from ridge.*

β	n	r/h	
		$E = 10E_0$	$E = 100E_0$
0	0.500	0.01	10^{-4}
30°	0.545	.0075	4.8×10^{-5}
60°	0.600	.0048	1.5×10^{-5}
90°	0.667	.0020	2×10^{-6}
120°	0.750	.0003	3×10^{-8}
150°	0.857	6×10^{-7}	6×10^{-14}
180°	1.000	0	0

These results may be used to calculate the field distribution over the square end of the wire of the experiment of Fig. 7. The actual wire may be approximately represented by a cylinder with rounded end on which is superimposed a square ridge with $\beta = 90°$ and $h = 1/10$ of the diameter of the wire, *i.e.*, $h = 0.0022$ cm. The average field E_0 over the surface was 350,000 volts cm^{-1}. The field was at least 10 times greater than this for a distance of 4.4 10^{-6} cm from the vertex of the ridge, giving a total area of 6 $(10)^{-7}$ cm^2. Since the current was 10^{-5} amp, the average current density over this area would have been 17 amp. cm^{-2}. A field of 100 E_0, *viz.*, 3.5 $(10)^7$ volt cm^{-1} extended for a distance $r = 4.4$ $(10)^{-9}$ cm according to the data of Table VIII, and to give the required current the current density would have been 1.4 $(10)^4$ amp. cm^{-2}.

Obviously we cannot expect to apply this theory when the value of r is less than the diameter of the atoms constituting the surface. Actually, the

---

* That this approximation gives reasonably accurate results follows from the fact that the field E at the summit of a hemispherical boss on a plane can be calculated in this way to be $4E_0$, whereas a rigorous calculation, which may be made for this case, gives $E = 3E_0$.

emission of fine pencils of cathode rays proves that the emission cannot occur from a ridge but from the serrated points along such a ridge. The theory, however, aids in forming a conception of the magnitude of the effects to be expected from surface irregularities.

Some experiments under unusually good vacuum conditions were carried out by W. D. Coolidge in 1923 (unpublished work). Two short V-shaped filaments were mounted in a small bulb so that the tips of the V's came within about 0.1 mm. One of these filaments was one mil diameter (0.0025 cm) and the other one was 8 mil diameter (0.020 cm). The tube was well exhausted and the filaments were degassed at very high temperature. During much of the work with the tube, it was immersed completely in liquid air to improve the vacuum still further.

The following are some of Coolidge's observations. With the bulb in liquid air after the filament has been heated to high temperature and allowed to cool, the filament is very inactive. If the voltage is gradually raised to the neighborhood of 10,000 volts until an appreciable field current can be measured on the galvanometer and the voltage is then kept constant, the current gradually increases at a rapidly accelerating rate but suddenly becomes constant and remains so. The filament is then in an "active" condition. The filament remains active if the voltages are taken off for a long time and reapplied. If the filament is heated to 1600° for 10 or 15 seconds, or to 2400° for one second, the filament becomes inactive but can be made active again by applying a sufficiently high voltage until the current again rises to its limiting value. With continued experimentation, the voltage required to activate the filament gradually increases. Heating the anode filament (the large filament) even to 2500° while the bulb is in liquid air has no effect on the field currents obtained from the small filament.

After the liquid air is removed, as the bulb temperature rises, the field currents at a given voltage first decrease and then, as the temperature approaches room temperature, the currents increase greatly. Heating the filament above 1600°K still caused a great decrease in activity.

In some experiments oxygen at a pressure of a few microns was introduced. Usually this caused no marked increase in activity if the bulb was in liquid air or at room temperature, but if the bulb was then heated moderately the filament became very active. This suggests that traces of alkali metal escaped from the glass and are held by a monatomic oxygen film on the tungsten. Heating the filament above about 1600° drives off some of the oxygen from the tungsten surface and renders the film inactive.

In general, the filament could be rendered active by raising the voltage sufficiently to draw fairly large currents. This activation was often accompanied by a crackling sound suggesting that disruptive discharges over the surface of the glass caused gas evolution which altered the cathode in such a way as to make it active. Activation also occurred as mentioned above by heating the bulb after oxygen treatment. Introduction of hydrogen seemed to have no effect on the activity. The cathode was rendered insensitive by heating to 1600 or 1800°K and sometimes by drawing excessively large currents (a few milliamperes).

The difference in the voltages necessary to draw currents from the inactive and from the active filaments frequently differed in a ratio as great as 10 to 1 or even 20 to 1.

These results emphasize the importance in future work on field currents, of exceptional care in controlling surface conditions of the cathode. After each measuring of field current it would seem desirable to test the condition of the filament by measuring its electron emission at a suitable testing temperature.

Finally, attention may be called to two very recent papers[127] dealing on the basis of wave mechanics with field currents, and especially with the modification introduced into Eq. (36) by the presence of a thin adsorbed layer of electropositive material. Comparison with experiments indicates a possibility of satisfactory interpretation of complications due to surface layers and indicates stable films of thicknesses of the order of $2.5\ (10)^{-8}$ cm.

(7) **Electron emission due to electron bombardment** is one of several phenomena which have been described as *secondary electron emission*, although it was originally called *delta ray* emission.[128] It is impossible to tell whether a secondary electron is simply a reflected primary, or whether it is an electron, originally of the metal, which has been ejected by the primary. For all practical purposes these two possibilities need not be differentiated. The fact however, that the number of secondaries sometimes exceeds the number of primaries proves that real emission does occur.

The main facts of this secondary emission may be summed up as follows: (a) The secondary emission depends considerably on the surface treatment of the metal, being generally reduced by heat treatment and degassing and increased by contamination, especially with electropositive impurities. (b) The emission increases from a low value (perhaps zero) for zero velocity of the primary electrons, rises to a maximum for primary electrons of a few hundred volts energy, and then slowly diminishes with further increase of energy of the primaries. (c) The maximum ratio of the *number of secondary electrons per primary electron* is between about 1.0 and 1.5 for well degassed ordinary metals; it may reach values of 3 or 4 for metals not specially treated. For electropositive metals this ratio is greater. For films of alkali metal on an oxidized metal surface, the number of secondaries per primary may be as large as 8 or 10. (d) Although the general trend of secondary emission with voltage is as described, there are superimposed small variations of the nature of subsidiary maxima which suggest the existence of *critical potentials* at which secondary emission by new processes set in. (e) The *velocities of the secondary* electrons are, for the most part, quite small, amounting to only a few volts even for primary electrons of a thousand volts. (f) The *directions of emission* of the secondary electrons appear to be distributed more or less at random. (g) Except for its effect in conditioning the surface, moderate *temperature variations* of the surface appear to have little effect. (There is

---

[127] Stern, Gossling and Fowler, Proc. Roy. Soc. **A124,** 699 (1929); Stern, Proc. Camb. Phil. Soc. **25,** 454 (1929).

[128] Campbell, Phil. Mag. **22,** 276 (1911); **25,** 803 (1913); **28,** 286 (1914); **29,** 369 (1915).

indication, however,[129] that the critical potentials mentioned under (d) are strongly emphasized if the surface is extraordinarily well freed from adsorbed gases, as by keeping it continually hot in a good vacuum.) The foregoing characteristics have been established by many observers.[130] A number of these agree in finding indication of about 0.50 of incident electrons of very low velocity reflected from ordinary metal surfaces, though the interpretation of results is particularly uncertain for very low velocities.

In view of the importance of reflecting power in the theory of thermionic emission (see section B 1), it is of interest to note the following strong evidence *against* a reflecting power of the order of 50% at low velocities. Langmuir and Jones[131] in their studies of ionization phenomena between an axial tungsten cathode in a cylindrical molybdenum collector measured the fraction of the primary electrons which left the cathode that were collected by the cylinder without having lost energy by inelastic collisions (see also section D 2b). If the logarithm of this fraction is plotted as ordinate against the pressure, straight lines are obtained whose slope is R/λ_1 where R is the radius of the cylinder and λ_1 is the free path of the electrons for inelastic collisions at unit pressure.

The intercept of this line gives the fraction of the electrons that would be collected if there were no collisions. This should be unity if it were not for the reflection of electrons incident on the cylinder. Actually, the intercepts that are found experimentally range from 0.77 to 0.83 and are independent of the nature of the six different gases used. This result proves that with molybdenum surfaces which have been cleaned by bombardment by positive ions the reflection coefficient, for electrons striking the surface normally with energies corresponding to 10 to 20 volts, lies between 0.17 and 0.23.

The shapes of the curves obtained by Langmuir and Jones were in good agreement with the empirical equation

$$1/(1-r)=1+0.0645V^{1/2}$$

where r is the reflection coefficient of electrons having an energy corresponding to V volts. Their data are wholly inconsistent with any increase in r as V decreases. The results thus indicate that the reflection coefficient becomes very small for low velocity electrons.

The electric image theory of the forces acting on an electron close to the surface of the metal also gives strong reasons for the view that the reflection coefficient should approach zero as the velocity of the incident electrons becomes very small. Consider, for example, electrons in equilibrium with a surface at 2000° which impinge on the tungsten surface. These electrons will

---

[129] Krefft, Phys. Rev. **31**, 199 (1928).

[130] Gehrts, Ann. d. Physik **36**, 995 (1911); Hull, Phys. Rev. **7**, 1, 141 (1926); McAllister, *ibid.* **21**, 122 (1923); Farnsworth, *ibid.* **20**, 358 (1922); **25**, 41 (1925); Petry, *ibid.* **26**, 346 (1925); **28**, 362 (1926); Gill, Phil. Mag. **45**, 864 (1923); Horton and Davies, Roy. Soc. Proc. **97**, 23 (1920); Phil. Mag. **46**, 129 (1923); Stuhlman, Phys. Rev. **25**, 234 (1925). Tate, *ibid.* **17**, 394 (1921).

[131] Langmuir and Jones, Phys. Rev. **31**, 401 (1928). See particularly Fig. 15.

have, on an average, energies of about 0.2 volt, but as they approach the metal they are acted on by the attractive force corresponding to the electric image. If the work function, 4.5 volts, is entirely due to the electric image force, the electrons will have an energy of about 4.7 volts by the time they reach the actual metal surface. If they should lose only 0.2 of a volt or about 4 percent of their energy, they will be unable to escape from the surface. According to some modern theories involving wave mechanics, the electric image force may be equivalent to energies of 10 or even 15 volts which is partly balanced by the electron pressure within the metal. On this basis, energy losses of much less than 4 percent would prevent the reflection of the electrons.

It was pointed out by Langmuir[132] that from the heat conductivity of a metal the time of relaxation of the electrons can be calculated. For tungsten this time is of the order of 10^{-15} seconds. This is about the time that it takes for an electron, having unusually high energy, to lose all but $1/\epsilon$th of its excess energy. A 0.2 volt electron which has an energy of 4.7 volts when it reaches the metal, is traveling with a velocity of 1.2×10^8 sec. and therefore when it penetrates within the metal to a distance of only a single atomic diameter, remains in the metal about 0.4×10^{-15} sec. and thus should lose about half of its energy because of the normal heat conductivity of the metal. Thus only an extremely small part of the electrons should lose less than 4 percent and only these can be reflected from the surface.

There is another effect, however, which must also greatly decrease the probability that low velocity electrons will be reflected. When an impinging electron has penetrated within the surface layer of atoms, all other free electrons are repelled from it, leaving a slightly greater positive charge than before the incident electron arrives. This is a kind of internal image force analogous to that postulated by Debye and Hückel in their theory of electrolytes. The length of time it takes to bring about this redistribution of charge can be estimated roughly as follows. In a metal of specific resistance ρ consider a charge e brought to the center of a sphere. Let t be the time that it takes for the charge within the sphere to fall to $1/\epsilon$th of its original value. We thus find $t = 10^9\rho/4\pi c^2$ where c is the velocity of light. For tungsten $\rho = 5 \times 10^{-6}$ and thus we find $t = 4 \times 10^{-19}$ sec. The redistribution, therefore, within the metal occurs in 1/1000 of the time of transit of the electron. At some slight distance from the surface where the electron concentration is lower, the time of relaxation will be comparable with the rate of passage of the electron and there will be relatively large hysteresis effects which will lead to considerable energy dissipation and thus tend to prevent reflection.

Besides being of importance in certain very special types of discharge (Lilienfeld X-ray tube,[133] Hull dynatron[134]) and in equilibrium theories of thermionic and photo-electric emission, electron reflection has recently become of great interest in the interpretation of the electron itself and the foundations of the quantum theory. This latter aspect developed from

---

[132] I. Langmuir, Phys. Rev. **8**, 171 (1916).

[133] Lilienfeld, Ber. d. König. Saechs. Ges. d. Wiss. **66**, 76 (1914).

[134] Hull, Phys. Rev. **7**, 141 (1916); Proc. Inst. Rad. Eng. **6**, 5 (1928).

studies six or eight years ago by Davisson and Kunsman[135] of the angular distribution of that very small fraction of rather fast primary electrons incident on a metal surface which are reflected with practically the entire original energy. Since then the phenomenon has been carefully investigated by Davisson and Germer[136] using reflection from the faces of nickel crystals. These experiments show strong reflection at particular angles of incidence and reflection which are related by the ordinary laws of diffraction of waves by a crystal lattice, and prove that the electrons behave like trains of waves of wave-length $\lambda = h/p$, where h is Planck's constant and p is the momentum of the electron. Furthermore it is found that the refractive index of the crystal for these waves is not unity, but that the crystal possesses a sort of "dispersion" curve for electrons of various equivalent wave-lengths. This "wave nature" of electrons is strikingly confirmed by the experiments of G. P. Thomson, who has shown that electrons in passing through thin films of metal, or when incident at grazing angle on a sputtered film on quartz, are scattered as if diffracted characteristically for waves of length $\lambda = h/p$ by the atomic lattice grating.[137]

Under the influence of electron bombardment secondary electrons may be emitted not only from metallic surfaces but from the *surface of insulators.* High velocity electrons striking glass surfaces may cause more than one secondary electron to be emitted per incident electron. Thus the glass surface becomes positively instead of negatively charged. In most high vacuum, high voltage discharge tubes, especially when operated at higher voltages than normal, spots of blue or green fluorescence are seen on the glass which owe their origin to pencils of cathode rays pulled out from the cathode by the intense fields. There is marked heat evolution at such fluorescence spots proving that these spots are at relatively high positive voltages with respect to the cathode. Since these phenomena occur in tubes in which no appreciable current can be carried by positive ions, it follows that the positive charge is maintained by secondary electron emission.

Langmuir[137a] has described experimental studies of these effects of secondary electron emission from glass surfaces. In general, two types of discharge are possible. First, those in which the walls become negatively charged and thus repel all further electrons except those few necessary to balance the small positive ion current. Fluorescence under these conditions, in presence of traces of gas, may be produced by positive ion bombardment. There are some indications that the red fluorescence sometimes observed with low pressures of oxygen is due to such positive ion bombardment. In the second type of discharge, secondary electron emission keeps the walls positive so that they continue to receive electrons, and a large part of the energy of the discharge may be then liberated in the form of heat at the walls.

---

[135] Davisson and Kunsman, Science, **64,** 522 (1921); Phys. Rev. **22,** 242 (1923).

[136] Davisson and Germer, Phys. Rev. **30,** 705 (1927); Proc. Nat. Acad. Sc. **14,** 317 (1928); Davisson, Jour. Frank. Inst. **205,** 597 (1928).

[137] G. P. Thomson, Nature **122,** 279 (1928); Proc. Roy. Soc. **A117,** 600 (1928); **119,** 651 (1928); **125,** 352 (1929).

[137a] Langmuir, Gen. Elec. Rev. **23,** 513 (1920).

A repetition[137a] of Lilienfeld's experiments[138] proves that his high vacuum discharges through long glass tubes are dependent entirely upon secondary electron emission from the walls of the tube.

(8) **Electron emission due to impact of metastable atoms** was for some years suspected of producing a part of the electron emission from a cathode, in the presence of an excited gas, which had at first been ascribed entirely to photoelectric action of the radiation. It was first definitely proved by Webb[139] and Miss Messenger,[140] who interposed screens of quartz and fluorite of measured optical transparency between the excited gas and electron emitting electrode, and from the amount of diminution of emission they were able to evaluate the relative importance of emission due to impact of metastable atoms and due to light in various parts of the speçtrum. They showed that the effect of metastable atoms is comparable with, and in some conditions considerably more effective, than photo-electric action in liberating electrons.

Recently Oliphant[141] has shown that the beam of positive ions of helium, which are shot through an orifice in a negatively charged Langmuir plane collector, may be largely transformed into a beam of metastable helium atoms of similar speed by allowing the ions to impinge at a glancing angle upon a metal surface. These metastable atoms, in turn, were found to liberate electrons upon impact with a second metal surface. The probability of liberation was at least several percent, and the simplest interpretation of the results is given by supposing that every metastable atom which reverted to the normal state at a metal surface set free one electron. Also a certain percentage of these metastable atoms was reflected at the surface, this percentage decreasing with depth of penetration, *i.e.*, with speed and with glancing angle, and increasing as the surface was heated. The amount of reflection was generally beween 10 and 50 percent. The electrons liberated by these metastable atoms possessed kinetic energies lying between a maximum value of $V_0 - \phi$ (where V_0 is the energy of the metastable state and ϕ is the work function of the metal) and a minimum value of about 2 volts, which may have significance in connection with Sommerfeld's theory of metals. Apparently the energy of emission of the electrons had no relation to the kinetic energy of the impinging metastable atoms.

Very significant evidence regarding the secondary emission of electrons from a negative cold electrode in a discharge has recently been obtained by Uyterhoeven and Harrington.[142] They introduced into a region of uniformly ionized neon gas, whose ionization was maintained by supplementary electrodes, the system of electrodes shown in Fig. 8. A circular disk electrode *D* was surrounded by an ample guard ring *G* and was pierced at its center by a pinhole. Close behind this pinhole was a Faraday box *F*. Between *D* and *G*

---

[138] Ann. d. Physik **32,** 673 (1910); *ibid.* **53,** 24 (1914); Leipziger Ber. **63,** 34 (1911).

[139] Webb, Phys. Rev. **24,** 113 (1924).

[140] Messenger, Phys. Rec. **28,** 962 (1926).

[141] Oliphant, Proc. Roy. Soc. **A124,** 228 (1929).

[142] Uyterhoeven and Harrington, Phys. Rev. **35,** 124 (1930); also more recent unpublished work.

was a narrow open gap as shown. There was no communication between the main discharge and the region below these electrodes except through this gap and the pinhole. Facing D was another Faraday box B, exclosed by glass except on the open end facing D. This box B could be moved vertically to various distances from D. The experiments which are of immediate significance are the following:

(1) Whatever the potential of the electrodes DG with respect to the ionized gas above them, there was always a considerable current between F and G, *which would pass in either direction* according to the sign of the field between F and G, and which was quite independent of the potential of DG with respect to the gas. Furthermore, applying a field between D and G had very little effect on this current. These observations proved that the conductivity between F and G was not due to charged particles passing from the main discharge into the region below DG. The currents, moreover, were of such a magnitude as probably to exclude their explanation as of photo-electric origin, especially in view of the complicated reflection which would have been involved in producing photo-electric emission from the under side of G. The only reasonable explanation of the currents between F and G thus seems to be action of long-lived metastable atoms which had diffused through the gap.

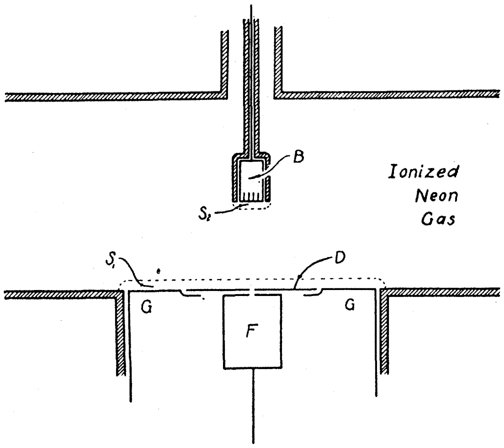


Fig. 8. Apparatus of Uyterhoeven and Harrington for study of electron emission due to positive ions and metastable atoms. Nickel electrodes.

(2) The collector B was used to prove the existence of a very considerable electron emission from the upper surface of the disk D which was exposed to the main discharge. To do this, the collector B was made negative with respect to the surrounding space by some definite amount, say 100 volts. It was then surrounded by a positive space charge sheath S_2 and it collected ions but not electrons from the surrounding ionized gas. Keeping this condition constant, the potential V of the electrodes DG was now varied from a small to a large negative value. So long as V was less negative than 100 volts, the elec-

trodes *DG* were practically without influence upon the current to *B*. Just as *V* was raised to 100 volts, a considerable negative current was received by *B*. Making *V* still more negative had relatively little further effect. This negative current to *B* must have been an electron current proceeding from *D*, and the fact that it came in definitely just when the potential of *D* became more negative than *B* proves that these electrons must have originated at the surface of *D* itself. If they had originated within the space charge sheath S_1, rather than at the electrode *D*, their velocity distribution would not have been so homogeneous.

Now these electrons may have been emitted by the action of light, of metastable atoms or of positive ions. Without doubt all three processes contributed. But the following reasons indicate that the metastable atoms exerted by far the preponderating effect. The amount of this electron current density was about half the total current density to *D*, indicating that approximately half the current to *D* was due to these secondary electrons and the other half to the incoming positive ions. The evidence in the following section (B 9) is that electron emission due to positive ion bombardment is far less effective than this. The same conclusion may be drawn from the fact that the results were essentially the same whether the potential of *B* was 50, 100 or 200 volts. Similarly no photo-electric effects of this order of magnitude have ever been recorded. Consequently we seem left with action of metastable atoms as the only adequate explanation.

This work is still in progress, obtaining additional data for a variety of gases, and also measuring electron free paths and the fraction of the current to the cathode which is carried by positive ions.

Some earlier work by Uyterhoeven[143] with apparatus similar to parts *D* and *G* of Fig. 8 led to results in He, Ne and A which, in the main, can be similarly explained, and whose significance in regard to electron emission due to positive ion impact is discussed in the following section (B 9). These conclusions are substantiated by Found,[143] who has used the characteristics of a cylindrical collecting electrode to evaluate the importance of emission of electrons by action of metastable neon atoms in the positive column of a neon discharge. The positive ion current to the negative collector is proportional to the area of the surrounding sheath, whereas the electron emission from it due to metastable atoms depends only on the area of the collector itself and hence is constant. In a positive column of 5 cm diameter in neon at pressure 0.225 mm, operating at 0.4 amp., the secondary electron emission from a negative tungsten collector is 7.5 milliamps/cm^2 compared to a positive ion random current density of 0.82 milliamps/cm^2. The current to a 2 mil collector at 100 volts negative to the discharge was thus approximately two-thirds due to secondary emission and one-third due to positive ions.

(9) **Electron emission due to positive ion bombardment** is another phenomenon which has long been suspected, but only recently proved, and really very little is known about it. Practically all of the older work is vitiated by unrecognized complicating effects.

---

[143] Uyterhoeven, Proc. Nat. Acad. Sc. **15**, 32 (1929); also thesis for Cal. Inst. Tech. 1929; Found, Phys. Rev. **34**, 1625 (1929).

The simplest conditions obtain when a metal surface is bombarded by positive ions in a high vacuum, and the resulting electron emission is measured after suitably allowing for positive ion reflection. Klein[144] and Jackson[145] have done this, using heated strips emitting positive ions of alkali metals as ion sources. The results of the two authors are in serious disagreement, due, we believe, to an unrecognized complication arising from the experimental arrangement in the former case. Jackson found, for K ions impinging perpendicularly on Al, Ni and Mo, no detectable electron emission (*i.e.*, less than 0.5 percent) for ion velocities below 200 volts for Al, 300 volts for Ni, 600 volts for Mo after degassing of these metals by heat treatment. Above these velocities the electron emission increased regularly to 7.0% for Al, 4.2% for Ni and 3.8% for Mo at 1000 volt velocities. Without the heat treatment the emission was detectable at about half the above minimum velocities and was about double the above values at 1000 volts. Positive ions of Cs were slightly more, and those of Na and Rb somewhat less effective than those of K. The electrons thus emitted were very slow, practically all of them being stopped by a retarding field of one volt.[146]

In the above experiments not more than 4% of the incident *ions were reflected*. At more glancing angles, however, and particularly with degassed surfaces, the percentage of reflection may be much greater, and the reflected ions possess a complicated distribution of directions and of retained energies.[147]

A very decisive test of the effectiveness of alkali ions in producing secondary electron emission from bombarded metal surfaces can be made by utilizing the remarkable constancy of the ion currents from a sufficiently hot filament in contact with the alkali metal vapors, since such currents depend only on the rate at which vapor atoms strike the filament and are entirely independent of applied voltage, provided this is sufficient to overcome space charge.[148] It is observed that if such a current of caesium ions from a filament to a surrounding axial cylinder is saturated at 50 volts, a sudden increase of voltage to 250 volts causes no perceptible change in the current. This proves that there is no change as large as a fraction of one per cent in the secondary electron emission in the range 50–250 volts, which makes it extremely probable that the total secondary electron emission itself is negligible.

It is particularly important to know the magnitude of this phenomenon in mercury vapor. Langmuir and Mott-Smith[149] found that the current to a negative nickel collector bombarded by Hg ions showed no evidence of secondary electron emission due to bombardment up to 1160 volts, though their conditions were such that an emission of not over 10% would not have

---

[144] Klein, Phys. Rev. **26,** 800 (1925).

[145] Jackson, Phys. Rev. **28,** 524 (1926); **30,** 473 (1927).

[146] See also Baerwald, Ann. d. Physik **60,** 26 (1919).

[147] Read, Phys. Rev. **31,** 155 (1928); Gurney, *ibid.* **32,** 467 (1928).

[148] Langmuir and Kingdon, Science **57,** 58 (1923); Killian, Phys. Rev. **27,** 578 (1926). Note particularly the flat saturation curves in Figs. 5, 6, p. 585 of Killian's paper.

[149] Langmuir and Mott-Smith, G. E. Rev. **27,** 544 (1924).

been detected on account of uncertainties in the "edge correction" to the currents to the collector. Then Dällenbach, Gerecke and Stoll[150] showed that Hg^+ ions incident on an iron electrode with energies up to 3000 volts are not more than perhaps 1 percent effective in liberating electrons from the electrode.

In some recent unpublished work, Langmuir and Sweetser have measured the variation of current to a negative collector with voltage far more accurately than in the work of Langmuir and Mott-Smith. The collector was of molybdenum of the guard-ring type. The outer diameter of the guard-ring was 1.92 cm while the diameter of the inner part of the collector was 0.64 cm, the separation between the two collectors being less than 0.005 cm. Both parts of the collector were always kept at the same voltage, but the current was measured only for the central part. The fractional variation of current per volt change in collector potential, which we may represent by β, was measured under a wide range of conditions. The largest observed variation ($\beta = 0.001$) was found only under conditions where the sheath thickness (x) was very large (0.20 cm). By varying x by altering the intensity of ionization, for example by changing the cathode current, it was found that β varied with x according to the equation

$$\beta = \beta_0 + 1.65x^2/(Vr_0^2) \tag{49}$$

where V is the negative voltage on the collector and r_0 is the radius of the outer perimeter of the guard-ring. In this equation the term involving x^2 is of the form to be expected for a residual edge correction due to an insufficiently large guard-ring. This equation was found to express the results for discharges for both argon and mercury vapor.

With a greater intensity of ionization the term involving x^2 becomes quite small as compared with β_0 and thus the value of β_0 could be found with reasonable accuracy. For the discharges in mercury vapor $\beta_0 = 0.0002$ volt^{-1}. For argon $\beta_0 = 0.0006$ volt^{-1}. In these experiments the voltage of the collector was varied from 50 to 150 volts. In this whole range of 100 volts, therefore, it may be concluded that if there is any electron emission produced by positive ion bombardment it varied by about 2 percent for mercury and 6 percent for argon, these being expressed as percentages of the total positive ion current flowing. (Experiments with collectors designed to catch the electrons emitted from the surface of a negatively charged collector are now in progress by Tonks and Sweetser).

Similar experiments by Uyterhoeven,[143] at rather lower pressures, do not agree very accurately with Eq. (49), but if this equation is used as a rough approximation then values of β_0 may be computed. Typical values are: He–Ni, 0.0020; A–Ni, 0.00095; A–C, 0.0012.

It should be noted that these are "apparent" values, based on the assumption that the total collector current is a positive ion current. They would be raised if part of this current is due to emitted electrons,—doubled for example

---

[150] Dällenbach, Gerecke and Stoll, Phys. Zeits. **26**, 17 (1925).

if half the current is due to electrons as in the case of Ne–Ni investigated by Uyterhoeven and Harrington.[142]

The most direct investigation of electron emission due to positive ions of a gas discharge is by Penning,[151] who projected neon ions, from a discharge, through a tube and allowed them to strike a copper, silver or iron electrode after the desired speed regulation in an auxiliary field. The resulting probability of electron emission as a function of the ion energy is shown by Fig. 9. It is interesting to note the emission even at zero velocity of impact. Extrapolation of the experimental curve gives the probability at zero velocity somewhere between 2 and 2.5%. Penning suggests that this will be found

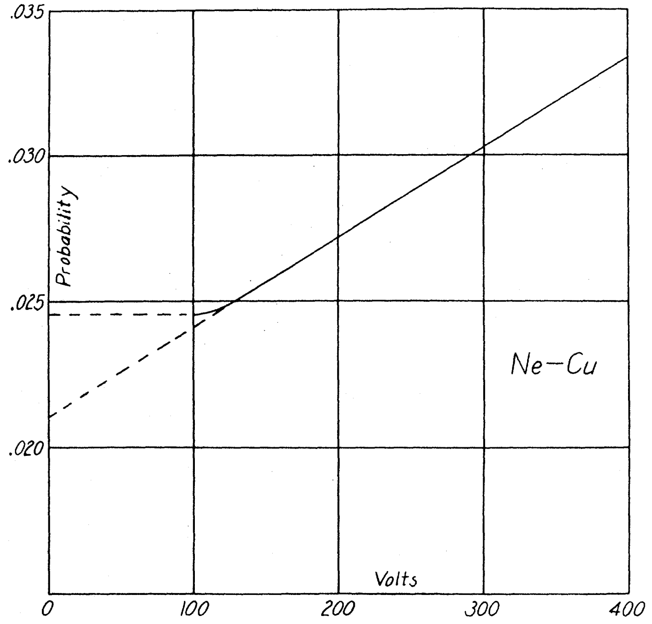


Fig. 9. Probability of electron emission by positive ion bombardment at V volts. (Neon ions, copper electrode.)

whenever the ionizing potential of the gas atom exceeds twice the work function of the electrode, $V_i > 2\phi$, because the ion must possess enough energy to extract an electron to neutralize itself, and also another electron. Oliphant[141] points out that Penning's results probably include a contribution from metastable atoms produced as in his own work. Nevertheless the increase of emission with ion velocity indicates that Penning has observed a true electron emission due to slow speed ions, even though his values may be too high on account of the complication mentioned by Oliphant.

(It is perhaps significant, in support of Penning's views, that cold cathode discharges in Hg vapor require a surprisingly high voltage in comparison with

---

[151] Penning, Vers. K. Ak. Amsterdam **36** (1927); Physica, **8,** 13 (1928); Proc. Amst. Acad. **31,** 14 (1928).

other gases whose ionization is known to be more difficult. This may be because the inequality $V_i > 2\phi$ is considerably less pronounced in the case of Hg than in the case of the gases in question, so that the positive ions are less effective in ejecting electrons from the cathode. If this be true, discharges in K vapor should be still more difficult, provided the cathode is of a material like oxygen-free zinc which will not adsorb K atoms or ions and thereby lower its work function.)

Finally, the yield of electrons liberated from cathodes by positive ion impact has been estimated indirectly and on questionable grounds by Klemperer,[152] from data on the minimum sparking voltage between parallel metal planes, combined with values of the "*effective*" (not minimum) ionizing potentials of the gases.[153] These estimates involve the assumption that every electron ionizes *every* time it falls through this "effective" ionizing potential, this being the characteristic of and the explanation of the minimum sparking voltage (an assumption and a statement which are not obvious). This estimate agrees in order of magnitude with calculations based on the Holst and Oosterhuis theory of sparking (see Part II). Klemperer's values of percentage yield of electrons per positive ion impact are given in Table IX.

TABLE IX. *Yield of secondary electrons per positive ion.* (*Estimated indirectly.*)

gas	air	CO_2	H_2	A
Yield	0.66%	0.09%	0.74%	0.7%
"u"	5.8	8.4	2.4	3

"u" = kilovolts/cm. ÷ pressure in cm Hg and is a measure of the mean energy acquired by the ions in passing through the gas between the plane parallel electrodes.

(10) **Emission due to chemical action** probably plays a very minor role in gas discharges. The phenomena are varied in nature. For example, air, especially when moist, when in contact with phosphorous is charged with both positive and negative ions of such low mobility that they obviously contain very complex products of the chemical reaction. Hot platinum in contact with phosphorous vapor emits positive ions but no appreciable negative ions or electrons. Gaseous products of electrolysis are ionized, though this is probably due to bubbling through the electrolyte rather than to chemical action.

Electrons are emitted by chemical action of a number of gases on such electropositive metals as sodium, potassium, amalgamated aluminum. Among the gases investigated are H_2S, HCl, CO_2, H_2O, $COCl_2$, $CSCl_2$, O_2, Cl_2, Br_2. Cases of emission of as many as one electron for every 1600 reacting molecules have been observed.[154] The emitted electrons have velocities of the same ordre as those ordinarily observed in photo-electric emission, but with that absence of saturation which we have shown to be characteristic of a composite surface.

---

[152] Klemperer, Zeits. f. Physik **52,** 650 (1928).

[153] Lehmann and Osgood, Proc. Roy. Soc. **A115,** 609 (1927); Lehmann, *ibid.* **115,** 624 (1927).

[154] Haber and Just, Ann. d. Physik **30,** 411 (1909); **36,** 308 (1911); Zeits. f. Elektrochem. **16,** 275 (1910).

Doubtless some cases of emission ascribed to chemical action are really thermionic emission arising from high temperatures produced by the reaction, while others may be of photo-electric origin associated with chemiluminescence. There appears to be no reason, however, for excluding electron emission by chemical action as a real phenomenon, since activated molecules are known to exist as intermediate products in chemical reactions,[155] and these activated molecules should be able to cause electron emission if their energy is sufficient, just as such emission occurs at contact of metastable atoms with electrodes.

An excellent discussion of ionization and chemical action is given by Richardson in his "Emission of Electricity from Hot Bodies."[156]

C. DISAPPEARANCE OF ELECTRONS AND IONS

Electrons and ions may be lost by any given element of volume of ionized gas by recombination, by absorption or by neutralization at the surfaces of electrodes, or by motion away from this element by volume. This latter process will be discussed in the following section entitled, "The Motions of Electrons and Ions."

(1) **Disappearance of electrons and ions at the electrodes and walls** involves, of course, their motion to the electrodes, which will be treated later. In addition to this, there are certain phenomena characteristic of the actual absorption or neutralization process. Of these phenomena, reflection and secondary emission of new charged particles have already been discussed (B 7, 8, 9).

Absorption of electrons by electrodes involves heating of the electrodes by the amount $e(\phi+\bar{V})-2kT$ per electron,[157] where $\bar{V}$ is the average energy of the energy of the incident electrons (in equivalent volts) and T is the excess in temperature of the electrode above its external connection. $\bar{V}$ does not include the energy gained close to the electrode surface as the result of surface forces, since this is included in ϕ. The term $2kT$ (which amounts only to e times 1 volt for $T=5886°$) is generally negligible. If the electrons reach the electrode in a retarding field, so that secondary emission and reflection of electrons occur, these phenomena alter the heating in an obvious manner, the net heating per incident primary electron being

$$H=e(\phi+\bar{V})-n_s e(\phi+\bar{V}_s)-(1-n_s)2kT \qquad (50)$$

where n_s is the number of secondary electrons per primary, and $\bar{V}_s$ is the average initial energy of the emitted secondary electrons. If the incident energy $\bar{V}$ is of the order of 10 volts, the term $n_s e(\phi+\bar{V}_s)$ is probably less than 10% of the term $e(\phi+)\bar{V}$. At higher incident energies n_s increases (up to a maximum when $\bar{V}$ is of the order of 300 volts), but $\bar{V}_s$ remains so small relative to $\bar{V}$ that it is very doubtful if the cooling effect of the second term can

---

[155] Smyth, Proc. Nat. Acad. Sc. **11,** 679 (1925).

[156] Richardson, "Emission of Electricity from Hot Bodies," Chap. IX.

[157] Richardson and Cooke, Phil. Mag. **20,** 73 (1910); **21,** 404 (1911), with the correction of $2kT$ in place of $(3/2)kT$.

ever equal the heating effect of the first term. The more important terms of Eq. (50) have been tested both for electrodes in *vacua*[157] and in ionized gases.[158]

Absorption or neutralization of positive ions at electrodes involves more complicated energy relations. Consider the cycle of Fig. 10. A positive ion of negligible kinetic energy reaches the surface, is neutralized, and liberates energy $e\phi_+$. Or, alternatively, an electron escapes from the surface absorbing energy $e\phi_-$, unites with the ion liberating energy eV_i, and the neutral atom *may* remain on the surface liberating the heat of absorption eL of the neutral atom. Comparing these equivalent processes, we get

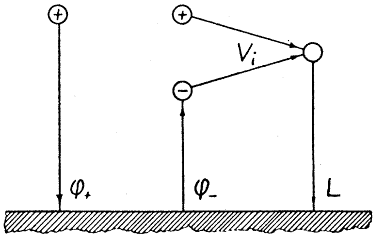


Fig. 10. Heat of neutralization ϕ_+ of a positive ion.

$$\phi_+ = V_i - \phi_- + L, \tag{51}$$

which is the relation originally proposed by Schottky, except for the inclusion of the term L (which vanishes if the ion-atom is not permanently deposited on the electrode).

While this equation is correct as regards total energy, it is not necessarily correct as regards *heat gained by the electrode*, because a part of the energy V_i may be radiated away in the process of combination. The process of neutralization may *actually* be somewhat similar to that shown on the right in Fig. 10, since, when the ion has approached within a distance of about ten atomic diameters of the surface it attracts electrons with a force sufficient to extract them from the surface. The subsequent time before the ion strikes the surface is of the order of 10^{-12} sec., and therefore much smaller than the average duration τ of a free atom in an excited state (A 3). Nevertheless, at or near the surface the combining ion must part with energy V_i, and it is quite possible that a fraction r of this is radiated. Perhaps this radiated energy accounts for the faint continuous glow often observed at the surfaces of cathodes,[159] detected in certain experiments by its photo-electric action and suggested by J. J. Thomson as producing the electron emission caused by positive ion impact.[160] Thus we should have, for the heat of neutralization,

$$\phi_+ = (1-r)V_i - \phi_- + L. \tag{52}$$

---

[158] Schottky and von Issendorff, Zeits. f. Physik **26,** 85 (1924); Compton and Van Voorhis, Proc. Nat. Acad. Sc. **13,** 336 (1927); Van Voorhis, Phys. Rev. **30,** 318 (1927).

[159] Geiger u. Scheel, "Handbuch der Physik," XIV, pp. 173, 183–188, 234.

[160] Thompson Phil. Mag. **48,** 1 (1924); **2,** 675 (1926).

The fraction (r) would be expected to be >0.5, from considerations of reflecting power and subtended solid angle of the metal surface. Compton and Van Voorhis' conclusion[158] that ϕ_+ is very nearly zero must now be retracted in the light of further evidence which has proved that their original results were affected by an unsuspected new complication now to be described. All that can at present be said is that ϕ_+ must be given by Eq. (52), with $1>r>0$.

A second factor which complicates and may considerably reduce the heating of electrodes by positive ions, and which appears to have been neglected in previous discussions of this question, is the *retention by the neutralized ion (atom) of a portion of its incident kinetic energy.* It has hitherto been assumed that the neutralized particle, if it was not permanently adsorbed on the electrode, departed from it with negligible energy (as, for example, in thermal equilibrium with it). However, this is not the typical behavior of neutral molecules incident upon a surface of different temperature, for it is found that such molecules only partially come into thermal equilibrium with the surface (except in the case of adsorption followed by evaporation, which is probably not the behavior of neutralized ions since these in general have kinetic energies far in excess of the heat of adsorption). The degree to which a reflected molecule adjusts its energy to that of the reflecting surface is described by its *accomodation coefficient,* defined by

$$a=(E_i-E_r)/(E_i-E_s) \tag{53}$$

where E_i, E_r and E_s are, respectively, the kinetic energy of incidence, that of reflection and that characteristic of the temperature of the reflecting surface. Thus complete adjustment at impact, as in case of adsorption and reevaporation, is described by $a=1$, while specular reflection corresponds to $a=0$. Some values of accomodation coefficient are given in Table X.

TABLE X. *Accomodation coefficients a.*

Gas	Metal	Metal Temperature	a	Ref.
H_2	Pt	20°C	0.26	161
CO_2	Pt	"	0.87	"
N_2	Pt	"	0.87	"
H_2	Pt	−100	0.25	162
H_2	Pt	+200	0.15	"
He	Pt	−100	0.49	"
He	Pt	+200	0.37	"
H_2	W	+1500	0.19	163
N_2	W	+1500	0.60	"
H_2	Pt	~20	0.278	164
O_2	Pt	"	0.800	"
CO_2	Pt	"	0.807	"
He	Pt	"	0.338	"
A	Pt	"	0.857	"
Ne	Pt	"	0.653	"

---

[161] Knudsen, Ann. d. Physik **34,** 593 (1911).
[162] Soddy and Berry, Proc. Roy. Soc. **84,** 576 (1911).
[163] Langmuir, J. Am. Chem. Soc. **37,** 425 (1915).
[164] Knudsen, Ann. d. Physik **46,** 641 (1915).

Compton and Van Voorhis, in some unpublished work still in progress,[165] have shown that the heating of a cool tungsten cathode by 50 volt positive ions of A, Ne and He is of the order of only 0.8, 0.65 and 0.43, respectively, of the expected watts input given by current to cathode times accelerating voltage drop. This is under conditions in which there is no possibility of energy dissipation by collisions of the incoming ions with gas molecules. It also neglects any contribution of the heat of neutralization ϕ_+ whose inclusion would tend further to diminish the above fractions. These fractions are strikingly similar to the corresponding accomodation coefficients, which is probably a coincidence, since the atom energies in this case are about a thousand times those of the atoms referred to in Table X and it would be quite surprising if a did not vary considerably over this range. The unexpectedly low heating is due to two factors (1) this effect of an accomodation coefficient less than unity and (2) the fact that part of the current is not incoming ion current, but outgoing electron current arising from action of excited atoms on the electrode,—as has been proven by supplementary tests.[142] Further possible evidence of this retention of energy by the neutralized particles is cited in the following section.

Thus far no quantitative estimates of the accomodation coefficient appropriate to impact of ions against electrodes are available. Until these have been determined, all estimates of the heating of cathodes by ion bombardment must be held in abeyance. However, the equation for this heating per positive ion of initial energy $\bar{V}$ may be stated as

$$H_+ = a\overline{V}_+ + \phi_+ = a\,\overline{V}_+ + (1-r)V_i - \phi_- + L. \tag{54}$$

Momentum transfers at electrodes due to impact of charged particles against electrodes, do not cause a pressure against the electrodes if, as is usual, these particles acquired their momenta entirely as the result of attraction by these electrodes, since the momentum gained by the electrode by attraction is exactly neutralized by the impact. Pressure against an electrode may, however, arise from impact of particles whose speeds were acquired in a field between other electrodes, or from the reaction of spontaneously emitted particles such as thermoelectrons from a hot cathode[166] or neutral atoms from a volatilizing electrode.[167]

Furthermore, if ions which are drawn to an electrode by an adjacent field, retain after neutralization a portion of their incident kinetic energy, as in case of an accomodation coefficient less than unity, the momentum of escape would be imparted to the electrode producing a pressure upon it. This would offer a reasonable explanation of the rather large pressure against the cathode of a copper vacuum arc, which led Tanberg[168] to the rather unprepossessing

---

[165] Compton and Van Voorhis, to be reported at the April meeting of the American Physical Society.

[166] Duffield, Burnham and Davis, Proc. Roy. Soc. Lon. **97**, 326 (1920).

[167] Beer and Tyndall, Phil. Mag. **42**, 956 (1921); Tyndall, *ibid.* **42**, 972 (1921); Sellerio, *ibid.* **44**, 765 (1922).

[168] Tanberg, Phys. Rev. **35**, 294 (1930).

conclusion that the copper atoms which evaporate from the surface, have kinetic energies characteristic of about 500,000°C. For example, the observed order of magnitude of this pressure would follow if half the current at the cathode is carried by positive ions, and if these retain on the average one-tenth of their kinetic energy after neutralization.

Langmuir[169] has discussed the related problem of momentum imparted to the gas, and the resulting pressure in discharge tubes.

"Sputtering," or distintegration of an electrode subjected to positive ion bombardment is a well known and often troublesome phenomenon. Although discovered[170] as early as 1852 its behavior and explanation both remain rather obscure.

Most investigations have dealt with the rate of loss of weight of the cathode in a glow discharge, as a function of the nature of the metal, nature of the gas, cathode fall, current density, gas pressure, cathode temperature or geometry of tube. The most striking observation is the great difference observed with different metals and gases. Some of these observations are shown in Table XI.

TABLE XI.

Observer	Gas	Rate of sputtering in descending order
Crookes[171]	air	Pd, Au, Ag, Pb, Sn, Pt, Cu, Cd, Ni, Ir, Fe, Al, Mg
Kohlschütter[172]	N_2	Ag, Au, Pt, Pd, Cu, Ni
Blechschmidt[173]	A	Cd, Ag, Pb, Au, Sb, Sn, Bi, Cu, Pt, Ni, Fe, W, Zn, Si, Al, Mg
Güntherschulze[174]	H_2*	Bi 1470, Te 1200, As 1100, Tl 1080, Sb 890, Ag 740, Au 460, Pb 400, Zn 340, Cu 300, C 262, Sn 196, Fe 68, Ni 65, W 57, Co 56, Mo 56, Mn 38, Cd 32, Al 29, Cr 27, Ta 16, Mg 9
"	O_2*	Zn 1030, Tl 650, Ag 614, Au 423, Pb 320, Cu 236, Sn 227, Fe 86, Mo 80, W 49, Ni 52, Cd 28

* Note: Numbers give rate of sputtering in Mg/amp. hr. under the conditions of cathode fall $V_c=770$ volts and current density about 7 milliamps. per cm^2.

A relation which holds with fair accuracy with most gases gives the mass of cathode material sputtered in unit time[175]

$$m=K(V_c-V_0)\,, \tag{55}$$

where K and V_0 are constants characteristic of the gas and metal and V_c is the cathode fall. Thus the rate of sputtering is about proportional to the excess

---

[169] Langmuir, Jour. Frank. Inst. **196,** 751 (1923).

[170] Grove, Phil. Trans. 1852.

[171] Crookes, Proc. Roy. Soc. Lon. **50,** 88 (1891).

[172] Kohlschütter, Zeits. f. Elektrochem. **15,** 316 (1909); Jahrbuch d. Radioakt. **9,** 355 (1912)

[173] Blechschmidt, Ann. d. Physik **81,** 999 (1926).

[174] Güntherschulze, Zeits. f. Physik **36,** 563 (1926); **38,** 575 (1926).

[175] Grandquist, Kgl. Akad. Stockholm, **54,** 595 (1897); Holborn and Austin, Wiss. Abhand. d. Phys. Tech. Reichsanstalt, **4,** 101 (1903).

of cathode fall of potential above V_0. V_0 usually lies between 350 and 550 volts and is generally about 450 volts. The constant K is roughly proportional to the fourth root of the atomic weight of the gas,[176] unless the rate of sputtering is accelerated by chemical action.[177] There have been suggestions[172] also that $K=K_0A/n$, where A is the atomic weight of the metal, n is an integer between 1 and 4 which is in some cases (but not always) equal to the valency, and K_0 is a constant characteristic of the gas. The value of K_0 for N_2 is about 0.0004.

The approximate validity of Eq. (55) does not necessarily imply that the rate of sputtering is causally related to the cathode fall V_c, since, in order to vary the cathode fall, the gas pressure or current density were varied. Güntherschulze[177] found that the rate of disintegration of the cathode depends on the distance of the anode, and also on the gas pressure and geometry of the cathode, in such a way as to suggest that the cathode loses weight by the process of diffusion of metal atoms away from the region of their maximum partial pressure just outside the cathode surface toward the anode where their partial pressure is zero. According to him, at constant current density

$$m=CV_c/pD \tag{56}$$

where C is a constant characteristic of the gas, p is the gas pressure and D is the distance to the anode.

All the above relations and experiments, while useful empirically to describe the rate of cathode disintegration in ordinary glow discharges, are ill adapted to yield information regarding its fundamental cause, on account of the complexity of the conditions. Much more incisive are experiments which give the rate of distintegration caused by bombardment of ions of known energy under conditions in which collisions of sputtered atoms with gas molecules do not occur to retard their escape. Such experiments have been performed by The General Electric Co., Ltd.[178] and by Kingdon and Langmuir.[179] Here electrons from a hot filament were used to ionize the gas whose pressure was too low appreciably to interfere with the escape of the atoms sputtered from the cathode. The positive ions were drawn to the cathode with known and fairly homogeneous velocities. The results again led to a relation $m=(V-V_0)$ like Eq. (55) but with much lower values of V_0, indicating that in the case of the glow discharge the positive ions striking the cathode have lost by collisions with gas molecules most (at least three-fourths) of the energy gained in the cathode fall.

The General Electric Co., Ltd. found no case in which V_0 exceeded 100 volts. The effectiveness of gas ions in disintegrating a tungsten cathode increase in the order H_2, He, N_2, Ne–He, Hg, A. Kingdon and Langmuir tried the effect of ion bombardment in disintegraing the monatomic layer of thor-

---

[176] Kohlschütter and Müller, Zeits. f. Elektrochem. **12,** 365 (1906); Kohlschütter and Goldschmidt, *ibid.* **14,** 221 (1908); Blechschmidt, Ann. d. Physik. **81,** 999 (1926).

[177] Güntherschulze, Zeits. f. Physik. **38,** 575 (1926).

[178] General Electric Co., Ltd. Phil. Mag. **45,** 98 (1923).

[179] Kingdon and Langmuir, Phys. Rev. **22,** 148 and 357 (1923).

ium on tungsten and found, for 150 volt impacts, that one thorium atom was knocked off for every 700,000 impacting ions of He, 45 of Ne, 23 of Hg, 12 of A, 12 of Cs, and that hydrogen ions were entirely ineffective. The very small sputtering power of hydrogen and helium is believed to be due to the relatively great penetrating power of these atoms, so that their energy is dissipated too deep within the metal to cause surface disintegration. Fig. 11 gives some illustrative data.

Holst[180] has observed sputtering of tungsten in argon rectifiers at voltages as low as 25 volts.

Oliphant[141] gives reasons for suspecting that it is not alone the kinetic energy of the impacting ion which is responsible for sputtering, but that the fact that the ion is an electric charge is also a factor.

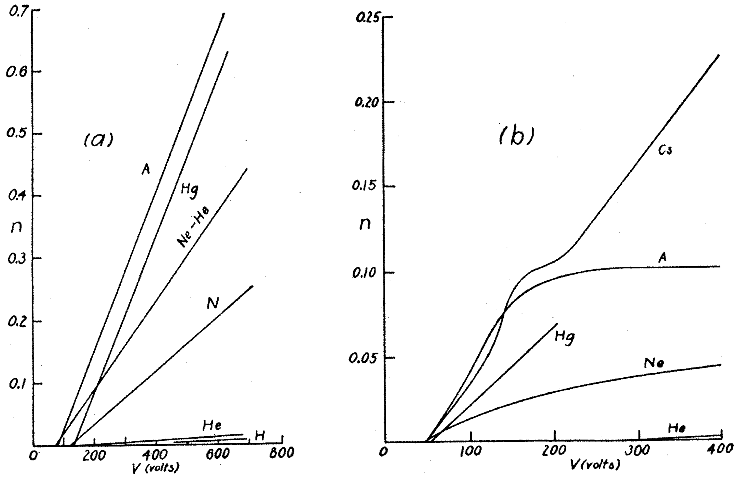


Fig. 11. (a) Sputtering of W (General Electric Co., Ltd.); (b) sputtering of surface Th atoms from a W filament (Kingdon and Langmuir). $n =$ number of sputtered atoms per impinging positive ion.

There is spectroscopic and magnetic deflection evidence that sputtering may consist in the expulsion of neutral atoms, whose velocities are of the order of those occurring in evaporation processes,[181] although these may acquire charges, coalesce into aggregates, etc., in their subsequent history. Tungsten, molybdenum and carbon sputtered from filaments of these materials in argon are capable of acquiring either positive or negative charges. This results in a very interesting type of discharge, the streamer discharge, which may occur when these materials are sputtered in arcs in argon (also in neon).[182]

When thermionic currents of 50 to 100 volts are passed through argon at pressures of only a few microns, a tungsten filament sputters rapidly and the

---

[180] Holst, Physica **4**, 68 (1924). See also A. W. Hull, Trans. Amer. Inst. E.E., **49**, 753 (1923).

[181] von Hippel, Ann. d. Physik **80**, 672 (1926); Baum, Zeits. f. Physik **40**, 686 (1927).

[182] I. Langmuir, Science **60**, 392 (1924)

sputtered material deposits on the bulb particularly behind the anode, indicating that it becomes negatively charged.[183]

There are two principal theories of sputtering, the theory of local high temperatures and the theory of direct momentum transfers. The theory of local high temperatures has been developed most extensively by von Hippel[184] on the idea that the energy of the impinging ion raises an area around the point of impact to a temperature which is instantaneously very high, but which sinks rapidly as the energy spreads out and is dissipated by the thermal conductivity of the metal. He finds

$$m \propto \frac{i}{e(1+C_e)T}\epsilon^{-q/RT}\Delta F\Delta t,$$

where i is the current density, e is the electronic charge, C_e is the number of secondary electrons emitted per impinging positive ion, T is the average temperature of the average area ΔF from which evaporation occurs during a time Δt, R is the gas constant and q is the heat of evaporation of the metal. ΔF, T and Δt may be estimated from considerations of the kinetic energy of the ion and the thermal conductivity of the metal as shown in the second reference (184). While this equation gives the right general sort of variation among the parameters, it rests on necessarily very crude approximations. An apparently serious objection to any such high temperature evaporation theory lies in the fact that it would predict, in the case of a metal like tungsten, an enormous secondary (thermionic) electron emission in proportion to the amount of sputtering, whereas this is not found to be true. It is possible, however, that such emission is limited to a small value by space charge on account of the extremely small dimensions ΔF of the effective emitting areas.

Kingdon and Langmuir[179] showed that the rate of sputtering of thorium from a tungsten surface can be quite accurately explained, and the minimum sputtering voltage (about 50 volts) roughly calculated on the following assumptions: As the first step in the process, a surface atom of thorium is struck by an ion and driven into the underlying tungsten, forming a depression. When this depressed thorium atom is struck by a second ion, the ion is elastically reflected and, on its way back, may strike one of the surrounding thorium surface atoms and dislodge it, provided the energy which it can communicate to the atom, according to the laws of momentum transfer, exceeds the atomic heat of evaporation. The total chance of removing a thorium atom as the result of N ion impacts against any particular atom is given by

$$(1-\theta)=\mu(3P_2+5P_3+6P_4+6P_5), \tag{57}$$

where

$$P_n=\frac{1}{n!}(Np)^n\epsilon^{-Np}$$

---

[183] I. Langmuir, Phys. Rev. **2,** 475 (1913).

[184] von Hippel, Ann. d. Physik **81,** 1043 (1926); Blechschmidt and von Hippel, *ibid.* **86,** 1006 (1928).

is the probability that the same atom will be struck n times while N ions strike the surface, in terms of the probability p that a given ion strikes a given atom. θ is the fraction of the surface covered by thorium atoms and μ is the probability that an ion which has been reflected from a depressed thorium atom will remove one of the neighboring atoms on its rebound. Similarly, the minimum voltage $\bar{V}_s$ for sputtering is given in terms of the atomic heat of evaporation of thorium E_v from tungsten (1.40 $(10)^{-11}$ ergs/atom) by

$$V_s=\frac{300E_v}{4em_gm_c}\left[\frac{(m_g+m_c)^2}{m_g-m_c}\right]^2 \tag{58}$$

where m_g and m_c are the masses of the impacting ion and the target (cathode) atom, respectively.

Equation (57) accurately fits the experimental data when reasonable values of the parameters p and μ are chosen. Equation (58) gives about the right value of V_s for Ne and A, but too high values for H, He, Cs and Hg ions. The evidence cited above indicates that the discrepancy with H and He is probably due to their great penetrating power, while the discrepancy with the heavy ions of Hg and Cs may well be due to their driving the thorium atom so far into the tungsten at the first impact that the reaction to the second impact is by the entire tungsten wall rather than by the thorium atom alone, as assumed in Eq. (58).

Holst's observation of sputtering of tungsten in argon rectifiers at voltages as low as 25 volts led him to postulate a mechanism different from that assumed to explain the sputtering away surface thorium atoms. He suggests that it depends upon the transfer of the requisite amount of energy to a tungsten atom at a single direct impact, according to which

$$V_s=\frac{300E_v}{4e}\,\frac{(m_g+m_c)^2}{m_gm_c}\,. \tag{59}$$

This expression gives very small values for V_s, (*e.g.*, W in A, 16; W in Ne, 27; Pt in A, 10; Pt in Ne, 17; Cu in A, 3.3; Cu in Ne, 4.2). The accuracy of these values is very uncertain.

These remarks will serve to emphasize the fact that cathode sputtering, though an important phenomenon of gas discharge, is still very inadequately understood. It may be significant that the ion bombardment fractures the surface crystalline layer. (See micrographs of Baum[181] and evidence from electron emission by Reynolds).[105] If sub-microscopic dust were thus produced, it would be quickly evaporated when it passed into the discharge by the heat of recombination of ions and electrons on its surface. In the case of tungsten the evaporation is very slow and such incandescent centers of recombination can actually be seen (and investigated optically by a Tyndall beam) when tungsten is sputtered in argon.[182] In the case of the more volatile metals, such a process might possibly explain the atoms of sputtered material which have been taken as proving the evaporation theory of sputtering.

(2) **Disappearance of electrons and ions by recombination.** That electrons and ions may recombine has been known ever since their existence in a conducting gas was recognized. In fact all emission of light from glowing gases was at one time ascribed to this process. Yet attempts to produce light by mixing together ions and electrons under controlled conditions have proved singularly fruitless. Within the last ten years, however, certain restrictions on recombination have become apparent, and their recognition has greatly simplified the interpretation of the hitherto seemingly conflicting observations. These restrictions, whose realization is due principally to Bonhoeffer and Franck, are based upon the following idea.

Free electrons in an ionized gas possess translational kinetic energies anywhere from the value characteristic of the gas temperature upward, depending upon the magnitude of the electric field and gas pressure and the initial conditions of their formation. Whenever one of these electrons comes within the range of attraction of a positive ion, it would be expected, on classical theory, to move past the ion in an hyperbolic orbit. But permanent attachment (recombination) involves settling down into an elliptic orbit, which can only occur if the electron loses a part of its energy. The only ways of losing energy are by collision with a third body during the interval of close approach, or by radiation. The first of these involves a three body collision which is extremely improbable except under very special conditions which will be discussed below. The second involves the radiation of energy outside of the regular line spectrum, and the observed weakness of such radiation proves that recombination in this manner also is highly improbable. Thus we conclude that recombination of electrons and ions is a far less probable occurrence than was formerly supposed, when it was believed that every approach of an electron to an ion resulted in its capture. We shall proceed to a closer investigation of recombination under these restricted conditions.

Recombination on surfaces is a three body process in which the surface acts as the third body to absorb excess energy and momentum. The electrons and ions do not need to arrive simultaneously at a point on the surface, but one may arrive first and remain on the surface as a surface charge until the other arrives to combine with it. Herein is the explanation of the effectiveness of surfaces in causing disappearance of ions by recombination. Dust particles, submicroscopic particles sputtered from electrodes, insulating surfaces or floating electrodes all act in this way. As will be pointed out in detail later, insulated surfaces are charged with respect to the surrounding gas to a positive or negative potential, depending on whether ions or electrons carry the maximum random current density. Except in very special cases near cathodes, the random current of the electrons is always in excess owing to their small mass and resulting rapid motion. Thus isolated surfaces in general take up negative potentials with respect to the surrounding gas to such a degree that the electrons are repelled and the positive ions are attracted sufficiently to cause electrons and ions to arrive at equal rates and combine at the surface. Such surfaces in an intensely ionized gas may become highly heated, small floating metallic particles being often evaporated or heated to incandescence. The energy comes from the heat of combination, the initial kinetic energies of the combining charges, and the energy gained by the positive ions in falling through the difference of potential between the surface and the surrounding space.

Recombination in the gas may occur, in a manner analogous to that described in the case of surfaces, by two *successive* impacts involving three bodies, (as distinguished from the simultaneous impact of three bodies), or it may occur by the direct union of an electron and ion without interaction of a third body. The first of these processes occurs in the following way: Electron attachment, *i. e.*, the formation of negative ions may occur at the collision of an electron with a neutral molecule. Then, if this negative ion collides with a positive ion, the electron transfers its attachment to the ion, releasing the neutral molecule. The neutral molecule may carry away the excess energy, if any, but we shall see that there often is no excess energy in such a case. The rapidity of this recombination process is limited, of course, by the rapidity of the slower one of the two cooperating processes (1) electron attachment to form negative ions, (2) combination of negative and positive ions.

Electron attachment to form negative ions has been studied most extensively by Loeb and his pupils.[185] The probability of attachment at an impact differs so enormously in different gases and is relatively so large in some gases and vapors which are very difficult to eliminate as impurities, that most of the conclusions are qualitative rather than quantitative. N is the total number of collisions made per second by an electron in the gas at atmospheric pressure and ordinary room temperature, assuming the electron mean free path to be the classical value of $4\sqrt{2}$ times that of a gas molecule. The attachment "constant," is not really a constant, since it is somewhat dependent upon the electron velocities. Furthermore it is not always an additive property in gaseous mixtures, since water vapor appears to cause more attachment when present as an impurity than would be expected from the value of n given in Table XII. n does not seem to be related with any obvious property of the molecules, unless it be roughly with their electronegative character. A prevalent idea that the molecular dipole moment is the controlling factor is obviously untenable, NH_3 and H_2O possessing strong moments and N_2 and Cl_2 no moments, to take extreme examples.

Several interesting deductions may be drawn from Table XII. In pure gas at atmospheric pressure an electron would remain free on the average for only about $7\ (10)^{-4}$ sec. in CO, about $4.7\ (10)^{-9}$ sec. in Cl_2, unless strong fields should so speed up the electrons as to render attachment still more improbable. Obviously most experimental work which has been done on ion mobilities and all the early work on recombination have been done

---

[185] Loeb, Kinetic Theory of Gases, pp. 507–515; J. Frank. Inst. **197,** 45 (1924); Wahlin, Phys. Rev. **19,** 173 (1922); Cravath, *ibid.* **33,** 605 (1929).

under conditions in which ions, rather than electrons, were the negative carriers of charge. In "vacuum tube" discharges, on the other hand, with pressures of the order of 1 mm or less, the average free life of electrons in many gases is sufficiently long to insure that most if not all the phenomena of negative charge are due to free electrons, even neglecting the increased effectiveness at low pressures of the electric field in maintaining electrons in the free state. (This effectiveness is a function of E/p.) Also the tremendous effect of some impurities on electron attachment is obvious. For example the rate of attachment CO would be increased *at least* 100 percent by the presence of 0.025 percent of oxygen or water vapor.

TABLE XII. *Attachment constant n (average number of electron impacts which result in one attachment to form a negative ion), compared with number N of electron impacts per second against gas molecules.*

Gas	n	N
Noble gases, N_2, H_2		
CO	$1.6\ (10)^8$	$2.22\ (10)^{11}$
NH_3	$9.9\ (10)^7$	2.95
C_2H_4	$4.7\ (10)^7$	3.75
C_2H_2	$7.8\ (10)^6$	4.12
C_2H_6	$2.5\ (10)^6$	4.85
N_2O	$6.1\ (10)^5$	3.36
C_2H_5Cl	$3.7\ (10)^5$	5.45
Air	$2.0\ (10)^5$	2.17
O_2, H_2O	$\sim 4.0\ (10)^4$	2.06, 2.83
Cl_2	$<2.1\ (10)^3$	4.50

Combination of negative and positive ions is not restricted, since the neutral molecule to which the electron is attached may function as the third body to carry off energy in excess of that corresponding to some excited state of the combining positive ion and electron. There is no direct evidence regarding the probability of such an energy transfer, and therefore no knowledge regarding the probability of combination of two oppositely charged ions which collide with a relative velocity greater than that which they would acquire in falling together from infinity. The two principal theories of ion combination neglect this probability, and assume that the combining ions have lost a part of the energy, gained by their mutual attraction, at collisions with neutral molecules, so that once they come within each other's sphere of influence, they remain there until recombination is effected.

The rate of ion recombination is jointly proportional to the concentrations n_1 and n_2 of the positive and negative ions, and is therefore

$$-\frac{dn_1}{dt} = -\frac{dn_2}{dt} = \alpha n_1 n_2, \tag{60}$$

where α is the "*coefficient of recombination.*" Table XIII gives some typical values:

TABLE XIII. *Coefficient of recombination α at atmospheric pressure and ordinary temperature in units of cm³ sec⁻¹. (Ionization produced by X-rays).*[186]

Gas	Air	CO_2	O_2	H_2	SO_2	N_2O	CO
$(10)^6$	1.71	1.67	1.61	1.44	1.43	1.42	0.85

From Table XIII we see that, if there were n positive and n negative ions per cm³ in air, the rate of recombination would be 1.71 $(10)^{-6}$ n^2.

The number of collisions between gas molecules of types 1 and 2 is given by kinetic theory as[187]

$$\text{no. collisions} = 2(2\pi/3)^{1/2} n_1 n_2 \sigma_{12}^2 (C_1^2 + C_2^2)^{1/2} \text{ cm}^{-3} \text{ sec}^{-1} \tag{61}$$

where C_1 and C_2 are their root mean square velocities and σ_{12} is the sum of their effective collision radii. From this we find that in air at room temperature, the number of collisions per cm³ sec. between 2 n molecules is 1.6 $(10)^{-10}n^2$. Comparing this with the value 1.71 $(10)^{-6}n^2$ above, we see that the *actual rate of recombination is about 10,000 times greater than it would be if due simply to ordinary kinetic theory collisions of positive with negative ions.* It is therefore concluded that mutual electrostatic attraction greatly accelerates the process of recombination. This effect of attraction has been differently handled by Langevin and Thomson.

Langevin's theory of recombination of ions[188] is based on the assumption that neighboring oppositely charged ions are drawn toward each other with velocities determined by the attractive force and by their mobilities* μ_1 and μ_2. When their distance apart is r, the attractive field is e/r^2 and the relative velocity of approach is $e(\mu_1+\mu_2)/r^2$, provided there are no other ions within a distance comparable with r. If there are n_2 negative ions per cm³, the rate at which negative ions will cross the surface of a sphere of radius r about a positive ion is

$$4\pi r^2 \cdot n_2 \cdot e(\mu_1+\mu_2)/r^2 = 4\pi e n_2(\mu_1+\mu_2),$$

which is independent of r. Thus the average time required for a negative ion to reach this particular positive ion is $1/4\pi\ e n_2\ (\mu_1+\mu_2)$ sec. But since there are n_1 positive ions, the average time interval between combinations

---

[186] Calculated from values collected by Thomson, "Conduction of Electricity Through Gases," 3 ed., p. 40.

[187] See Jeans, "Dynamical Theory of Gases," 2 ed., p. 275 and also Eq. (83) in Section (D 1 b) of this article. Thomson, "Cond. Elec. Through Gases," 3 ed., p. 43 uses an equation whose coefficient is 2.45 times too large.

[188] Langevin, Ann. de Chem. et de Phys. **28**, 287, 433 (1903); Townsend, "Electricity in Gases," pp. 206–220, in which Langevin's theory is extended and certain limits of applicability are discussed.

* The "mobility" is the constant μ in the relation $\bar{v} = \mu E$ between the field strength E and the average rate of drift $\bar{v}$ in the direction of the field. As pointed out below, μ is not in general a constant, but is itself a function of E. At high gas pressures and weak fields, μ is sensibly independent of E.

with *any* positive ion is $1/4\pi\ e\ n_1\ n_2\ (\mu_1+\mu_2)$. The reciprocal of this gives the rate of recombination, and therefore α, as

$$\alpha n_1 n_2 = 4\pi e(\mu_1+\mu_2)\cdot n_1 n_2. \tag{62}$$

This theory implicitly assumes that ions recombine whenever they are drawn together, which is self consistent since it is only justifiable to use mobilities when the moving ions lose energy so rapidly by collisions that they are always in or near a state of terminal speed and under such conditions the kinetic energy retained by the ions is insufficient to cause their separation once they have come close together. This consideration suggests that Langevin's theory should be most applicable at high gas pressures, and should fail at low pressures, as is the case. Also, since μ_1 and μ_2 vary inversely with pressure, α should also vary thus according to the theory. This is true at high pressures (such as several atmospheres) but not at low pressures. The absolute values of α calculated from Eq. (62) are approximately correct at high pressures, but are as much as 100 times too large at the lower pressures at which measurements of α and μ are made (such as 0.1 atmosphere).

Townsend[188] has extended Langevin's theory to include approximately the effect of thermal agitation, for so long as the ions have not approached so closely that the work to separate them greatly exceeds the energy of thermal agitation, it is always possible for the ions to escape combination. This fact, and the influence of neighboring ions, introduce corrections to Langevin's theory in the right direction. The most elegant treatment of thermal energies is, however, due to Thomson.

Thomson's theory of recombination of ions[189] is based on the idea that combination occurs if one of two neighboring ions of opposite sign collides with a neutral molecule and loses so much kinetic energy that it cannot escape against the attraction of the other. If v is the relative velocity of the two ions of masses M_1 and M_2 at a distance r apart, then they will execute closed orbits about each other and ultimately combine provided r is less than r_0 in the relation

$$\frac{1}{2}\,\frac{M_1 M_2}{M_1+M_2}v^2 = \frac{e^2}{r_0}.$$

Thomson now assumes that the mean velocities u_1 and u_2 immediately after one of the ions has collided with a molecule are those characteristic of thermal agitation. (This is certainly not true if the ions have been drawn close together, but it appears to be sufficiently justified at the critical distance r_0 which alone is important for the present purposes.) Then, since $v^2 = u_1^2 + u_2^2$,

$$\tfrac{1}{2}M_1 u_1^2 = \tfrac{1}{2}M_2 u_2^2 = \tfrac{3}{2}kT$$

$$v^2 = 3kT\left(\frac{M_1+M_2}{M_1 M_2}\right),$$

---

[189] Thomson, Phil. Mag. **47**, 337 (1924); "Conduction of Electricity Through Gases," 3 ed. pp. 44–57.

whence the critical distance r_0 is given by

$$\frac{e^2}{r_0}=\frac{3}{2}kT \tag{63}$$

and is seen to vary inversely as the absolute temperature T.

Now the chance that ion 1 will collide with a molecule while passing ion 2 within the critical distance r_0 is found in terms of its mean free path λ_1 to be

$$w_1=1+2\left[\frac{(\epsilon^{-2r_0/\lambda_1}-1)}{(2r_0/\lambda_1)}+\frac{\epsilon^{-2r_0/\lambda_1}}{(2r_0/\lambda_1)}\right]$$

and a corresponding expression holds for the chance w_2 that ion 2 will collide. Thus the total chance that one of the two ions which come within a distance r_0 will collide while within this distance is

$$w_1+w_2-w_1w_2,$$

the last term which represents the chance of *both* ions colliding being already included in w_1 and w_2.

Finally, the number of times that ions come within a distance r_0 of each other is approximately $\pi r_0^2 n_1 n_2 (u_1^2+u_2^2)^{1/2}\text{cm}^{-3}\ \text{sec}^{-1}$. Since every one of these that collides is supposed to enter into recombination with its neighboring ion, the rate of recombination is

$$\alpha n_1 n_2=\pi r_0^2(u_1^2+u_2^2)^{1/2}(w_1+w_2-w_1w_2)\cdot n_1 n_2.$$

Substituting for r_0 from Eq. (63) we obtain

$$\alpha=\frac{4\pi e^4}{9k^2T^2}(u_1^2+u_2^2)^{1/2}(w_1+w_2-w_1w_2). \tag{64}$$

At high pressures w_1 and w_2 approach unity, so that α should increase with pressure, but approach a constant value at high pressures. Actually this is found to be true[190] except that at still higher pressures α is found again to diminish with increasing pressure. This marks the point at which Langevin's theory begins to describe the phenomena more accurately than Thomson's.

Quantitatively, Eq. (64) fits the facts throughout a considerable range of pressures as accurately as could be expected in view of the very considerable uncertainty regarding the ionic mean free path and the exact nature (mass) of the ions,[191] which may often be ions of impurities or of clusters.

In Langevin's theory the rate of recombination is limited by the rate at which ions are drawn together by their mutual attraction; in Thomson's theory it is limited by the rate of diffusion of ions into regions in which the attractive force can hold them together. Additional support of Thomson's

---

[190] Langevin, Comptes Rendus **137**, 177 (1902); McClung, Phil. Mag. **6**, 283 (1902).

[191] Loeb, Phys. Rev. **32**, 81 (1928).

theory as against Langevin's for pressures of the order of an atmosphere and downward has recently been deduced by Loeb and Marshall[192] from the observation[193] that recombination is abnormally rapid for a short time after the formation of the ions, especially if the ionizing agent is one, like α particles, which creates an uneven distribution of ions. This was correctly explained[194] as due to the fact that the actual effective initial ion concentrations are much greater than the value calculated on the basis of even distribution throughout the entire volume, and it was shown that the correct values of α are those taken after lapse of sufficient time to permit uniform distribution. Loeb and Marshall pointed out that the very fact that an even distribution is attained shows that diffusion is a more important element in the life of the ions than is inter-ion attraction. They further analyzed the problem by considering the ions as executing Brownian movements subject to the action of their electric fields and showed that, at atmospheric pressure and room temperature, their mutual fields were practically a negligible factor, as compared with diffusion, in bringing the ions together from distances beyond about one free path. At several atmospheres, however, the field is important.

Recombination of free electrons and positive ions[195] is that type of recombination which, next to recombination on surfaces, is of the greatest interest in gas discharges. Its existence cannot be assumed simply because of the production of light in gas discharges because it is readily shown that light is principally due, in most cases, to excitation of atoms rather than to recombination. For example, the positive column of a glow discharge emits more intense light than does the negative glow. Yet measurements show[196] that electron and ion concentrations are each of the order of 100 times larger in the negative glow than in the positive column, and their velocities are lower. If light in both regions were due to recombination, it should be 100^2 times more intense in the negative glow because of greater concentrations, and still more than this because of the lower velocities which favor recombination. Thus, certainly, recombination plays a negligible role in the production of light in the positive column. In further support of this conclusion we shall see in Part II of this article that the radial concentration and potential gradients as well as the relation between axial potential gradients and tube diameters in cylindrical positive columns are such as to prove that all other types of recombination in the positive column with low pressures of gas are negligible in comparison with recombination on the tube walls.

This does not prove, however, that the negative glow light may not be due appreciably or perhaps mostly to recombination. That recombination is important here is proved by the fact that spectrum lines from the negative

---

[192] Loeb and Marshall, J. Frank. Inst. **208,** 371 (1929).

[193] Plimpton, Phil. Mag. **25,** 65 (1913); Rümelin, Ann. d. Physik **45,** 821 (1914).

[194] Plimpton, Phil. Mag. **25,** 65 (1913); Townsend, "Electricity in Gases," p. 200.

[195] For an excellent review of this subject see Seeliger, Phys. Zeits. **30,** 329 (1929); also a discussion of some calculated orders of magnitude by Atkinson, Zeits. f. Physik **51,** 188 (1928).

[196] Compton, Turner and McCurdy, Phys. Rev. **24,** 597 (1924).

glow show a Doppler widening[197] of the magnitude to be expected if the radiating atoms are moving with velocities of the same order as positive ion velocities,—distinctly more rapidly than molecular velocities,—whereas lines from the positive column have widths appropriate for emitters with ordinary thermal velocities. In fact, from Miss Dewey's experiments one would infer that, at least in her apparatus, practically all the negative glow light is due to recombination.

There are two additional criteria by which a recombination spectrum may be recognized. One of these, used effectively by Miss Hayner[198] and Kenty[199] is the relatively large intensity of the higher members of spectral series, as compared with their intensities in spectra due to excitation. This is explained by the fact that in combining, every electron has a chance to make transitions between the higher energy states as well as the lower ones, whereas in excitation most of the atoms are excited only as far as the lower states,—a fact proven by direct observation of intensities of excitation spectra under conditions of such low ion concentration as to make recombination completely negligible.

Kenty's observations with argon are particularly illuminating. He ionized the gas intensely by a low voltage arc from a hot cathode, then cut off the voltage (or else reduced it to a second value much too low to maintain the arc) and during this second period simultaneously photographed the spectrum and measured the velocity distribution of the electrons by Langmuir's probe method. A rotating sector disk and commutator enabled these intervals to be rapidly repeated and continuous measurements to be made. The intensity of high series members was a measure of the rate of recombination, and this was found to be greatly reduced as the mean velocities of the electrons was increased by means of the post-arc voltage. With no post-arc voltage the mean electron energy was 0.4 volt, the electron and ion concentrations were of the order of 10^{12} per cm^3, and the coefficient of recombination α was found to be about $2\ (10)^{-10}$. The number of kinetic theory collisions between positive ions and electrons may be calculated by Eq. (61), assuming the effective collision radius to be that of an argon atom and it is found that the actual rate of combination is 1/375 of the rate at which electrons and ions would be thus calculated to collide, which may be taken as a very rough upper limit to the *probability of combination* of argon ions with 0.4 volt electrons. We saw that positive and negative *ions* may combine 10,000 times faster than the rate of kinetic theory collisions, whereas positive ions and electrons combine several hundred times slower than the kinetic theory collision rate, even under the exceptionally favorable condition of unusually low velocity electrons.

Table XIV gives an example of the relatively greater intensity of higher series lines in the recombination spectrum.

---

[197] Dewey, Phys. Rev. **32,** 918 (1928).

[198] Hayner, Zeits. F. Physik **35,** 365 (1926).

[199] Kenty, Phys. Rev. **32,** 624 (1928).

TABLE XIV. *Intensities of argon lines* $2p_{10}-md$ *(Kenty)*.[199]

m	Intensity Recomb. Spectrum	Arc Spectrum
5	15	20
6	14	8
7	10	1
8	8	0
9	2	—
10	3	—

The other criterion of recombination is the existence of continuous bands stretching to the short wave-length side of series limits. Fig. 12 shows results of a photometric measurement of the intensity distribution in these bands in the case of caesium vapor[200] in the neighborhood of the absorption limits $3\ D_{2,3}$ and $2\ P_{1,2}$ and $1\ S_0$.

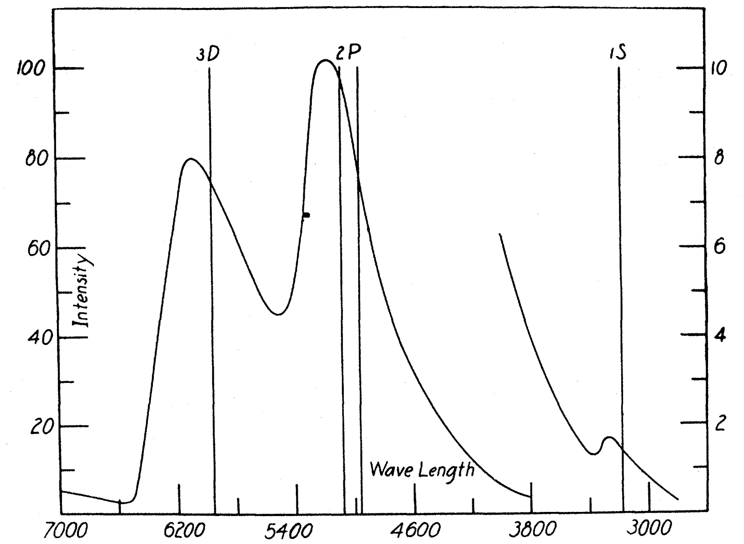


Fig. 12. Intensities of continuous recombination spectra beyond absorption limits in Cs vapor.

The interpretation of these bands is simple: The frequency associated with a state of energy $h\nu_i$ of an atom is the high frequency limit of the spectral series due to the falling of electrons into state i from states of higher energy. If an electron, whose kinetic energy was zero at a great distance, were to combine with an ion and fall directly into the energy state i, the emitted light would have the frequency ν_i of this series limit. But, actually, the electrons which combine have energies $\frac{1}{2}m\ v_2$ greater than zero. On classical theory these could not combine since they would execute hyperbolic orbits about the ion. But on quantum theory there is a certain probability,

---

[200] Mohler, Phys. Rev. **31**, 187 (1928); see especially Phys. Rev. Supp. **1**, 216 (1929).

which is a function of v, that they will combine. An electron of velocity v which combines causes emission of light of frequency ν given by

$$h\nu = h\nu_i + \tfrac{1}{2}mv^2. \tag{65}$$

Since the velocities v are continuously distributed (frequently with a Maxwellian distribution) it is obvious that ν will have all values from ν_i upward,[201] giving the continuous band.

The intensity distribution in the band depends obviously on two factors, (1) the distribution of electron velocities and (2) the probability of combination, or recombination coefficient characteristic of each velocity. The former factor $N(v)$ may be measured by Langmuir's probe method, so that the band intensity measurements may be used to estimate the coefficient of recombination $\alpha(v\,\nu_i)$ for electrons of any given speed v to form atoms in the energy state i. The equation for this may be written*

$$I(\nu)d\nu = h\nu \cdot \alpha(v\nu_i) N^+ N^-(v)dv \tag{66}$$

where $h\ d\nu = m\ v\ dv$ and $I(\nu)\ d\nu$ is the energy of frequency between ν and $\nu + d\nu$ radiated per second per unit volume and $N^-(v)\ dv$ is the concentration of electrons with velocities between v and $v+dv$. The recombination coefficient $\alpha(v\,\nu_i)$ is frequently written $v\ q(v\,\nu_i)$, where $q(v\,\nu_i)$ is the effective cross section for recombination of electrons of velocity v going into the i electron energy state of the atom. The total recombination coefficient $\alpha(v)$ for electrons of velocity v is, of course, $\alpha(v) = \sum(v\,\nu_i)$, and the ordinary total recombination coefficient is $\alpha = \int_0^\infty \alpha(v)\ dv$.

Mohler[202] has made a careful study of recombination spectra in caesium and helium by this method, and has shown that the coefficient of recombination $\alpha(v\,\nu_i)$ varies with electron velocities according to an equation of the form

$$\alpha(v\nu_i) = \frac{K}{\nu(\nu-\nu_i)^{1/2}} \quad \text{or} \quad \frac{K}{\nu^2(\nu-\nu_i)^{1/2}} \tag{67}$$

and depends so much more on the term $(\nu-\nu_i)^{1/2}$ than on the term ν^n that it is impossible to say with certainty whether $n=1$ or 2, although the agreement is slightly better with $n=2$. Thus the recombination coefficient approaches infinity very close to a series limit, but diminishes rapidly at higher frequencies. In Eqs. 66, 67, ν and v are, of course, related by Eq. (65).

According to a general relation based on the principle of detailed statistical balancing between the probability of recombination $\alpha(v\,\nu_i)$ and the probability of absorption $B(\nu\,\nu_i)$ at a frequency ν corresponding to v by Eq.

---

[201] The fact that the bands are observed to extend a slight distance to the long wave length side of ν_i is probably due to a blurring of the limits by the Stark effect in highly ionized gases. (Robertson and Dewey, Phys. Rev. **31**, 973 (1928)).

* We here assume, for simplification, that continuous spectra associated with different limits do not overlap. If they do overlap, Eq. (66) may be expressed as a summation, or the experimental contributions from the different bands may be separated by extrapolation.

[202] Mohler, Phys. Rev. **31**, 187 (1928); Research Paper No. 46, U. S. Bureau of Standards, March 1929.

(65), Milne[203] has derived a relation $\alpha(v\nu_i) = K'B(\nu\ \nu_i)\nu^3/(\nu-\nu_i)^{1/2}$. Also it is well known[204] that $B(\nu\ \nu_i)$ is very closely proportional to $1/\nu^4$, at least in the X-ray region well beyond an absorption edge. Hence we should expect approximately $\alpha(v\ \nu_i) = K/[\nu(\nu-\nu_i)^{1/2}.]$ which is in quite satisfactory agreement with Eq. (67). It is this quantity $B(\nu\,\nu_i)$ which expresses the probability of photo-ionization. (See section A(2) .) The experiments on recombination are in rather better accord with the theory than are those on photo-ionization.[205]

It seems likely that the above theory of recombination is on a fairly satisfactory basis in so far that it enables recombination coefficients to be calculated from spectral data, and that such experimental discrepancies as exist may be due to insidious errors which are very difficult to eliminate in work requiring such refined technique. The experimental work up to the present has, however, only just begun to give the information which may ultimately be secured. While others[206] have made interesting qualitative observations, Mohler alone has obtained all the information necessary to calculate recombination probabilities by this method.

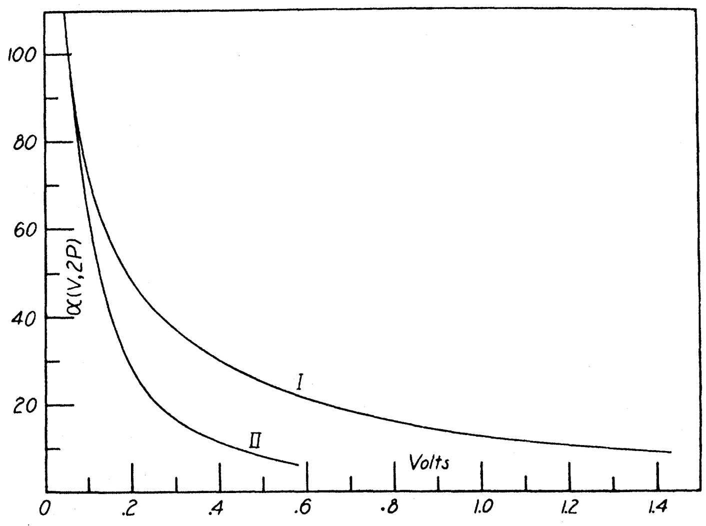


Fig. 13. Probabilities of recombination of an electron into the 2*P* states of caesium as a function of electron kinetic energy in volts. (Calculated from intensities of recombination spectra I; from photo-ionization II.)

---

[203] Milne, Phil. Mag. **47,** 209 (1924).

[204] Compton, "X-rays and Electrons," pp. 189–198. Oppenheimer, Zeits. f. Physik **41,** 268 (1927). Note that the absorption coefficient is proportional to ν^{-3}. The energy absorbed in one absorption act is $h\nu$. Thus the probability of absorption varies as ν^{-4}.

[205] Mohler, Foote and Chenault, Phys. Rev. **27,** 37 (1926).

[206] Paschen, Berlin Berichte, p. 135 (1926); Herzberg, Ann. d. Physik **84,** 553, 565 (1927); Mierdel, *ibid.* **85,** 612 (1928); Balasse, Comptes Rendus **184,** 1002, 1927 (1927).

In Fig. 13 are given experimental values of the relative probabilities of recombination into the $2P$ state in Cs as a function of the average electron energy. The absolute scale is given roughly by the estimate that $\alpha=5.4(10)^{-14}$ at $V=0.2$ volt. This value means that about 1 collision in 5000 results in recombination into the $2P$ state, for 0.2 volt electrons. Curve I, determined from the recombination spectrum, is in very close agreement with Eq. (67). Curve II is calculated from measurements on photo-ionization. The cause of the discrepancy between these curves is not understood.

Further theoretical work on the problem of recombination may only be mentioned. Milne[207] was led by a statistical equilibrium argument to conclude that, for small electron velocities, the effective combining cross section $q(v)$ must be of the form C/v^2. Since this is related to the absorption coefficient by $\alpha(v)=v\cdot q(v)$ we have

$$\alpha(v)=C/v. \tag{68}$$

If v is expressed in terms of ν and ν_i by Eq. (65) we have directly Eq. (67) except for the omission of the factor ν(or ν^2), which is practically a constant for small electron velocities, where ν only slightly exceeds ν_i.

This also is in satisfactory agreement with the conclusions of Morse and Stueckelberg,[208] who have calculated $\alpha(v\ \nu_i)$ by wave mechanics and found, for every state, $\alpha(v\ \nu_i)=C/v=D/(\nu-\nu_i)^{1/2}$ as the asymptotic value for low velocities. Further, they obtained actual numerical values of C(or D) for the lower states and showed that the sum over all states is finite and varies as $1/v$ but cannot be expressed in simple form.

Kramers,[209] and Eddington[210] and Rüchardt[211] have derived theories for the combination of free electrons with stripped atomic nuclei, and that of Kramers contains only fundamental constants. The two former theories find their most interesting applications in X-rays and theories of the interior of stars; the latter has been applied to describe the neutralization of canal rays.

It may be noted in passing that three devices have proven particularly advantageous in enhancing the spectrum due to recombination. These are: (1) Schüler cathode,[212] a hollow cathode in a glow discharge from within which is emitted light characteristic of recombination (Paschen[206]); (2) the electrodeless ring discharge, from whose center the recombination light is emitted (Herzberg, Mierdel[206]); (3) a low voltage arc between a hot cathode of great electron emissivity and very small dimensions and a surrounding anode of large area. All of these arrangements are particularly favorable

---

[207] Milne, Phil. Mag. **47,** 209 (1925); see also Becker, Zeits. f. Physik **18,** 325 (1923).

[208] Morse and Stueckelberg, Phys. Rev.; **35,** 116 (1930); see also Oppenheimer, Zeits. f. Physik **55,** 725 (1929), who developed a method and obtained general equations by wave mechanics, but whose results were not worked out for the particular problem here considered.

[209] Kramers, Phil. Mag. **46,** 836 (1923; Wentzel, Zeits. f. Physik **27,** 257 (1924).

[210] Eddington, Inner Constitution of the Stars.

[211] Rüchardt, Zeits. f. Physik **15,** 164 (1923).

[212] Schüler, Zeits. f. Physik **35,** 323 (1926); **37,** 728 (1926).

for the production of large electron and ion concentrations in regions of such small electric field that the electron velocities are low.

Finally, the *capture of electrons by swiftly moving α particles* has very recently been investigated by Davis and Barnes[213] with most interesting and surprising results. It has been known[214] that fast α particles do not capture electrons from the molecules through which they pass until their velocity has decreased below a certain limiting value, suggesting that capture is impossible if the relative velocity exceeds this critical value.[215] For example it was found that α particles whose original velocity was 2.06 $(10)^9$ cm/sec. did not capture any electrons until their speed had fallen to about 0.82 $(10)^9$ cm sec. and did not capture the second electron to become completely neutralized unless the velocity were less than about 0.31 $(10)^9$ cm/sec. In order to examine this point more closely, Davis and Barnes projected a beam of α particles into an evacuated vessel in which also a stream of electrons from a hot cathode was passed with regulated speed in the same direction. Thus each α particle found itself accompanied in its onward flight by a cloud of electrons whose speed, relative to itself, could be adjusted at will. Particles which had captured electrons were then sorted out from the rest by action of a magnetic field, and the number of particles which did not capture electrons was counted on a fluorescent screen.

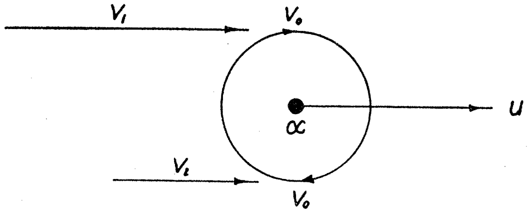


Fig. 14. Conditions for capture of electrons by α particles. u = velocity of α particle; v_0 = orbital velocity which an electron would have in any one of the Bohr orbits of He^+; v_1 and $= v_2$ velocities of free electrons.

With this arrangement it was found that there was a relatively high probability of capture when the relative velocity of electrons and α particles had certain definite characteristic values, and that these characteristic velocities were related to the orbital velocities of electrons in He^+ in the simple way illustrated in Fig. 14. The condition for capture of a free electron by an α particle is that $v_0 = v_1 - u$ or $v_0 = u - v_2$. In other words, the relative velocity between electron and α particle must equal the velocity which an electron would have in an orbit, if captured. But this relative velocity refers to conditions *before* the electron is accelerated toward the α particle by the Coulomb field in the process of its capture. Thus another way of express-

---

[213] Davis and Barnes, Phys. Rev. **34**, 152 (1929); Barnes, *ibid.* **34**, 1224 (1929); **35**, 217 (1930).

[214] Henderson, Proc. Roy. Soc. **A102**, 496 (1923).

[215] Davis, Nature, May 26, 1923.

ing the situation is to say that capture is probable if the total energy relative to the α particle is twice the energy in some one of the Bohr orbits. In addition to this, capture is possible if the relative velocity is zero. Similar energy relations hold for the simultaneous capture of two electrons, with the interesting fact that the condition for recombination appears to be simply that the sum of the energies of the two electrons must equal the total negative energy of the final state of the helium atom.

There is as yet no satisfactory explanation of these experiments. That the experiment should have yielded any results at all is surprising in view of the fact that, to effect the captures which were found, it is necessary that an electron with suitable velocity is captured if its trajectory carries it within a distance of the order of 10^{-5} cm from the α particle,—a distance much larger than the kinetic theory atomic radius. In other words, these experiments indicate an effective atomic cross section for recombination of the order of a million times larger than the ordinary kinetic theory atomic cross section, for the specified relative energies including zero relative energies. For the recombination when the relative velocity is close to zero this is quite to be expected according to the above theories, but recombination at other energies appears to involve quite a different process from any at present recognized.[216]

D. Motions of Electrons and Ions

(1) **Classical kinetic theory** will be understood as referring to that type of treatment of particle kinetics which has been used with considerable success in the problem of molecular motions in the kinetic theory of gases. We shall first outline the more important relations which can thus be derived, then consider experimental tests of this classical theory, and finally mention some attempts to apply the new methods of quantum mechanics to the problem.

(a) *Maxwell's distribution of velocities,*[217] so well known in kinetic theory, is found experimentally to describe very closely the motions of electrons in most regions of a discharge, and we shall see also that there is every theoretical reason for expecting it also to describe motions of ions except in extreme circumstances. The distribution law may be variously expressed in terms of the number of particles per unit volume N:

$$Nf(u)du = N\left(\frac{hm}{\pi}\right)^{1/2} \epsilon^{-hmu^2}du \tag{69}$$

is the number with velocity components between u and $u+du$ in a given direction;

$$Nf(uvw)dudvdw = N\left(\frac{hm}{\pi}\right)^{3/2} \epsilon^{-hm(u^2+v^2+w^2)}dudvdw \tag{70}$$

---

[216] Stueckelberg and Morse, Phys. Rev. **35**, 116 (1930); Adams, *ibid.* **34**, 537 (1929).

[217] Jeans, "Dynamical Theory of Gases," 2 ed. Chap. II.

is the number with perpendicular velocity components lying between u and $u+du$, v and $v+dv$, w and $w+dw$;

$$NF(cdc)=4\pi N\left(\frac{hm}{\pi}\right)^{3/2}\epsilon^{-hmc^2}c^2dc \tag{71}$$

is the number with speeds (irrespective of direction) lying between c and $c+dc$. By integration of this equation between any assigned value c and infinity, one can find the number of particles with velocities greater than c. Furthermore,

$$Nuf(u)du=N\left(\frac{hm}{\pi}\right)^{1/2}u\epsilon^{-hmu^2}du \tag{72}$$

is the number *which cross any plane* with velocity components perpendicular to the plane lying between u and $u+du$.

The constant h may be written in terms of the average kinetic energy $\overline{E}$, or the temperature T, or the mean square molecular speed C^2 by

$$\overline{E}=\frac{1}{2}mC^2=\frac{3}{2}kT=\frac{3}{4h} \tag{73}$$

where k is the Boltzmann gas constant.

By integration of Eq. (72) over all values of u, the total number of particles crossing unit area in either direction is, per second

$$n=N\frac{1}{2(\pi hm)^{1/2}}=N\left(\frac{kT}{2\pi m}\right)^{1/2}. \tag{74}$$

The average speed $\bar{c}$ and the root mean square speed C are related by

$$\bar{c}=(8/3\pi)^{1/2}C=0.921C. \tag{75}$$

Comparing Eqs. (72 and 74) it is seen that

$$u\epsilon^{-hmu^2}du \tag{76}$$

represents the fraction of the particles crossing a surface which possess velocity components perpendicular to the surface lying between u and $u+du$. From this, we find that the average energy of those particles *which cross a surface* is 2 kT, whereas the average energy of the particles *in a given volume* is $(3/2)kT$. The difference is due to the fact that, for the particles which cross a surface, the average energy associated with each of the two coordinates parallel to the surface is the usual value 1/2 kT, but that associated with the coordinate perpendicular to the surface is kT. This increased value is due to the fact that relatively more fast particles than slow ones cross the surface.

If any two regions are separated by a layer in which there is a force field of such a nature that a definite amount of work W would be done by every particle in passing from the first region to the second, then it can be shown by direct integration[218] of Maxwell's equations that, if the particles in the first region possess a Maxwell's velocity distribution, those which pass through the retarding layer enter the second region also with a Maxwellian distribution characteristic of the same temperature. Indeed, by *Boltzmann's equation*,[219] the only effect of such a force field is to alter the concentrations of the particles in the two regions in the ratio

$$\frac{n_1}{n_2} = \epsilon^{-W/kT} \tag{77}$$

where W is the difference in the potential energies of a particle in the two regions.

Mott-Smith and Langmuir[220] have proven an analogous theorem which applies to a more general case of particles with a Maxwellian distribution of velocity which cross a surface into a region of *either retarding or accelerating* field toward some second surface, and which is applicable to problems of collecting electrodes. It shows that in this case also the Maxwell-Boltzmann equations apply to the particles reaching the second surface, *but only to certain groups in such a distribution.* Consider a conservative system consisting of a large number of particles moving in an enclosed space and continually exchanging energy and momentum with each other so that the state of statistical equilibrium described by the Maxwell-Boltzmann distribution law is reached. In this space we imagine to exist a region A in which there is no interaction by collision or otherwise between the particles, and in which there is a field of force acting on the particles. Any interior boundary surfaces of A (such as surfaces of collectors) we shall first assume to be perfectly reflecting. The particles penetrating into A from the exterior will then describe "orbits" (perhaps including reflections at the interior surfaces) and eventually escape again across the exterior boundary. There may, in addition, be some orbits within A which never intersect the outer boundary. This would be true, for example, if there were a force directing the particles inward into A, and we were to introduce particles within A with kinetic energies too small to permit their escape. Now consider all possible orbits, such as we would have if we imagined particles to pass every point within A with every velocity between zero and infinity. Out of this group of orbits, some will intersect the outer boundary. Others *may* be present (as in case of a field accelerating particles inward) which lie entirely within the space A. These paths which never carry the particles outside of A we shall call "interior orbits." The theorem is now as follows:

"If the field A has no interior orbits, the distribution of particles and their velocities throughout it will conform to the Maxwell-Boltzmann distribution law. If interior orbits exist, the distribution will also conform to the Maxwell-Boltzmann law except for an excluded class of particles, these being the particles which, if present, would describe the interior orbits."

[218] Richardson, Phil. Mag. **18,** 695 (1909).

[219] See, for example, Richardson, "Electron Theory of Matter," Chap.

[220] Mott-Smith and Langmuir, Phys. Rev. **28,** 727 (1926); see especially pp. 756–758.

The first case includes the case of electrons or ions which cross the boundary of a plane or convex sheath within which they are retarded and drawn back to the boundary. The second case is illustrated by electrons or ions entering a sheath within which they are accelerated toward an interior collecting electrode or repelled back to an enclosing surface, as in a hollow collector.

If the interior surfaces are absorbing instead of perfectly reflecting, then the distribution is modified in that the group of particles which would have velocities coming from that surface is missing. The simplest case is that of a plane collector surrounded by a space charge sheath with a parallel boundary. Here the concentration of particles of such speeds as would carry them to the collector is just half what it would be if the collector were perfectly reflecting. For the particles which are *drawn* in, there is just a half (or "one way") Maxwell distribution after exclusion of all particles which would have interior orbits. For the particles which penetrate *against* the field within the sheath, there is everywhere the full Boltzmann distribution for those particles which cannot penetrate to the inner absorbing surface, and a half Boltzmann distribution for those which can so penetrate. There are numerous possible applications of this theorem to the condition of ions in the neighborhood of electrodes of various shapes and at various potentials with respect to the surrounding ionized gas.

(b) *The mean free path*[221] is the average distance moved by a particle between collisions. For real molecules its value obviously depends on our definition of a *collision*. For hard spherical particles, which are so often discussed in kinetic theory as a convenient approximation, there is no question; two particles (1 and 2) collide whenever their centers approach each other to within the distance $\sigma_{12}=\sigma_1+\sigma_2$, the sum of their radii. The mean free path λ_1 of particles of type 1 which collide with particles of type 2 is then

$$\lambda_1=\frac{1}{\pi N_2\sigma_{12}^2(1+h_1m_1/h_2m_2)^{1/2}}=\frac{1}{\pi N_2\sigma_{12}^2(1+C_2^2/C_1^2)^{1/2}}$$

$$=\frac{1}{\pi N_2\sigma_{12}^2(1+\bar{E}_2m_1/\bar{E}_1m_2)^{1/2}} \qquad (78)$$

provided both types of particles possess Maxwellian velocity distributions characteristic of mean energies $\bar{E}_1$ and $\bar{E}_2$ respectively,—or velocities C_1 and C_2. In problems of kinetic theory of gases, the mean energies of admixed gases are equal, and hence the factors h_1/h_2 and E_2/E_1 drop out of Eq. (78), but this is not true of electrons or ions in gas discharges. Eq. (78) reduces to simpler forms in important special cases:

$$\lambda_1=\frac{1}{2^{1/2}\pi N_2\sigma_{12}^2} \qquad (79)$$

---

[221] Jeans, "Dynamical Theory of Gases," 2 ed., Chap. X.

if both particles are of the same type;

$$\lambda_1 = \frac{1}{\pi N_2 \sigma_{12}^2} \tag{80}$$

irrespective of velocity distributions if the velocity of type 1 is much greater than that of type 2, as in the case of electrons colliding with gas molecules;

$$\lambda_1 = \frac{1}{4/(2)^{1/2}\pi N_2 \sigma_2^2} \tag{81}$$

if the collision radius σ_2 of the target particle so exceeds that of the projectile particle that it may be substituted for the sum of the radii of the colliding particles in Eq. (79).

If σ_2 is the radius of a molecule, a comparison of Eqs. (80, 81) shows that

$$\lambda_{\text{electron}} = 4(2)^{1/2}\lambda_{\text{molecule}}, \tag{82}$$

since the contribution of the electron radius σ_1 to the sum σ_{12} for electron and molecule is negligible. Eq. (82) defines the so-called "*kinetic theory mean free path of an electron.*" Some values thus calculated from accepted values of molecular free paths are shown in Table XV, together with their reciprocals $\nu = 1/\lambda$ which give the average numbers of collisions per centimeter path.

TABLE XV. *Kinetic theory mean free paths λ and numbers of collisions ν per centimeter path in gas at pressure $p = 1$ mm at 25°C.*

Gas	λ (electron)	λ (molecule)	ν (electron)	ν (molecule)
Hg	0.0149 cm	0.00263 cm	67.0	380.0
A	0.0450	0.00795	22.2	125.9
Ne	0.0787	0.01390	12.7	72.0
He	0.1259	0.02221	7.95	45.0
H_2	0.0817	0.01444	12.2	69.1
N_2	0.0425	0.00751	23.5	133.0
O_2	0.0455	0.00805	22.0	124.2
HCl	0.0322	0.00570	31.0	175.6
CO	0.0420	0.00743	23.8	136.5

Closely related to these expressions is[187]

$$\nu_{12} = 2\pi^{1/2} N_1 N_2 \sigma_{12}^2 \left(\frac{1}{h_1 m_1} + \frac{1}{h_2 m_2}\right)^{1/2} \tag{83}$$

for the total number of collisions per unit volume per unit time between particles of type 1 and those of type 2.

When the particle whose free path we are considering is an ion, there is an attraction between it and all neighboring uncharged particles due to the electric doublet induced in each. The magnitude of this force between an ion and a neutral molecule distant r is,

$$F = \frac{K-1}{4\pi N}\frac{e^2}{r^5} = Ar^{-5} \tag{84}$$

where K is the dielectric constant and N is the number of molecules per unit volume.[222] This attraction both increases the number of times that the center of an ion comes within the distance σ_{12} of the center of a molecule, and also deflects the path of the ion when ion and molecule pass near each other, but not near enough to collide. Each of these effects reduces the diffusion and mobility of the ion. Since the diffusion constant D and mobility constant μ are proportional to the mean free path in the absence of attraction, we may use their reduction to define the mean free path in the presence of attraction, *i.e.*,

$$\frac{\lambda'}{\lambda} = \frac{\mu'}{\mu} = \frac{D'}{D}$$

where the primed symbols represent the values in the presence of attraction and the unprimed symbols represent the values which would be obtained if there were no attraction. Langevin[223] has calculated μ and D for smooth elastic sphere ions moving among smooth elastic sphere molecules both with and without attraction when the ions and molecules are in thermal equilibrium, and hence have the same average kinetic energies $\bar{E}$. The effect of attraction is found to depend on the ratio $A/4\sigma_{12}^4\bar{E}$. $A/4\sigma_{12}^4$ is the work required to separate an ion and molecule from contact to infinity against the force of Eq. (83). It is therefore the *energy of dissociation of an elementary cluster ion*. The following table shows the magnitude of the effect:

TABLE XVI.

$\dfrac{A/4\sigma_{12}^4}{\bar{E}}$	$\dfrac{\lambda'}{\lambda} = \dfrac{\mu'}{\mu} = \dfrac{D'}{D}$
∞	0
10	0.076
5	.15
2.5	.311
1.0	.732
0.5	.93
0.3	.97
0.0	1.00

Had we defined mean free paths by energy loss instead of by diffusion and mobility, these values would be somewhat different, but the general conclusion would remain unchanged. This conclusion is that *the ion free path is not appreciably diminished by the fact of its charge unless the mutual kinetic energy is of the order of the cluster dissociation energy, or less.* Hence in ionized gases in which ion clusters do not occur to an appreciable extent, we do not

---

[222] Langevin, Ann. d. Chem. et de Phys. **28,** 316 (1903).

[223] Langevin, Ann. d. Chim. et de Phys. **5,** 245 (1905); Hassé, Phil. Mag. **1,** 139 (1926).

need to consider the effect of the ion charge upon its free path. Apparently then this phenomenon plays no appreciable role in ordinary vacuum discharge tubes or any discharges which dissipate large amounts of energy density. It may be important in phenomena of feeble electrical conduction through gas at considerable pressure.

(c) *Collisions and single scattering* are most simply, and for many purposes rather satisfactorily, handled in the kinetic theory of gases by considering collisions to be like those of elastic spheres.

Energy losses at collisions are easily calculated for impacts of *elastic sphere.* Assume a target sphere of mass M at rest before being struck at random by a projectile sphere of mass m and original velocity v. Let θ be the angle between the original trajectory of m and the radius vector in M to the point of impact. The results of the impact are determined by the momentum and energy equations

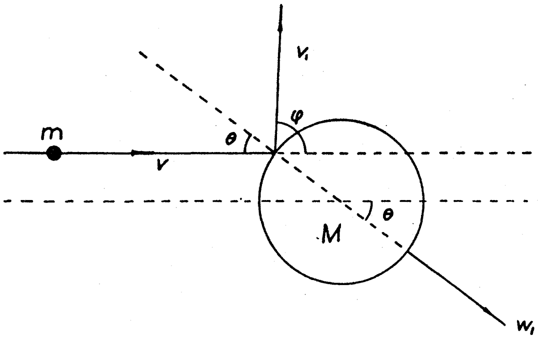


Fig. 15. Collision of elastic spheres.

$$\begin{gathered} mv - mv_1 \cos\phi = Mw_1 \cos\theta \\ mv_1 \sin\phi = Mw_1 \sin\theta \\ \tfrac{1}{2}mv^2 - \tfrac{1}{2}mv_1^2 = \tfrac{1}{2}Mw_1^2 \end{gathered} \tag{85}$$

from which

$$f_\theta = \frac{\frac{1}{2}mv^2 - \frac{1}{2}mv_1^2}{\frac{1}{2}mv^2} = \frac{4Mm}{(M+m)^2}\cos^2\Theta \tag{86}$$

is the fraction of its initial energy which is lost by the projectile particle at this collision specified by θ. The projectile particle may strike the target particle at any point of its surface specified by θ between 0 and $\pi/2$. Multiplying f_θ by the probability of striking at an angle between θ and $\theta + d\theta$, and integrating over all values of θ from 0 to $\pi/2$ gives the *average fraction of energy lost at a collision*

$$f = \frac{2Mm}{(M+m)^2}\,. \tag{87}$$

From this theory we predict that electrons impinging against molecules lose, on the average, a fraction $f=2m/M$ of their energy (where $m \ll M$). Ions, on the other hand, colliding with molecules of the same mass, are expected to lose one-half their energy, on the average.

When the target particles are also in motion, the average fraction of energy lost by the impinging projectile particles is less than that given by Eq. (87). If the projectile particle is moving quite rapidly and has small mass m compared with the target particle M, Compton[224] showed that the average fraction of energy lost by a projectile particle at impact is

$$f=2\frac{m}{M}\left(1-\frac{E_m}{E_M}\right) \tag{88}$$

where E_m and E_M are the kinetic energies of the projectile and target particles, respectively. This expression should be applicable to electrons colliding with molecules (as elastic spheres) provided the velocities of each of the two types of particle were homogeneous.

More recently Cravath[225] has succeeded in solving the analogous problem for the general case of particles with Maxwellian distributions and with no restrictions upon the masses or average energies of the two groups. He finds

$$f=2.66\frac{mM}{(m+M)^2}\left(1-\frac{E_m}{E_M}\right) \tag{89}$$

for the *average fraction of the average energy* E_m lost by particles m at a collision with one of the particles M whose average energy is E_M. Thus the previous applications of Eq. (88) to problems of electron mobility should be corrected by substituting a factor 2.66 in place of 2.

Single scattering is easily handled in case the colliding particles behave like *elastic spheres*. From Eqs. (85) we find a general relation between the angle of incidence θ and the angle of scattering ϕ,

$$m[\sin(\phi-\theta)\sin(\phi+\theta)+\sin^2\theta]=M[\sin^2(\phi-\theta)-\sin^2\theta]. \tag{90}$$

The probability of colliding at an angle between θ and $\theta+d\theta$ is $2\sin\theta\cos\theta\, d\theta$, whence the probability of deflection through an angle between ϕ and $\phi+d\phi$ is found by substitution of ϕ for θ in this expression according to their relation in Eq. (90). For the two most important cases of impacts of electrons against molecules ($m \ll M$) and impacts of ions against molecules of equal mass ($m=M$) we thus find for the relation between θ and ϕ, and for the probability $P(\phi)\,d\phi$ that a particle which collides is deflected through an angle between ϕ and $\phi+d\phi$

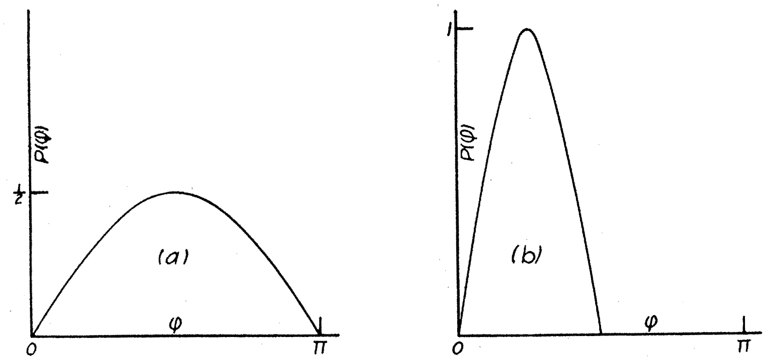
$$\begin{aligned}&\text{for electron } \phi=2\theta \text{ and } P(\phi)d\phi=\tfrac{1}{2}\sin\phi\, d\phi\\&\text{for ion } \phi=\pi/2-\theta \text{ and } P(\phi)d\phi=\sin 2\phi\, d\phi.\end{aligned} \tag{91}$$

---

[224] Compton, Phys. Rev. **22,** 333 (1923).

[225] Cravath, to be published, probably in the Physical Review 1930.

We see, among other things, that the most probable deflection of an electron is at 90° and of an ion is at 45°; also that no ions are deflected backwards, and that the paths of the ion and molecule after collision are at right angle to each other. The distributions of scattering are shown graphically in Fig. 16. By referring to Eq. (86) one can easily find the energy transmitted to the molecule for any angle of impact or of deflection.



(a) electron impact (b) ion impact

Fig. 16. Distribution of scattering angles for elastic spheres.

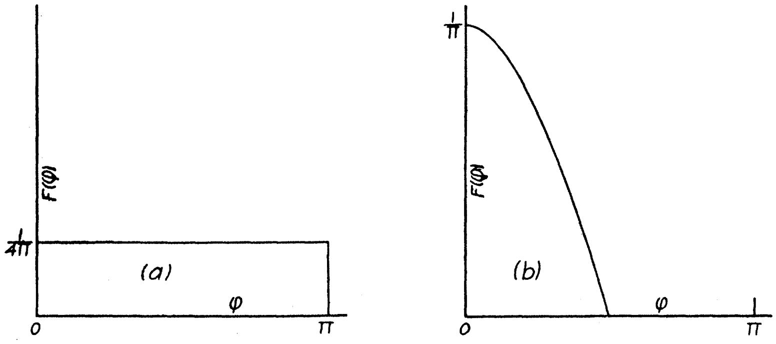
In these expressions no distinction is made in regard to the azimuth of deflection, all azimuths at a given angle ϕ contributing to $P(\phi)$. It is sometimes desirable to express these distributions differently, in terms of the relative probabilities of deflection within a given element of solid angle for various orientations of this element about the axis of the original trajectory. In other words, if radius vectors were drawn from a common point for every collision, what would be the density of these vectors in different directions. This is readily found from Eqs. (91) by dividing each value of $P(\phi)\,d\phi$ by the element of solid angle included between ϕ and $\phi+d\phi$, *i.e.*, by $2\pi \sin \phi d\phi$. Calling the result $F(\phi)$, meaning the fraction of deflections per unit solid angle in the direction ϕ, we have:

$$\text{for electrons } F(\phi)=1/4\pi \text{ ; for ions } F(\phi)=(\cos\phi)/4 \qquad (92)$$

showing that electrons are scattered equally in all directions in space, while ions are scattered most densely in the forward direction. Fig. 17 shows these distributions.

A more general classical case is that in which the particles exert on each other forces of the type $F \propto r^{-n}$. In this case there is no natural definition of a collision. The relative scattering at different angles can still be calculated, but this is now a function of the number and concentration of the scattering particles and of the velocities of the scattered particles. As an example consider:

Scattering of electrons by centers of inverse square force fields. Assume that an electron of kinetic energy $(1/2)mC^2=eV$ traverses a region in which there are N singly charged molecular ions per unit volume. The attraction of the electron to each ion is e^2/r^2. In a path of length l through this ionized gas the probability of deflection through an angle between ϕ and $\phi+d\phi$ as the result of the interaction with some one positive ion is[226]



(a) electron impact (b) ion impact

Fig. 17. Alternative graph of distribution of scattering angles.

$$P(\phi)d\phi=\frac{\pi e^2Nl}{4V^2}\cot\frac{\phi}{2}\cdot\csc^2\frac{\phi}{2}d\phi \tag{93}$$

and the fraction of deflections per unit solid angle in the direction ϕ is

$$F(\phi)=\frac{e^2Nl}{16V^2}\csc^4\frac{\phi}{2}\,. \tag{94}$$

If the energy is expressed as V volts, the coefficients of the trigonometric quantities reduce to 16.1 $(10)^{-5}$ Nl/V^2 and 1.28 $(10)^{-15}$ Nl/V^2, respectively These two distribution functions are illustrated in Fig. 18.

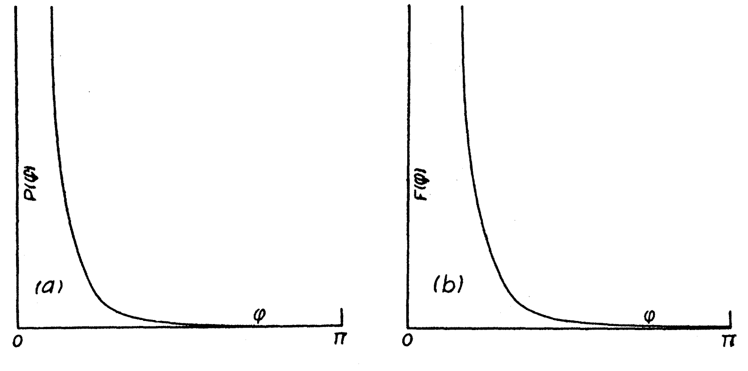


Fig. 18. Single scattering of electrons by ions (inverse square law).

---

[226] This is the well-known formula for single scattering as applied by Darwin to the scattering of α particles (Rutherford, Phil. Mag. **21,** 669 (1911); Millikan, "The Electron," Appendix F). Although in these references the scattering is worked out for an inverse square law of *repulsion,* the same method applied to the problem of *attraction* leads to the identical result.

Since collisions of elastic spheres are equivalent to deflections by centers of a force $F \propto r^{-\infty}$, it is obvious that for any other inverse power law of force higher than the second, the distribution functions would be intermediate in character beween those illustrated in Fig. 18 and those in Figs. 16a and 17a.

Finally, if we investigate the single scattering of *ions* by N ions per unit volume of the same mass we find,[227] in path

$$P(\phi)d\phi = \frac{2\pi e^2 Nl}{V^2} \cot\phi \csc^2\phi \, d\phi \tag{95}$$

$$F(\phi) = \frac{e^2 Nl}{V^2} \cot\phi \csc^3\phi$$

shown graphically in Fig. 19. With V in volts, the coefficients here are 129 $(10)^{-15} Nl/V^2$ and 20.5 $(10)^{-15} Nl/V^2$, respectively.

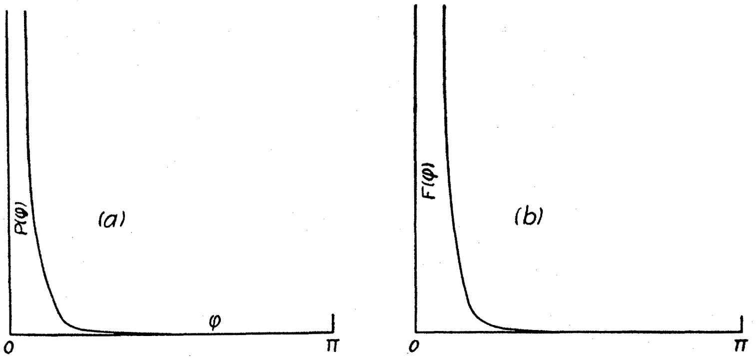


Fig. 19. Single scattering of ions by ions (inverse square law).

It will be observed that the scattering by elastic spheres differs in one important detail from that by force centers in that the expressions for $P(\phi)$ and $F(\phi)$ do not involve the concentration N of scattering centers. This is because the definition of a collision in the former case is perfectly precise, whereas in the latter case there is no distinction between a collision and a non-collision. Really to compare different types of scattering it is preferable never to speak of scattering at a collision, but rather of single scattering per unit path through the gas containing N molecules per unit volume. Then expressions (93, 94, 95) remain unchanged, but for elastic spheres we must modify Eqs. (91, 92) thus: The aggregate cross sectional area for collision offered by the N molecules in unit volume is $\pi\sigma_{12}^2 N$. In path l the chance of collision is $\pi\sigma_{12}^2 Nl$ and of non-collision is $(1 - \pi\sigma_{12}^2 Nl)$.

---

[227] By an adaptation of the methods developed for study of the recoil of light atoms at collisions with α particles. (Darwin, Phil. Mag. **27,** 499 (1914); Rutherford, *ibid.* **37,** 537 (1919); Proc. Roy. Soc. **97,** 374 (1920).

The former fraction of particles traversing path l is scattered according to Eqs. (91, 92). The latter fraction is not scattered at all. Thus we have:
for electrons:

$$P(\phi)d\phi=\begin{cases}(1-\pi\sigma_{12}{}^2Nl)\ldots\ldots\ldots\ldots\ldots\phi=0\\ \pi\sigma_{12}{}^2Nl\cdot\frac{1}{2}\sin\phi\,d\phi\ldots\ldots\ldots 0<\phi<\pi\end{cases}$$
$$F(\phi)=\begin{cases}\infty\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\phi=0\\ \dfrac{1}{4\pi}\pi\sigma_{12}{}^2Nl\ldots\ldots\ldots\ldots\ldots\ldots 0<\phi<\pi\end{cases}\tag{96}$$

for ions:

$$P(\phi)d\phi=\begin{cases}(1-\pi\sigma_{12}{}^2Nl)\ldots\ldots\ldots\ldots\ldots\phi=0\\ \pi\sigma_{12}{}^2Nl\cdot\sin 2\phi d\phi\ldots\ldots\ldots 0<\phi<\pi/2\end{cases}$$
$$F(\phi)=\begin{cases}\infty\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\phi=0\\ \pi\sigma_{12}{}^2Nl\cdot\dfrac{1}{\pi}\cos\phi\ldots\ldots\ldots\ldots 0<\phi<\pi/2.\end{cases}\tag{97}$$

Fig. 20 illustrates the application of these expressions to the case of single scattering of electrons in helium. The total area under each curve must, of course, equal unity. In the case of scattering by elastic spheres, the area *OABC* equals the fraction which have collided, and the line *CD* goes to infinity in such a way that the area under it has a finite area such that *OABCD* equals unity. For any inverse power law higher than the second, the curves lie intermediate between the two types shown.

(d) *Diffusion* is one of the two processes by which ions move in a discharge, the other process being the action of the field. The fundamental law of diffusion is[228]

$$D_{12}=\frac{1}{3}\,\frac{N_1\lambda_2c_2+N_2\lambda_1c_1}{N_1+N_2}\tag{98}$$

for the interdiffusion of gases 1 and 2, whose molecular concentrations, mean free paths and average speeds are denoted by N, λ and c, respectively. The number of molecules of type 1 which cross unit area in the direction of z in unit time is

$$n_1=-D_{12}\frac{\partial N_1}{\partial z}\tag{99}$$

and the rate of increase of their concentration in unit volume is

$$\frac{dN_1}{dt}=D_{12}\nabla^2N_1.\tag{100}$$

---

[228] Jeans, "Dynamical Theory of Gases," 2 ed. p. 326.

Substituting the values of λ from Eq. (78) and putting $N=N_1+N_2$ for the total number of molecules per unit volume, we obtain

$$D_{12}=\frac{4}{(3\pi)^{3/2}N\sigma_{12}^2}\left(\frac{\overline{E}_1}{m_1}+\frac{\overline{E}_2}{m_2}\right)^{1/2}$$

$$=\frac{0.921(C_1^2+C_2^2)^{1/2}}{3\pi N\sigma_{12}^2}$$

where the average velocity $\bar{c}$ is converted in to r.m.s. velocity C by Eq. (75) and $\overline{E}$ is the mean kinetic energy by Eq. (7 3). (We may note that, in substituting in Eq. (98) the values of λ_1, λ_2 given by Eq. (78), we have assumed that λ_1, λ_2 refer only to free paths of the *one* gas which are terminated by collisions with the *other* gas. We have neglected collisions between molecules of the same gas. This is legitimate, however, since collisions of this latter type do not, on the average, affect the rate of diffusion.)

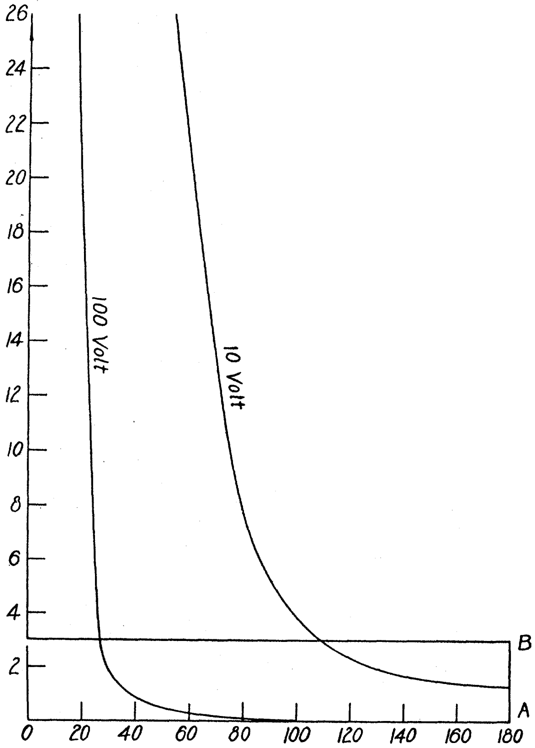


Fig. 20. Comparison of scattering as elastic spheres and as centers of inverse square force (electrons in helium). Ordinate is $F(\phi)/Nl(10)^{-17}$

In these equations let us introduce a quantity λ_0 defined by

$$\lambda_0=(\pi N\sigma_{12}^2)^{-1}. \qquad (102)$$

This is the free path which a particle would have if its speed were very large compared with the speeds of the target particles (Eq. (80)). Let us also limit ourselves to the special cases of electrons diffusing through the gas. ($m_1 \ll m_2$ and $C_1 \gg C_2$) and ions diffusing through the gas ($m_1 = m_2 = M$). Eq. (101) then reduces to

$$\begin{aligned} D_{\text{electrons}} &= 0.434\lambda_0(\bar{E}_1/m_1)^{1/2} = 0.333\lambda_0 c_1 \\ D_{\text{ions}} &= 0.434\frac{\lambda_0}{M^{1/2}}(\bar{E}_1{}^2+\bar{E}_2{}^2)^{1/2} = 0.333\lambda_0(c_1{}^2+c_2{}^2)^{1/2}. \end{aligned} \tag{103}$$

It is to be noted here that, for electrons, λ_0 is the "kinetic theory" mean free path; for ions the kinetic theory value of λ_0 is 1/4 of that for electrons owing to the negligible radii of the latter. λ_0 for ions is, however, $2^{1/2}$ times the molecular mean free path.

Equations (101, 103) are practically identical with those derived from direct consideration of "persistence of velocities," which phenomenon principally accounts for the departure of the numerical coefficient from the value 1/3 when the diffusing particles are of appreciable mass.[229] We have followed the Stefan-Maxwell method, which avoids the direct consideration of persistence of velocities as required by the alternative Meyer theory.

(e) *Mobility* μ is defined in terms of the electric field strength E and the average of ionic drift by the relation

$$\bar{v} = \mu E \tag{104}$$

which is useful even though μ is in general not a constant, but is a function of E. The value of μ has been deduced by a variety of methods,[230] whose results differ only in the numerical coefficient, whose value varies by a factor of about 2 between the extreme cases. A satisfactory method is to deduce it from the diffusion constant D as given in Eqs. (101) by use of the general relation

$$\mu = \frac{e}{kT}D \tag{105}$$

where $3kT/2$ is the average kinetic energy $\bar{E}$ of the ions. This relation was derived by Thomson[231] by equating the average rate of drift of ions across unit area caused by the electric field, $N\mu E$, to the drift which would be caused by a partial pressure gradient $-dp/dz$ sufficient to give the same force on the N ions of unit volume, *i.e.*, with $NeE = -dp/dz$. Hence $N\mu E = -(\mu/e)\,(dp/dz) = -(\mu kT/e)\,(dN/dz)$ in virtue of $p = NkT$. But this must be identical with the diffusion drift $-D\,dN/dz$, whence Eq. (105) follows immediately.

---

[229] Jeans, "Dynamical Theory of Gases," 2 ed., p. 328.

[230] Langevin, Ann. de Chim et de Phys. **5**, 245 (1905); **28**, 317, 495 (1903); Mayer, Ann. der Phys. **62**, 358 (1920); Loeb, "Kinetic Theory of Gases," Chap. XI; Townsend, "Electricity in Gases," p. 84.

[231] Thomson, "Conduction of Electricity Through Gases," 3 ed., p. 79.

In this manner Eqs. (73, 101, 105) lead to

$$\begin{aligned}\mu_{12}&=\frac{2e}{(3\pi)^{1/2}\pi N\sigma_{12}{}^2\bar{E}_1}\left(\frac{\bar{E}_1}{m_1}+\frac{\bar{E}_2}{m_2}\right)^{1/2}\\&=\frac{0.921e}{\pi N\sigma_{12}{}^2\cdot m_1C_1}\left(1+\frac{\bar{E}_2m_1}{\bar{E}_1m_2}\right)^{1/2}\end{aligned}\tag{106}$$

for the mobility of charged particles 1 moving through gas 2. If the average velocity c_1 is used instead of the r.m.s. velocity C_1, the numerical coefficient is 0.85 instead of 0.921.

Again introducing λ_0 from Eq. (102) we have in general

$$\mu_{12}=\frac{0.921e\lambda_0}{m_1C_1}\left(1+\frac{\bar{E}_2m_1}{\bar{E}_1m_2}\right)^{1/2}$$

for electrons

$$\mu=\frac{0.921e\lambda_0}{mC}=\frac{0.85e\lambda_0}{mc}\tag{107}$$

for ions

$m_1=m_2=M$

$$\mu=\frac{0.921e\lambda_0}{MC}\left(1+\frac{\bar{E}_2}{\bar{E}_1}\right)^{1/2}.$$

Comparing our derivation of μ_{12} with the most familiar mobility equation, that of Langevin[232]

$$\mu_{12}=\frac{0.815e\lambda_0}{m_1C_1}\left(1+\frac{m_1}{m_2}\right)^{1/2},\tag{108}$$

we notice two differences. The difference in the numerical factor arises from differences in the methods of averaging, and is typical of the variety of constants lying between 0.5 and 1.0 which follow the use of different degrees of refinement. We believe that the value here given is as reliable as any. The absence of the ratio of the mean energies in Langevin's (and all other) mobility equations arises from an implicit assumption of equipartition of energy in carrying out an integration, and has probably crept in because, when mobility equations were first derived, interest in mobility centered on cases where the ions were practically in equilibrium with the gas molecules.

The thing in Eqs. (107, 108) which is generally misunderstood is that λ_0 is not necessarily the mean free path, but is defined by Eq. (102) and is $2^{1/2}$ times greater than the mean free path if the velocities of the ions and molecules are of the same order.[233]

---

[232] Langevin, Ann. de Chim. et de Phys. **5**, 245 (1905); **28**, 495 (1903); Mayer, Ann. d Phys. **62**, 358 (1920).

[233] Loeb (Kinetic Theory of Gases, p. 447) calls particular attention to the correct definition of λ_0.

It should be remarked that Langevin has derived a more general mobility equation based on the assumption of inverse power attractive forces between ions and molecules.[234] Since we have already seen that attractive forces do not notably affect free paths when the ion energies are considerably too great to permit formation of "clusters," this refinement does not appear to be important for the theory of electric discharges in gases.

To the extent to which collisions may be treated as between elastic spheres, Eq. (107) should permit an estimate of mobilities accurate within the small uncertainty in the numerical coefficient, *provided the mean velocities and energies are known.* In strongly ionized gases these quantities can be measured directly for electrons and estimated with considerable precision for ions as the result of the development of special probe-wire methods[235] which will be described in Part II. Where this direct information is unavailable, Eq. (107) can only be used in connection with some supplementary theory for estimating the velocities and energies. This has been attempted in the following analysis, based on papers by Hertz[236] and Compton.[237]

Terminal speeds may be calculated by equating the rate of gain to the rate of loss of energy as a charged particle moves through a gas in a uniform field E. In advancing a distance dx in the direction of the field, each particle of charge e receives energy $edU = eEdx$, where U is the kinetic energy of the charged particle in terms of equivalent potential drop. In the same path dx the particle will lose energy $\nu' \cdot feU\,dx$, where ν^1 is the average number of collisions made while advancing unit distance and f is the average fraction of its energy lost at a collision as a result of momentum transfer. Thus

$$e\,dU/dx = e(E - \nu' f U) \tag{109}$$

is the net rate at which the particle acquires additional energy. The state of terminal speed is defined by $dU/dx = 0$, hence by the terminal energy U_t in

$$U_t = E/\nu' f. \tag{110}$$

From this the average number of collisions ν' made by a charged particle while advancing unit distance may be calculated thus:

In Eq. (107) put $eU = \bar{E}_1$ and $e\Omega = \bar{E}_2$ for the mean energies of charged particle and gas molecule, respectively. Then we have the average velocity of advance in the direction of the field E given by

$$\bar{v} = \mu E = \frac{0.921 e\lambda_0}{mC} E \left(1 + \frac{\Omega m}{UM}\right)^{1/2}. \tag{111}$$

---

[234] Langevin, Ann. de Chim. et Phys. **8,** 238 (1905); Thomson, "Conduction of Electricity Through Gases," 3 ed., p. 165.

[235] Langmuir and Mott-Smith, G. E. Rev. **27,** 449, 538, 616, 762, 810 (1924); also Tonks and Langmuir, Phys. Rev. **34,** 877 (1929).

[236] Hertz, Zeits. f. Physik **32,** 298 (1925); Physica, **2,** 15 (1922).

[237] Compton, Phys. Rev. **22,** 333 (1923).

But the average number of collisions made by a charged particle in unit time is c/λ. Hence the average number of collisions made while advancing unit distance is

$$\nu'=\frac{c/\lambda}{\mu E}=\frac{0.921C}{\lambda E}\;\frac{mC}{0.921e\lambda_0\left(1+\dfrac{\Omega m}{UM}\right)^{1/2}}$$

$$\nu'=\frac{2U}{\lambda\lambda_0 E\left(1+\dfrac{\Omega m}{UM}\right)^{1/2}}=\frac{2U}{\lambda_0^2 E} \tag{112}$$

by Eq. (78). Remembering that $1/\lambda_0$ is of the order of the number of collisions per unit path, we see that the number of collisions made while *advancing* unit distance is of the order of the square of the number made in unit path *along the trajectory.*

Returning now to Eq. (110) and substituting for f and ν' from Eqs. (89, 112) we obtain for the terminal energy of charged particles of mass m and mean free path λ in a medium whose molecules have mass M and average energy Ω,

$$U_t=\frac{\Omega}{2}+\left[\frac{\Omega^2}{4}+\frac{\lambda_0^2E^2(M+m)^2}{5.32Mm}\right]^{1/2}. \tag{113}$$

This reduces to the equipartition value $U_t=\Omega$ for very weak fields $E=0$, while in strong fields the terminal energy becomes nearly proportional to the field according to

$$U_t=\lambda_0E(M+m)/2.31Mm.$$

Since the root mean square speed is given by

$$C_1=(2eU_t/m)^{1/2}, \tag{114}$$

we substitute Eq. (113) into Eq. (114), and this value of C_1 into Eq. (107) to obtain the general mobility equation

$$\mu=\frac{0.921e\lambda_0}{(2em)^{1/2}}\left[\frac{\Omega}{2}+\left(\frac{\Omega^2}{4}+\frac{\lambda_0^2E^2(M+m)^2}{5.32Mm}\right)^{1/2}\right]^{-1/2}$$

$$\times\left[1+\frac{m}{M}\;\frac{1}{\dfrac{1}{2}+\left(\dfrac{1}{4}+\dfrac{\lambda_0^2E^2(M+m)^2}{5.32Mm}\right)^{1/2}}\right]^{1/2}. \tag{115}$$

In this, the first term in brackets is a generalization of an analogous expression previously derived by one of us.[237] The second term in brackets replaces the factor $(1+m/M)^{1/2}$ which has appeared in previous mobility equations (*e.g.* Langevin[232]). Apparently in previous equations the effect on the mean free paths of the fact that the mean ionic energy exceeds the mean molecular energy (see discussion of Eq. (78)) has been neglected in this term, which is of the nature of a correction term for persistence of velocities. Note that λ_0 is defined by $\lambda_0=(\pi\sigma_{12}^2N)^{-1}$ and is thus independent of velocities.

Eq. (115) reduces, for the two cases of chief interest, to: for electrons $m\ll M$, $\lambda_0=\lambda=$ electron mean free path,

$$\mu_{\text{electrons}}=\frac{0.921e\lambda_0}{(2em)^{1/2}}\left[\frac{\Omega}{2}+\left(\frac{\Omega^2}{4}+\frac{\lambda_0^2E^2M}{5.32m}\right)^{1/2}\right]^{-1/2} \tag{116}$$

for ions $m=M$, $\lambda_0=\sqrt{2}\lambda$ where $\lambda=$ molecular mean free path,

$$\mu_{\text{ions}}=\frac{0.921e\lambda_0}{(2eM)^{1/2}}\left[\frac{\Omega}{2}+\left(\frac{\Omega^2}{4}+\frac{\lambda_0^2E^2}{1.33}\right)^{1/2}\right]^{-1/2} \times\left[1+\frac{1}{\dfrac{1}{2}+\left(\dfrac{1}{4}+\dfrac{\lambda_0^2E^2}{1.33\Omega}\right)^{1/2}}\right]^{1/2}. \tag{117}$$

Both equations reduce to simple forms in the limiting cases of very small field and very large field.

The *effect of inelastic impacts* is to increase the mobility. This result is not paradoxical when one notes that inelastic impacts diminish the translational speed of the particles, and that this speed occurs in the denominator of the mobility equation (107). If all collisions made by electrons were completely inelastic, their mobility is shown to be[237]

$$\mu_i=\left(\frac{\pi\lambda e}{2mE}\right)^{1/2} \tag{118}$$

which is at least in qualitative agreement with observation.[238]

(2) **Comparison of these applications of classical kinetic theory with experiment** can be made at several points.

(a) *The Maxwell distribution* of velocities is found among electrons thermionically emitted from a hot body (as already discussed under B (1)). Also in many parts of discharge tubes the electrons are found[239] (by methods to be described in Part II) to have a Maxwellian distribution with a mean energy determined jointly by the ionization potential of the gas and by the discharge conditions, rarely exceeding one-third of the minimum ionizing potential. Frequently, in regions of intense ionization near the cathode, there are found two superimposed Maxwellian distributions, one of relatively high mean energy apparently consisting of primary electrons from the cathode which have been scattered and the other of much lower energy comprising secondary electrons which have been produced by ionization of the gas. The mechanism by which these Maxwellian distributions are so quickly established in an ionized gas is not understood.* It is well known that electrons drifting through a gas under the influence of a

---

[238] Compton, Phys. Rev. **22**, 333, 432 (1923).

[239] Langmuir and Mott-Smith, G. E. Rev. **27**, 449, 538, 616, 762, 810 (1924).

* See, however, section D (4).

uniform field, and subject to the laws of conservation of momentum, acquire a terminal speed in which they have a Maxwellian distribution of velocities with respect to a system of coordinates moving with their uniform rate of drift,[240] but calculation of the number of collisions required approximately to attain this condition shows that in an ionized gas some additional and more effective agency must be chiefly responsible for the scattering of velocities. Generally speaking, electrons are found to have very close to Maxwellian velocity distributions in all parts of discharges where there is considerable luminosity, and also in the Faraday dark space. Wide departures from complete Maxwellian velocities are sometimes found in the dark spaces between striations, and always in the regions of cathode and anode falls of potential.

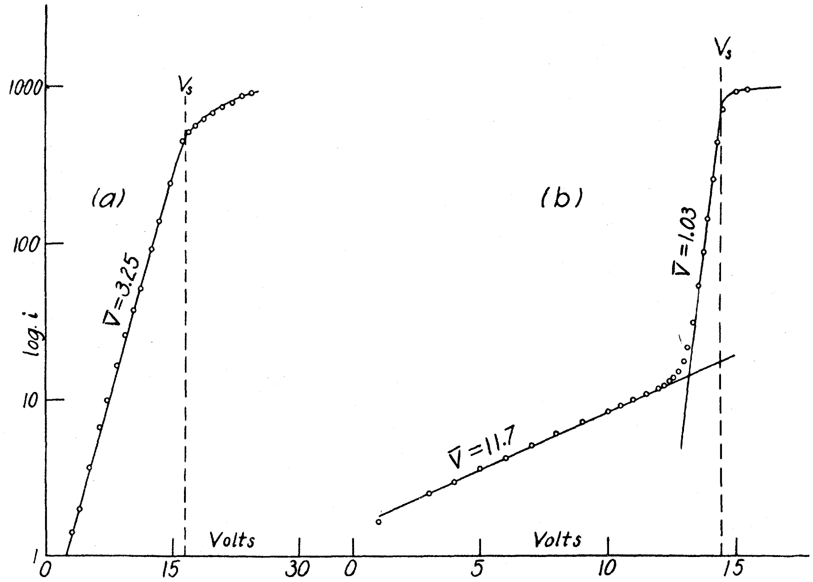


Fig. 21 (a) Showing one Maxwellian distribution. (b) Showing two superimposed Maxwellian distributions.

Fig. 21 shows two typical velocity distributions. The criterion of a Maxwellian distribution is that the graph of log i_- (electron current to a collecting electrode) against V (potential of collector) shall be a straight line in the region where V is negative with respect to space potential V_s. Its slope is $3/(2\bar{V})$ where $\bar{V}$ is the mean energy, in equivalent volts, of the electrons in the surrounding space. Fig. 21 (a) was obtained from an arc in argon, and 21 (b) from an arc in helium, both provided with incandescent cathodes as in tungar rectifiers.

---

[240] Langevin, Ann. Chim. Phys. **105,** 245 (1905); Boltzmann, "Gastheorie," Vol I, p. 114; Benade and Compton, Phys. Rev. **11,** 196 (1918).

Boltzmann's distribution of concentration is also found to hold for electrons in discharge tubes. A very pretty example of this will be found in a paper by Killian.[241]

(b) In the case of *mean free paths*, the experimental results point to a collision mechanism much more complicated than that assumed in the so-called "classical" kinetic theory case, discussed above; yet the results are in general of the same order of magnitude so that the classical kinetic theory values are useful for easy rough estimates or for use where no more accurate data are available or can be mathematically handled. There are three direct methods of measuring free paths of charged particles, due respectively to Lenard, Ramsauer, and Langmuir and Jones.

In *Lenard's* method[242] the charged particles are accelerated by a field to the desired velocity, a well defined beam of them is passed through a system of pinhole diaphragms into a chamber in which they may collide with gas molecules, and those which pass through undeflected are caught by a suitable receiving electrode. The number N getting through a distance x without deflection is $N_0\epsilon^{-x/\lambda}$ or $N_0\epsilon^{-px/\lambda_1}$, if λ_1 is the mean free path at unit pressure. The ratio of the numbers N' and N'' getting through at two pressures p' and p'', or at two distances x' and x'', is $\epsilon^{-x(p'-p'')/\lambda_1}$ or $\epsilon^{-p(x'-x'')/\lambda_1}$ respectively, whence the mean free path λ_1 at unit pressure is readily calculated.

It is necessary to examine what the mean free paths determined in any experiment really signify, since in each case the meaning of the mean free path is defined by the apparatus used to determine it. In the Lenard apparatus, a free path is one in which the angular scattering is very small,—too small to cause the particle to miss the collecting electrode. Energy losses are not involved, except in so far as they are accompanied by deflection.

In Ramsauer's method[243] Fig. 22, the charged particles are set free photoelectrically or thermionically as from the filament F, and are accelerated to the desired speed by an electric field between F and the electrode C. The beam emerging from the slit S_c is bent by a magnetic field to pass through the circular slit system S_1, S_2, S_3, S_4, S_5 and is finally caught in the Faraday box B.

The apparatus thus selects out a group of velocities very narrowly defined by the magnetic field and the slit system. The currents to the box B are measured for a series of different gas pressures and, as before, the ratio of currents at any two pressures is given by $\epsilon^{-x(p'-p'')/\lambda_1}$, where x is the length

---

[241] Killian, Phys. Rev. **35,** (1930).

[242] Lenard, Ann. d. Physik **12,** 714 (1903); Mayer, *ibid.* **45,** 24 (1914); **64,** 451 (1921); Compton and Benade, Phys. Rev. **8,** 449 (1916); Maxwell, Proc. Nat. Acad. Sc. **12,** 509 (1926); Jones, Phys. Rev. **32,** 459 (1928).

[243] Ramsauer, Ann. d. Physik **64,** 513 (1921); **66,** 546 (1921); **72,** 345 (1923); Jahrb. d. Radioakt. **19,** 345 (1922); Brode, Proc. Roy. Soc. **125,** 134 (1929); Phys. Rev. **34,** 673 (1929); Beuthe, Ann. d. Physik **84,** 949 (1927) probably vitiated by impurities; Brüche, *ibid.* **5,** 909 (1929); Jones, Phys. Rev. **32,** 459 (1928) compares Ramsauer's and Lenard's methods for electrons in Hg vapor; see particularly Ramsauer and Kollath, Ann. d. Physik **4,** 91 (1930) for latest knowledge of behavior at very low velocities.

of path from S_c to S_6. Brode[243] has pointed out certain necessary precautions and second order corrections.

In this method it will be noted that not only angular deflection but also energy loss even without deflection will cause a particle to be lost from the beam. For this reason, the absorption coefficient $1/\lambda_1$ measured by this method, is often called the *total absorption coefficient.*

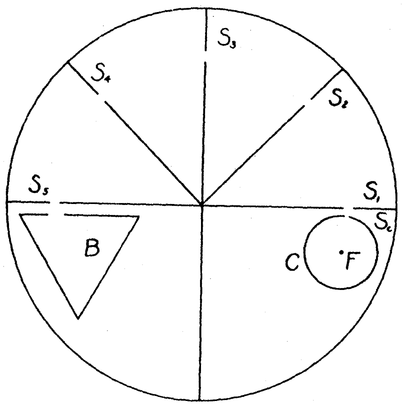


Fig. 22. Ramsauer's method for measuring mean free paths.

In *Langmuir and Jones' method,*[244] Fig. 23, ionization of the gas is maintained between an electron emitting equipotential hot filament *F* and anode plates *A* and *B*, while a surrounding coaxial cylinder *C* is used as a collecting electrode to which the current is measured at various potentials with respect to the filament. As will be shown in Part II, the main body of the enclosed ionized gas is at a nearly uniform potential, approximately that of the anode, and differences of potential between this body of gas and the electrodes are concentrated in "space charge sheaths," around the electrodes, whose thicknesses are relatively small if the ionization is fairly intense. Thus the electrons emitted by the filament are projected out radially into the gas with velocities corresponding to the cathode fall of potential in the sheath. If the collector *C* is negative with respect to the filament *F* (and therefore with respect to all parts of the discharge) positive ions flow into it through the surrounding space charge sheath, but all electrons entering the sheath are

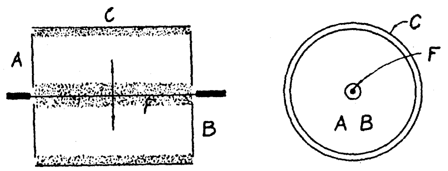


Fig. 23. Langmuir and Jones' method for studying electron collisions with gas molecules.

---

[244] Langmuir and Jones, Science, 59, 380 (1924); Phys. Rev. 31, 357 (1928).

forced back into the main body of the discharge, thus failing to reach the collector. But if the collector *C* is brought just to the potential of the filament, then those electrons from the filament which have lost no forward momentum are able to penetrate this sheath and reach the collector. For more positive potentials of the collector *C*, electrons which have lost some forward momentum are nevertheless able to reach it. Thus the current to this collector at its various potentials may be used to indicate the fraction of electrons leaving the filament which collide (lose forward momentum) while traversing the gas between filament and collector. Also this experiment yields much information regarding the nature of the collisions, as will be discussed in the following section. Fig. 24 shows a typical curve for nitrogen. In region *AB* only positive ions reach the collector *C*. At *BC* the cylinder is no longer negative in respect to *F* and the length $BC = \Delta$ is the relative change in current to the collector in passing from *B* to *C*. Then the fraction of primary electrons from the filament which reach the collector *C* without collision is

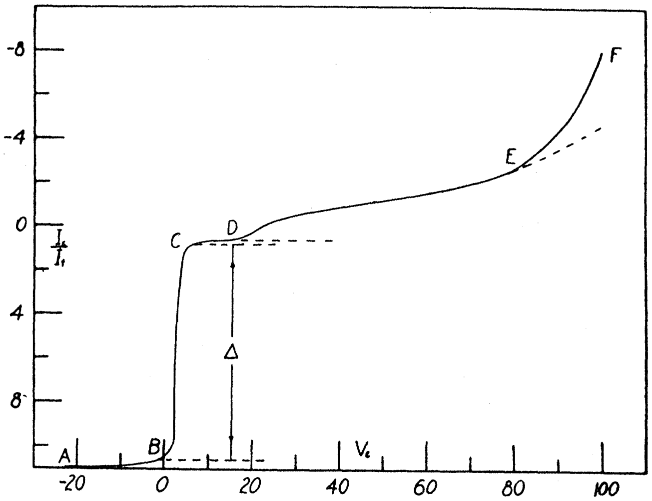


Fig. 24. Langmuir and Jones' results with nitrogen. Δ is the measure of the number of electrons which lose no forward momentum.

$$\frac{\Delta}{1-r+\beta_c} = \epsilon^{-ap/\lambda_1}$$

where r and β_c are small corrections due to reflection of a fraction r of the electrons incident on *C* and to change in the positive ion current to *C* due to the loss of this group of electrons as ultimate ionizing agents in the discharge, respectively, and a is the radius of the collector *C*. All these quantities may be measured or estimated with considerable certainty, whence λ_1 is found. Further information given by this method in regard to the nature of the collisions themselves is discussed in the following section.

Data of *electron mean free paths* from these three methods are shown in Figs. 25 and 26. Following common usage, the ordinates are "absorption coefficients" α of the gas at 1 mm pressure for electrons, or aggregate "effective" cross-sectional area of all the molecules in a cubic centimeter at 1 mm pressure, or average number of collisions made by an electron in 1 cm path through the gas at 1 mm pressure. These are all equivalent expressions and are equal to the reciprocal $1/\lambda_1$ of the mean free path at 1 mm pressure.

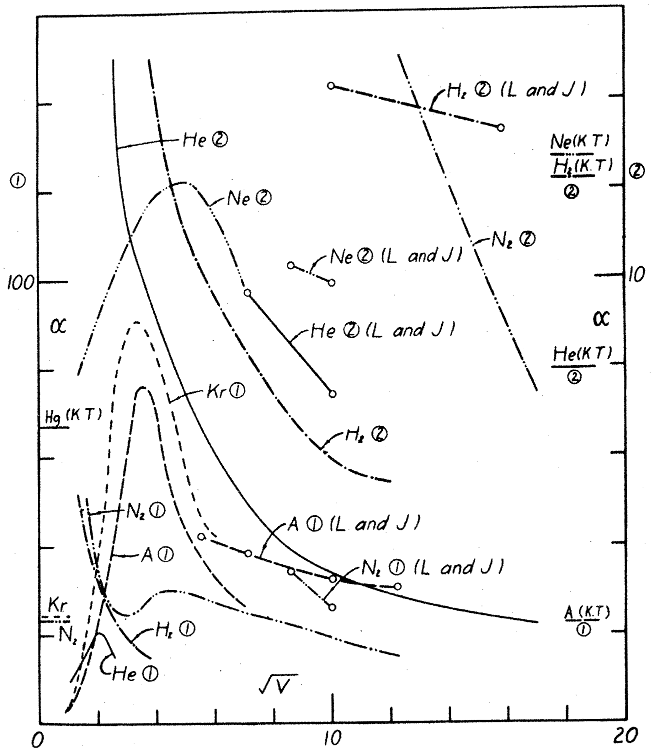


Fig. 25. Absorption coefficients $\alpha = 1/\lambda_1$ for electrons in gases at 1 mm, 25°C, as function of electron velocity. *K.T.* = Kinetic theory value from Eq. (82). Values by Ramsauer method. Values by method of Langmuir and Jones. (1) and (2) indicate scales of ordinates.

Data regarding *positive ion mean free paths* are very meager and are completely lacking in the most important case, that of positive ions moving among molecules of the same gas, except for protons moving through hydrogen.[245] Here Dempster found that protons of velocities between 50 and 2000 volts can pass through many hydrogen molecules without suffering appreciable velocity change, while Thomson found an angular distribution of scattering of the type which would be expected if the inverse cube law of force held during collisions. Similarly, for 900 volt protons in helium,

---

[245] Dempster, Proc. Nat. Acad. Sc. **11,** 552 (1925); G. P. Thomson, Phil. Mag. **1,** 961 (1926).

Dempster found abnormally long free paths [246] (or surprisingly small effects of collisions), while for protons of various velocities in helium and argon Thomson found maximum scattering (minimum free paths) at velocities of 1.4 $(10)^{-8}$ and 0.7 $(10)^{-8}$ cm/sec, respectively, in analogy with the "Ramsauer" effect for electrons.

More recently mean free paths of alkali ions in various gases have been studied. Kennard[247] and Thompson[248] have found that ions of lithium, sodium, potassium or caesium, moving in a beam through hydrogen, helium or argon, are much less scattered out of the beam than would be expected from consideration of the kinetic theory radii, and also that there is less scattering at high than at low velocities. Ramsauer and Beeck[249] found also rapidly decreasing scattering at higher velocities, but found that the scattering approached a limiting value at velocities of the order of 50 volts or more, and that this limiting value agreed quite well with kinetic theory predictions. That is, the mean free path $\lambda_1 = 1/\alpha$ is such as would be expected if the effective collision radius is the sum of the radii of the gas molecule

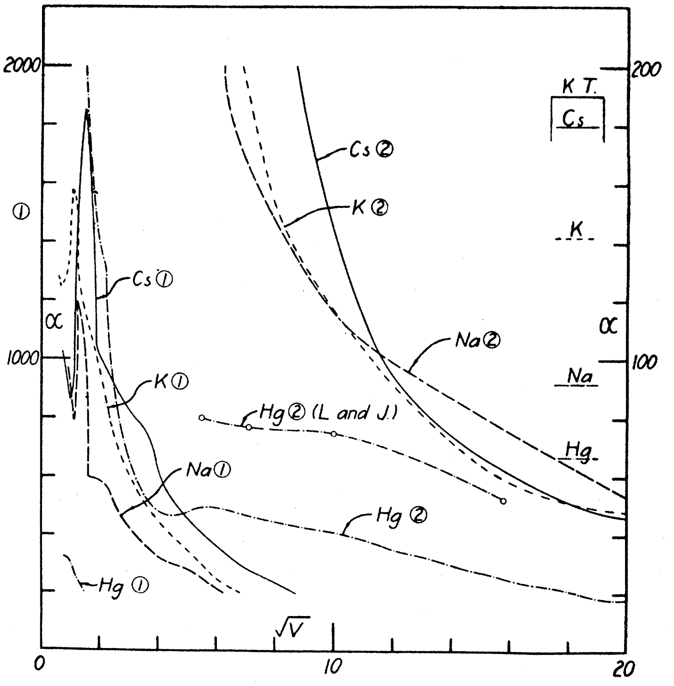


Fig. 26. Absorption coefficients α (see Fig. 25).

---

[246] Dempster, Proc. Nat. Acad. Sc. **12,** 96 (1926).
[247] R. B. Kennard, Phys. Rev. **31,** 423 (1928).
[248] J. S. Thompson, Phys. Rev. (in print).
[249] Ramsauer and Beeck, Ann. d. Physik **87,** 1 (1928).

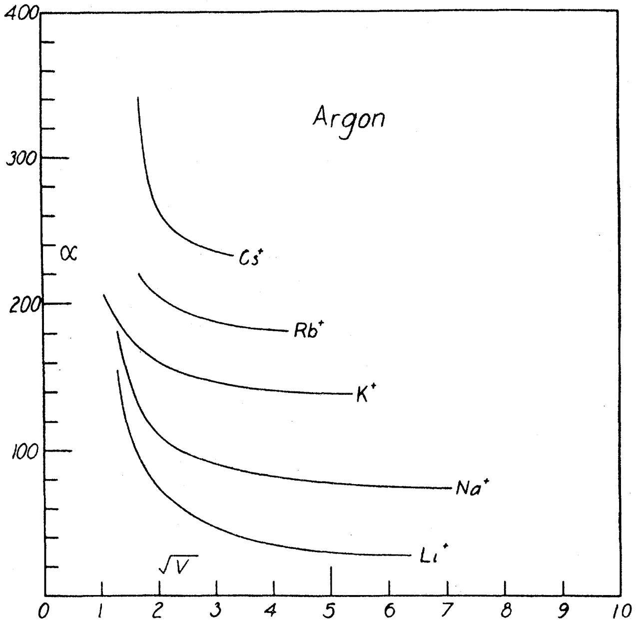


Fig. 27. Absorption coefficients $\alpha = 1/\lambda_1$ of alkali ions in argon gas.

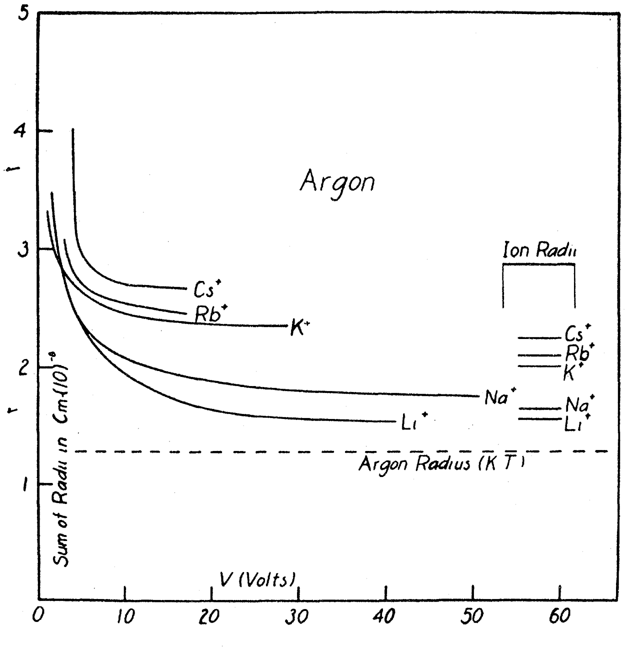


Fig. 28. Comparison of experimental with kinetic theory mean free paths of positive ions.

and the ion. (There is considerable diversity of evidence regarding the magnitudes of ion radii, as shown in the table on p. 22 of Ref. 249. The agreement is obtained if the "true sizes" of the ions are taken according to Fajans and Herzfeld.) Figs. 27 and 28 show a few of the results of Ramsauer and Beeck. In Fig. 28 the lines to the right of the curves and marked Cs^+, Rb^+, etc., indicate the sum of the radii of an argon atom and of each of these ions.

In order to reconcile the results of Thompson with those of Ramsauer and Beeck, it seems necessary to suppose that the mean free paths are actually of the order of those predicated by kinetic theory, especially at the higher velocities, but that the collisions result in loss of velocity without appreciable change in direction.

(c) *The nature of collisions and single scattering of electrons* by molecules has been investigated by two methods, the one devised by Dymond and the other by Langmuir and Jones. The former has the advantage of greater directness and resolving power, the latter of experimental simplicity. As will be seen, the two are in general agreement on the main features of electron scattering at collisions, though not in regard to some details.

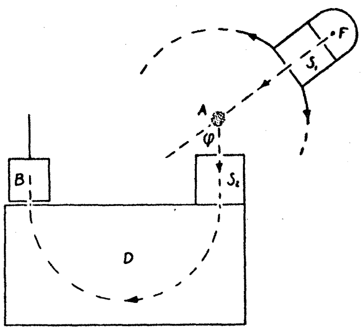


Fig. 29. Dymond's method of investigating electron scattering.

In *Dymond's method*[250] electrons from a hot filament F (Fig. 29) are accelerated to any desired velocity v_1 and reduced to a well defined beam by a slit system S_1. Those which collide with molecules in a small region A and are deflected through an angle ϕ pass through the evacuated slit system S_2 into the evacuated deflection chamber D where those of any desired velocity v_2 are sorted out and deflected into the Faraday detection box F by means of a magnetic field (Dymond) or an electrostatic field (Harnwell). The scattering angle of the observations can be varied by rotating the electron "gun" FS_1 about the axis A. Thus the probability of deflection through any angle, and of any energy loss, can be found for

---

[250] Dymond, Phys. Rev. **29,** 433 (1926); Dymond and Watson, Proc. Roy. Soc. **122,** 571 (1929); Harnwell, Proc. Nat. Acad. Sc. **14,** 564 (1928); Phys. Rev. **33,** 459 (1929); **34,** 661 (1929); **35,** 285 (1930); Kollath, Ann. d. Physik **87,** 259 (1928); Whiddington, Phil. Mag. **6,** 889 (1928); Arnot, Proc. Roy. Soc. **125,** 660 (1929).

electrons of any initial energy colliding with molecules of any gas. Typical results of this method are shown in Fig. 30.

From a series of experiments such as those in Fig. 30, the angular distribution of scattering in helium is found to be as shown in Fig. 31 where, for comparison there are also shown some theoretical curves. The observations are seen to agree acceptably with the new quantum theory of scattering,[251] but *not* with classical kinetic theory. Furthermore the area under each particular curve gives the absorption coefficient α (reciprocal mean free path) for the corresponding type of collision. The most striking feature of these results is the relatively large probability of scattering through small angles, except at the very lowest velocities.

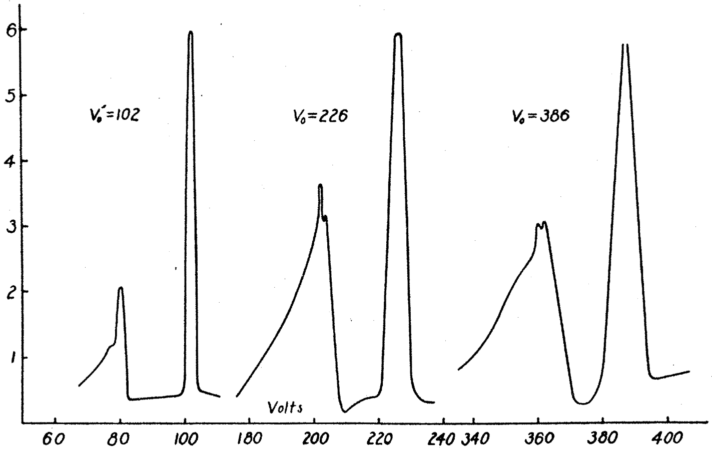


Fig. 30. Velocity distribution of electrons scattered at 10° by single impacts in helium, for initial velocities of 102, 226 and 336 volts. (Dymond and Watson [250].) The three high peaks represent elastic scattering; the pairs of lower peaks represent scattering with sufficient energy loss to excite one or the other of the two lowest excited states of the helium atom.

Harnwell's results[250] show that essentially the same characteristics are found in the scattering curves of helium, neon, atomic hydrogen, hydrogen and nitrogen. The average angle of elastic deflection appears to increase somewhat with increasing molecular weight.

In the Langmuir and Jones method[244] the apparatus of Fig. 23 was used to obtain data of the kind shown in Fig. 24. It will be recalled that the section *AB* of the latter figure represents positive ion current to the collector whose potential is V_c with respect to a homogeneous source of electrons which are projected at any desired speed directly toward the collector. When the collector changes from slightly negative to slightly positive with respect to

---

[251] For hydrogen, or in any Coulomb field, Born, Göttingen Nachrichten, p. 146 (1926); Zeits. f. Physik **38,** 803 (1926); Oppenheimer, Phys. Rev. **32,** 361 (1928); for scattering of particle or electron by a shielded nucleus, Sommerfeld, "Wellenmechanischer Ergänzungsband" p. 231. For scattering by helium, Mott, Proc. Camb. Phil. Soc. **25,** 304 (1929).

the source, those electrons Δ which have lost no forward momentum in the intervening distance become able to reach the collector. The information regarding the nature of collisions is obtained from a study of the shape of the current-voltage curve for positive values of V_c. The basis of interpretation of this curve is the following.

If all electrons which collided lost all their energy, it is obvious that the curve *CDEF* would be perfectly flat and would correspond just to those electrons which pass from source to collector without undergoing collisions. If, however, some electrons are slightly and elastically deflected, these will not be able to penetrate the space charge sheath surrounding the collector when $V = 0$, but they will be able to penetrate it when V is sufficiently positive to make the potential drop in this sheath less by an amount corresponding to the lost energy associated with the forward component of momentum. Thus the shape of the rising curve *CD* gives information in regard to the angular distribution of elastic scattering.

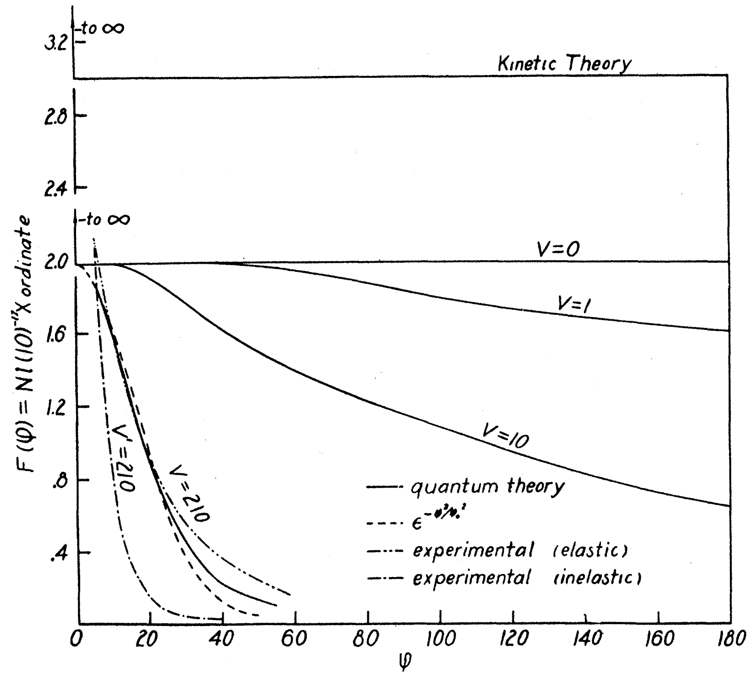


Fig. 31. Electron scattering in helium. $F(\phi)$ is the fraction scattered per unit solid angle at angle ϕ. Observations on *elastic* scattering of 210 volt electrons compared with quantum theory predictions. Also theoretical scattering at other voltages. Also observations on *inelastic* scattering of 210 volt electrons. *The observations are plotted to an arbitrary scale* which is the same for both elastic and inelastic scattering. Curve - - - is the graph of Eq. (119).

The break in the curve at D comes at about $V_c = 13$ volts. It is at this voltage V_c that an electron, which has lost just enough energy to excite a nitrogen molecule and has continued to move directly forward, is just able to penetrate the sheath and reach the collector. At still higher values of V_s electrons which have lost additional energy or been deflected in the process of exciting the atoms, can be collected.

In making the calculations, which are described in detail in the original paper, several secondary effects such as electron reflection at the collector and variation in total ionization as electrons are collected, must be taken into account. The experiment does not distinguish sharply between loss of energy and angular deflection, since loss of forward momentum is the quantity directly given. But some internal evidence, as well as supplementary experiments, justify the deduction of Table XVII.

The results are consistent with a probability law of angular scattering of the form

$$F(\phi)=F(\phi)_0\epsilon^{-\phi^2/\phi_0^2} \tag{119}$$

where $F(\phi)$ is the fraction of the electrons which, in traversing unit distance, are scattered per unit solid angle at the angle ϕ, $F(\phi)_0$ is this fraction at the angle $\phi=0$, and ϕ_0 may be called the *mean square angle of deflection.* Fig. 31 shows that such an equation is in approximate agreement also with Dymond and Watson's results in helium, the value of ϕ_0 there being 22.7°, for elastic scattering of 210 volt electrons. While this equation may not be exact, it is in fair accord with the facts and is of a form which can easily be handled in equations. It is suggested, therefore, that it may be quite useful in dealing with the influence of angular scattering in actual discharge devices. The appropriate constants to be used in this equation for several gases may be obtained from Table XVII, until more direct measurements are available as are now in the case of helium.

The total probability P of scattering as the result of a collision while going unit distance is given from Eq. (119) by

$$P=\int_0^\pi 2\pi\sin\phi\cdot F(\phi)_0\epsilon^{-\phi^2/\phi_0^2}d\phi=\pi\phi_0^2F(\phi)_0 \tag{120}$$

Thus, approximately,

$$F(\phi)=\frac{P}{\pi\phi_0^2}\epsilon^{-\phi^2/\phi_0^2}. \tag{121}$$

Values of P and ϕ_0 derived by substituting experimental results in this equation are given in Table XVII. From these, the value of $F(\phi)$ for any angle is calculable.

In some cases the curve above the first excitation potential was unsuitable for accurate estimates of ϕ_r. Since ϕ_r was found generally to be about equal to ϕ_e, it was assumed equal to ϕ_e in those more uncertain cases. These values are given in parentheses.

In applying Eq. (121) ϕ_0 is placed equal to ϕ_e or ϕ_r as the case may be, and the corresponding value of P is used.

TABLE XVII. *Summary of data on electron impacts in gases. (Langmuir and Jones.) P_k, P_e, P_r, P_i are the probabilities that an electron, while going 1 cm through gas at 1 mm pressure at 20°C, will collide inelastically, elastically, so as to excite the first excited state, or so as to ionize, respectively. ϕ_e and ϕ_r are the root mean square angles of deflection for elastic scattering and for scattering accompanying the first excitation respectively. $E_e = V\phi_e^2$ (volts radians^2) is found to be "approximately" a constant for each gas and is useful for predicting ϕ_e for other electron energies V (volts). Note that ϕ_e must be expressed in "radians" in the argument of Eq. (121). $P_k + P_e$ = total probability of colliding.*

Gas	Volts	P_k	P_e	P_r	P_i	ϕ_e	ϕ_r	E_e
He	50	7.7	2.1	2.8	0.9	25°	(25)°	9.5
	100	6.0	1.5	0.7	1.6	19	16	11.0
Ne	75	9.3	1.1	1.5	1.8	21	(21)	9.8
	100	9.2	.9	1.3	2.4	19	(19)	11.0
A	30	19.1	24.1	5.9	4.7	24	(24)	5.3
	50	18.4	20.8	1.9	9.5	18	(18)	5.2
	100	18.7	14.5	1.7	11.4	12	(12)	4.7
	150	18.4	12.8	2.7	11.4	10	(10)	4.5
Hg	30	48.0	33.3	17.3	13.6	17	(17)	2.5
	50	49.1	29.5	14.7	19.9	11	13	3.1
	100	50.3	25.9	16.7	21.7	10	12	3.3
	250	32.0	21.3	6.7	20.4	6	(6)	3.2
H_2	100	9.2	5.3	3.5	3.9	5	16	7.3
	250	7.2	6.3	2.1	3.6	9	5	6.7
N_2	75	20.2	14.9	5.3	9.3	16	(16)	5.9
	100	16.2	10.4	4.8	10.3	14	8	5.8

Comparison of these results with those of Dymond and Harnwell described previously, shows agreement in the preponderance of scattering through small angles and in the magnitude of the mean scattering angle. Langmuir and Jones find inelastic collisions relatively more probable than do Dymond and Harnwell. In both cases the observed distribution $F(\phi)$ for small velocities tends to approach that of spherical particles.

In the important case of scattering in mercury vapor, Table XVIII gives data by both methods.

TABLE XVIII. *Single scattering of electrons in mercury vapor. $F_e(\phi)$ is the number of electrons elastically scattered through angle ϕ per unit solid angle per primary electron per cm path per 0.001 mm pressure at 20°C. $F_k(\phi)$ is the corresponding quantity for inelastic impacts. 82 volt primary electrons.*

	Dymond's Method (Arnot[250])		Langmuir and Jones[244]	
ϕ	$F_e(\phi)$	$F_k(\phi)$	$F_e(\phi)$	Ratio
0°	—	—	0.226	—
5	0.127	0.167	.184	1.45
10	.051	.063	.102	2.00
15	.024	.025	.038	1.58
20	.0144	.0111	.0099	0.69
25	.0089	.0061	.0012	0.15
30	.0056	.0036	.0003	0.05
40	.0028	.0019	—	—
50	.0015	.0011	—	—
60	.0005	.0004	—	—

In Table XVIII the first values of $F(\phi)$ are calculated from the data in Arnot's paper. The latter values are calculated from data in Table XVII and Eq. (121), taking $P_e = 0.0204$, $\phi_e = 11.3° = 0.198$ radians.

(d) *Diffusion* of electrons and ions has never been studied experimentally with sufficient accuracy to serve as any test of theories such as were developed in section D(1d). It is much easier experimentally to measure mobilities, and thence to calculate diffusion constants by Eq. (105).

(e) *Mobilities* of positive ions have never been studied under conditions in which the nature of the ions has been sufficiently well established to make the results of much use in testing an equation such as Eq. (117). In this direction, therefore, there is more point in combining theory and experiment to investigate the nature of the ions than in testing the theory itself.

Mobilities of electrons are known in many gases over quite a range of fields and pressures and permit a test of theories. Here the only theory which pretends to a rigid derivation and which does not contain arbitrary constants is that expressed by Eq. (116). Following a common usage, this equation may be written in terms of the so-called "mobility constant" K (which is really not a constant, since it depends on temperature) defined as the mobility under standard conditions of temperature and pressure by

$$K = (p/760)(273/T)\mu. \tag{122}$$

If μ is substituted from Eq. (116) and values of constants are introduced, this becomes (since $\lambda = \lambda_0$ for electrons)

$$K = \frac{271,000\lambda_1(273/T)^{1/2}}{[1+(1+1,106,000M\lambda_1^2(E/p)^2)^{1/2}]^{1/2}} \tag{123}$$

where λ_1 is the electron mean free path at $p = 1$ mm and 273°K, M is the molecular weight on the basis of $M_H = 1$ and E is the field in volts per cm. The numerical constants are slightly different from those previously published[252] and are believed better to express the theory.

The experimental results come surprisingly near to the predictions of this theory, when one considers the rather large departures of actual collision phenomena from simple kinetic theory and fact that the equation contains no arbitrarily adjustable constants. Figs. 32, 33 show comparison of theory with experiment in two cases; other cases are discussed by Compton.[252]

These and similar results show that the theory gives results of the right order of magnitude and about the right type of variation of K with (E/p) even as regards the peculiar horizontal intercept of the curve with the axis at $E/p = 0$. Thus the general idea underlying the theory is probably correct and its inaccuracies are due to its use of the much too simplified kinetic theory idea of a collision. Just how the theoretical results would be modified by introducing experimental values of free paths is not immediately obvious. For example, Fig. 25 shows that experimental determinations of electron

---

[252] Compton, Phys. Rev. **22**, 432 (1923).

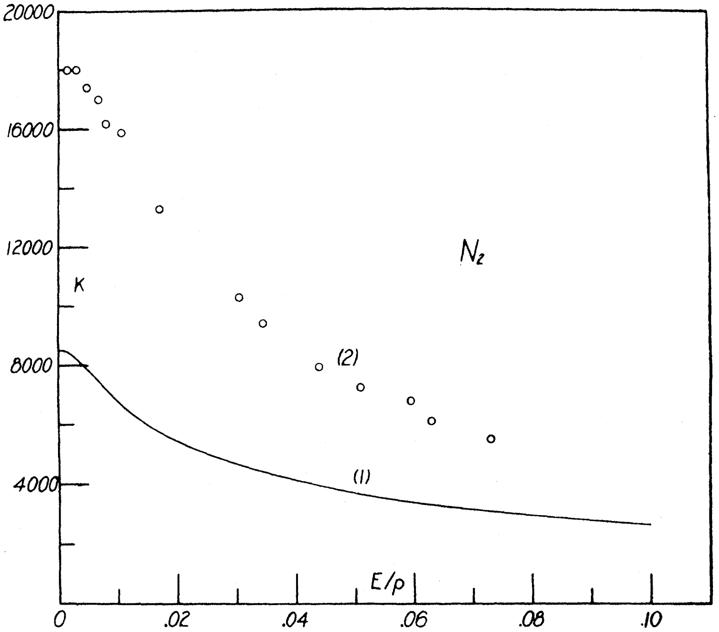


Fig. 32. Electron mobility "constant"; curve (1) theory by Eq. (123); curve (2) experimental results of Wahlin.[253]

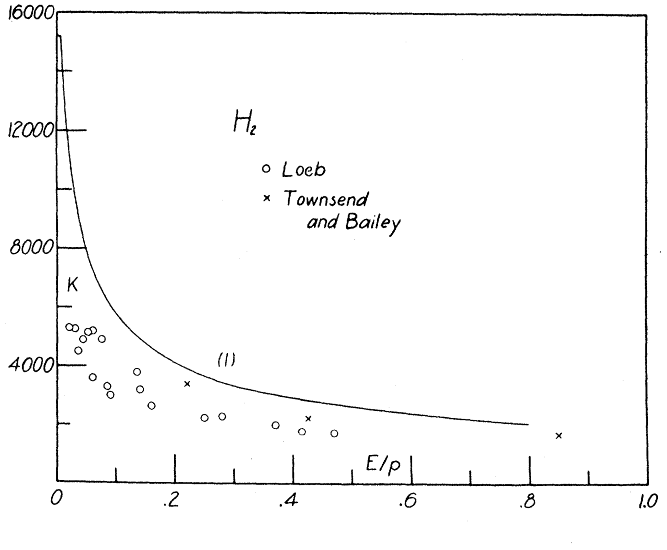


Fig. 33. Electron mobility "constant"; solid curve is theory by Eq. (123); experimental results by Loeb[254] and by Townsend and Bailey.[255]

---

[253] Wahlin, Phys. Rev. **23**, 169 (1924).

[254] Loeb, Phys. Rev. **19**, 24 (1922); **20**, 397 (1922) with small correction for wave form.

[255] Townsend and Bailey, Phil. Mag. **42**, 873 (1921).

mean free paths in N_2 give values considerably *smaller* than the kinetic theory value for such small velocities as are involved in mobility experiments. Introduction of such smaller free paths would, however, accentuate rather than remove the discrepancies shown in Fig. 32. Consideration of possible imperfect elasticity of impact will not bring agreement since it would not change the value of K for $E/p=0$, but would only modify the subsequent course of curve. In this case of nitrogen, however, the fact that scattered electrons are much more concentrated in the forward direction (small scattering angles) than would be true of elastic spheres would introduce a correction increasing the mobility and thus in the right direction to bring agreement between theory and experiment.

In hydrogen and helium, on the other hand, the experimental values of mobility constant are somewhat smaller than those predicted by the theory. In these cases, also, the experimental free paths at low velocities are much smaller than the kinetic theory values, which now is in the right direction to explain the discrepancy in Fig. 33, but the correction which would thus be introduced is somewhat too large, so that to obtain agreement it is again necessary to take account of the excess of scattering in the forward direction. In the case of hydrogen and helium, the quantum theory of scattering (which we have seen is well supported by experiments) predicts that this excess forward scattering is less pronounced at small than at large velocities and, for zero velocity, approaches uniformity of scattering through all angles, as in the simple kinetic theory case. It can fairly be said that such considerations seem adequate to modify Eq. (123) sufficiently to bring it into conformity with experiment, but no test of the theory along these lines has thus far been made.

Obviously a theory of mobilities based on the actual laws of electron scattering at low velocity impacts will be an extremely complicated thing. Perhaps, by assuming approximate analytical functions to represent the variation of free paths of and scattering angles with electron velocities, an approximate solution more satisfactory than Eq. (123) may be found.

There is another way of testing the mobility equations which avoids any consideration of terminal energy such as is involved in Eqs. (117, 123) and goes back to the more general Eq. (107), which involves only the assumptions that the distribution of velocities is Maxwellian and that all directions of motion are equally probable after a collision. The method of Langmuir and Mott-Smith already referred to[235] permits a test of the character of the velocity distribution and a determination of the average electron velocity in case the distribution is Maxwellian, provided the ionization of the gas is fairly intense. In such cases, Eq. (107) permits immediate calculation of the mobility μ if the mean free path is known, or vice versa. It is easy experimentally to determine μ since the total current carried by electrons equals $\int Ne\mu EdS$ integrated over the cross section of the current path, and N and E are given by exploring electrode measurements. Hence, in practice, the electron mean free path λ is calculated by applying the experimental results in Eq. (107). In mercury vapor it is found[256] that the mean free path thus calculated is somewhat smaller than the kinetic theory value. This again is consistent with the experimental values shown in Fig. 26 for the small velocities here involved (for the most part of the order of 2 volts or less). Further tests by this method for a greater variety of conditions and for other gases are very desirable.

(3) **Quantum theories of collisions and scattering** are being reviewed (by E. U. Condon) in a separate article for this journal, and will therefore be treated here only in so far as is necessary to complete the discussion of these phenomena, which are so important in gas discharges. There are three cases which have been treated with considerable success by quantum theory: (a) *mean free paths for very small deflections*, such as would be involved in mean free path measurements; (b) *distribution of angular scattering as a function of velocity*, which gives a theory for the type of scattering studied by Dymond and Harnwell; (c) *abnormal transparency of some molecules for very slow electrons*,—the "*Ramsauer effect*," as observed apparently for all atoms or molecules with completed outer shells of 8 electrons. All of these apply only to electrons but (a) could be extended to include deflection of positive ions. We shall discuss these three cases very briefly.

(a) *Electron mean free paths for very small deflections* were investigated by Zwicky[257] by applying the method of perturbations after the well-known methods of the older quantum theory. The problem may be stated thus: "how far from the center of a molecule must the initial trajectory of an electron pass in order that it shall undergo a deflection ϕ?" Since the present theory applies only to small values of ϕ, the perturbation method is used as follows: First assume that the electron continues undeflected in the direction of its original trajectory. While passing, it exerts a distorting force on the molecule. Then the force exerted on the electron by this distorted molecule is used to calculate its deflection. This force includes that due to polarization $(K-1)e^2/(2\pi N r^5)$ where K is the dielectric constant, N the number of molecules per unit volume and r the distance between electron and molecule. The force may also include a contribution from the permanent field of the molecule, if the latter is a permanent dipole, and if an electron in its orbit in the molecule has a period τ_1 which is comparable with the time τ_2 taken for the electron to pass the molecule, there will be a sort of resonance effect due to the behavior of the molecule as a dipole on account of the orbital electron, even though it would not act as a dipole in phenomena of much greater natural period. It is found that the deflection ϕ is proportional to

$$\phi \propto \frac{U(a)}{mv^2/2}\phi\left(\frac{\tau_1}{\tau_2}\right) \tag{124}$$

where $U(a)$ is the potential energy of the electron at the distance a, a is the closest distance of the molecule from the original trajectory of the electron, τ_2 is defined by $\tau_2 = a/v$, and ϕ is sort of "resonance function."

---

[256] Langmuir and Mott-Smith, G. E. Rev. **27,** 819 (1924); Killian, Phys. Rev. **35,** (1930).

[257] Zwicky, Phys. Zeits. **24,** 171 (1923); Proc. Nat. Acad. Sc. **12,** 461 (1926).

If the molecule possesses a high degree of symmetry the potential energy is due only to the polarization force above and

$$\phi \propto \frac{(K-1)e^2}{4\pi N a^4 m v^2} \cdot \tag{125}$$

Experimentally we find the fraction of electrons deflected through an angle greater than some particular ϕ_0 defined by the construction of the apparatus. That is, we find the fraction whose trajectories come within a distance from a molecule. This fraction is $Nq = N\pi a^2 = \alpha = 1/\lambda$, where q is the effective cross section of a molecule and α (see Figs. 25, 26) is the aggregate effective cross section of the molecules in unit volume. Thus, from Eq. (125) we find

$$\alpha v = \frac{v}{\lambda} = \text{const } (K-1)^{1/2} . \tag{126}$$

In Figs. 25, 26, the curve for H_2 is seen to resemble such a hyperbolic relation, and that for Hg is somewhat similar. In fact it is found that a quantitative evaluation of the constant in Eq. (126) leads to calculated values of α which are within about 10% of the actual values in the cases of H_2, Hg, Zn, Cd.

If, on the other hand, the molecule is a dipole of moment μ oscillating or rotating because of electron orbital motion of period $\tau_1 = 1/\omega$, then Eq. (124) takes the form

$$\phi \propto \frac{\mu e}{a^2 m v^2} \phi\left(\frac{v}{\omega a}\right)$$

or

$$\alpha v^2 = \text{const} \left[\phi\left(\frac{v}{\omega a}\right)\right]^{1/2} . \tag{127}$$

Here α should decrease with increasing v more rapidly than in the case of simply polarizable molecules, it should be larger than it would be if polarization alone were effective, it should increase with atomic volume for atoms in the same column of the periodic table, and it should reach a maximum value in the neighborhood of $v = \omega a$. All these characteristics are exhibited markedly by the rare gas and the alkali atoms and to a less degree by Hg and N_2.

It would seem, therefore, that this theory of Zwicky is based on those physical phenomena which are actually effective in producing electron scattering at collisions. The same considerations could be used in a theory of positive ion scattering through small angles, except that here mutual polarization would have to be considered.

(b) The *distribution of angular scattering of electrons as a function of velocity* has been treated by wave-mechanical methods for atomic hydrogen and other one-electron systems by Born[258] and Sommerfeld[259] and by Mott[260] for helium. Some results of this treatment have already been discussed in connection with Fig. 31. It would take us too far afield here to develop the wave mechanical theory of scattering, but the fundamental ideas and the results may be presented.

The electron of mass m and velocity v is treated as a plane wave of wave length $h/m\ v$ and amplitude ψ, the product of ψ by its conjugate $\bar{\psi}$ at any point being the measure of the average charge density, or the probability of the electron being at that point. The wave function satisfies the Schrödinger equation

$$\Delta\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \tag{128}$$

where E is the total and V is the potential energy of the electron. If proper values of E and V are substituted in this equation, and it is solved for ψ as a function of the coordinates, then the distribution of ψ gives the distribution of scattering. In applying this method, the values of V characteristic of the fields surrounding various types of atoms, must be known.

(c) *The Ramsauer effect*, or the great transparency of certain gases to electrons of low speed, is again rather well explained by wave mechanics.[261] This phenomenon is observed for those gases like Ne, A, etc., whose molecules are electrically so symmetrical that their electric fields fall off extremely rapidly with distance. Thus the function V of Eq. (128) has appreciable values only within a very small distance of each molecule. The molecule is, therefore, an object of very small linear dimensions in so far as V is concerned. On the other hand, an electron of very small velocity v has a relatively long equivalent wave length $h/m\ v$. Hence this combination of a molecule which possesses very small external field, and a slow electron of long equivalent wave length, presents a case analogous to that of a small obstacle in the path of a train of waves of large wave length: the obstacle has relatively little ability to scatter the waves, which pass by it practically unaffected.

(4) **Plasma oscillations of electrons and ions** constitute a unique type among the numerous kinds of oscillations which can be obtained with discharge devices, in that they are entirely independent of the constants L, C, R of the circuit and in other respects. They were first discovered by Penning,[262] were suggested as the cause of the unexpectedly rapid electron scattering

---

[258] Born, Göttingen Nachrichten, p. 146 (1926).

[259] Sommerfeld, "Atombau u. Spektrallinien, Wellenmechanischer Ergänzungsband," p. 231.

[260] Mott, Proc. Camb. Phil. Soc. **25**, 304 (1929).

[261] Faxen and Holtsmark, Zeits. f. Physik **45**, 307 (1927); Holtsmark, Naturwiss. **16**, 614 (1928); *ibid.* **17**, 365 (1929); Zeits. f. Physik **48**, 231 (1928); *ibid.* **55**, 437 (1929).

[262] Penning, Nature, August 28 (1926); Physica **6**, 241 (1926).

discovered in strongly ionized gases by Langmuir[263] and further studied by Dittmer,[264] and were partly explained by Langmuir and Tonks[265] as follows.

A "plasma" is defined as a region of ionized gas in which electron and positive ion concentrations are approximately equal. In such a region, if a group of electrons at x is displaced in the direction of x by an amount $\xi(x)$, subject to $\xi(x)=0$ at two parallel bounding planes, then there is created an electric force arising from the unbalanced space charges, which tends to bring these electrons back to the equilibrium condition of zero space charge. The change in electron concentration, and the resulting field given by Poisson's equation are,

$$\delta n = n\delta\xi/\delta x \quad \text{and} \quad dE/dx = 4\pi e\delta n$$

whence

$$dE/dx = 4\pi ne d\xi/dx$$

whose integral is

$$E = 4\pi ne\xi .$$

Since the restoring force Ee is thus proportional to the displacement ξ, it is obvious that the motion of each electron is simple harmonic according to the equation

$$m\ddot{\xi} + 4\pi ne^2\xi = 0,$$

whose solution gives the natural frequency

$$\nu_e = \left(\frac{ne^2}{\pi m}\right)^{1/2} = 8980n^{1/2}. \tag{129}$$

There is thus a natural oscillation frequency proportional to the square root of electron concentration n. An ordinary value of n in low pressure discharge tubes is $(10)^{10}$ cm^{-3}, which leads by Eq. (129) to $\nu_e = 9\ (10)^8$ cycles which corresponds to radio waves of about 33 cm wave-length.

The velocity of propagation of these waves is

$$v = \lambda\left(\frac{ne^2}{m\pi}\right)^{1/2}. \tag{130}$$

Since the velocity is proportional to the wave-length, the waves show high dispersion and the group velocity of the waves turns out to be zero. Thus, although the waves can propagate through space, they transmit no energy.

---

[263] Langmuir, Phys. Rev. **26,** 585 (1925).

[264] Dittmer, Phys. Rev. **28,** 507 (1906).

[265] Langmuir, Proc. Nat. Acad. Sc. **14,** 627 (1928); Tonks and Langmuir, Phys. Rev. **33,** 195 (1928).

The average field amplitude of these oscillations may be estimated by considering each volume element to be an independent harmonic oscillator in equipartition equilibrium with the electrons themselves, provided we know the lower limit of size of these volume elements. As a reasonable guess, we may assume it to be the cube of the "Debye" distance[266] given by

$$\lambda_D = \left(\frac{kT_e}{8\pi ne^2}\right)^{1/2} = 4.90\left(\frac{T_e}{n}\right)^{1/2} \text{cm} \tag{131}$$

where T_e is the "temperature" of the electrons. (λ_D is the distance at which the average potential near a charged plane in the ionized gas is $1/\epsilon$ of that of the plane.) With this assumption the total energy density of the electric field of the oscillations is

$$\frac{E^2}{8\pi} = \frac{3}{2}\left(\frac{1}{\lambda_D}\right)^3 kT_e$$

whence

$$E = 96^{1/2}\pi^{5/4}e^{3/2}n^{3/4}(kT_e)^{-1/4} \tag{132}$$

$$= 1.17(10)^{-6}n^{3/4}T_e^{-1/4} \text{ volts/cm.}$$

This relation probably gives too large a value of E since it is probable that the mimimum volume element should be larger than λ_D, though of this order of magnitude.

It is obvious that any homogeneous beam of electrons, in passing through an ionized gas, will tend to acquire a random distribution of velocities about the mean velocity on account of the fields of these plasma electron oscillations. These oscillations, therefore, provide a means of interaction between ions and electrons other than that arising from individual encounters or mutual forces.

The foregoing oscillations of the electron space charge with respect to the relatively inert positive ion space charge are the "plasma *electron* oscillations." There are also natural oscillations of the positive ions, which Langmuir terms "plasma *ion* oscillations." For this case a treatment along similar principles gives the frequency

$$\nu_p = \left(\frac{ne^2}{\pi M + ne^2 M\lambda^2/kT_e}\right)^{1/2} \tag{133}$$

Here, if the wave-length λ is small, the equation reduces to the form of Eq. (129), with the ionic mass M in place of the electronic mass m. For long waves, on the other hand, the frequency approaches $(kT_e/M)^{1/2}/\lambda$, which means waves travelling with velocity $(kT_e/M)^{1/2}$. These latter waves are analogous to sound waves travelling through the ionized gas and their

---

[266] Debye and Hückel, Phys. Zeits. **24**, 185, 305 (1923).

frequencies are usually lower than 5 $(10)^5$ per sec. The demarkation between these two types of plasma ion oscillations is roughly the Debye wave-length of Eq. (131).

In Part II of this article, the authors will discuss actual discharge types, such as arcs, sparks, glow discharges and coronas, and will attempt an interpretation of their characteristics in terms of the fundamental phenomena discussed in Part I.

In conclusion, the authors are glad to express their thanks to Mr. Edward S. Lamar for preparing the drawings and to Miss Anna E. Lahey for her assistance in preparing the manuscript.