The Quantitative Study of the Collisions of Electrons with Atoms

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A. GENERAL SURVEY

1. Introduction

When an electron is sent toward an atom there may be an interaction between the atom and the electron. For high speed electrons, it is possible to observe such a collision process by a Wilson cloud chamber. For low speed electrons, i.e., less than 1000 volts, we can send a stream of electrons through a random distribution of gas atoms and observe the distribution of electrons coming from the gas, the number of positive ions formed and the amount of radiation emitted by the atoms. Although we are working at pressures so low that only one collision, ionization or excitation is likely to occur in the volume of our gas, we are still concerned with a statistical problem that tells us only the probabilities of collision, excitation, and ionization. The theoretical solution of the problem by wave mechanics also can give us only the probability of these processes.

The collisions of electrons with atoms are divided into the two classes, elastic and inelastic. By an elastic collision we mean one in which the electron loses only that amount of energy necessary for the conservation of momentum in the collision process. In an inelastic collision the electron loses an amount of energy determined by the quantum states of an atom that is either excited or ionized. In a process involving ionization it is not possible to distinguish between the ejected electron and the ionizing electron after collision. It is moreover possible in an elastic collision for the electron sent at the atom to remain with the atom and one of the electrons of the atom to be ejected with the energy of the

impinging electron. Such interchange processes are considered in the theoretical studies of this problem. We are not concerned in this study with the evaluation of the energies involved in these inelastic collisions, but in the probability of such processes as a function of the energy or velocity of the electron.

2. Definitions and nomenclature

The *probability of scattering*, S, is defined as the number of electrons scattered, per unit electron current, per unit path length, per unit pressure at 0°C, per unit solid angle in the direction θ to the original beam.

This probability of scattering can be divided into three parts: (1) *probability of elastic scattering*, S_e; (2) *probability of scattering with excitation*, S_x; (3) *probability of scattering with ionization*, S_i. The total number of electrons that are scattered elastically and inelastically in all angles equals the number of collisions. Attachment of electrons to form negative ions, although an infrequent process, is to be classified as an inelastic collision.

The *probability of collision*, P_c, is the number of collisions, per unit electron current, per unit path length, per unit pressure at 0°C.

The *probability of ionization*, P_i, is the number of ions formed, per unit electron current, per unit path length, per unit pressure at 0°C.

The *probability of excitation*, P_x, is the number of excited atoms formed per unit electron current, per unit path length, per unit pressure at 0°C.

The probability of excitation must be specified as the probability of excitation to a particular energy state of the atom; and the probability of ionization must be specified as the probability of single ionization, P_{1i}, or the probability of double ionization, P_{2i}, etc.

The efficiency of ionization, E_i, is the total positive ion current per unit electron current, per unit path length, per unit pressure at 0°C.

The probability of excitation is related to the probability of scattering with excitation by the equation:

$$P_x = \int_0^\pi S_x 2\pi \sin\theta d\theta; \qquad (1)$$

also

$$P_i = \int_0^\pi S_i 2\pi \sin\theta d\theta \qquad (2)$$

and

$$P_c = \int_0^\pi (S_x + S_i) 2\pi \sin\theta d\theta + \int_\delta^\pi S_e 2\pi \sin\theta d\theta. \qquad (3)$$

The lower limit of the last integral must not be extended quite to 0 as the initial beam of particles that have passed through the gas without being influenced by the atoms would then be counted as having collided. Experimentally this difficulty in the definition of a collision is removed by the fact that as θ approaches zero, $S_e \sin\theta$ is observed to approach zero, and this enables one to extrapolate the value of the integral to $\theta = 0$, omitting the original beam.

The probability of a collision in a distance dx in a gas at a pressure p is $P_c p dx$. A current of electrons of strength I passing through the layer dx is decreased by

$$dI = -IP_c p dx.$$

Hence

$$I = I_0 e^{-P_c x p}, \qquad (4)$$

where I_0 is the initial electron current in the beam and I is the electron current after passing a distance x through the gas at a pressure p.

The mean free path, λ, is the average distance travelled before colliding and is given by $p \cdot \lambda = 1/P_c = \lambda_0$ the free path at unit pressure. The dimensions of P_c are $l^{-1}p^{-1}$ or $l^2 l^{-3} p^{-1}$ or area, per unit volume, per unit pressure. P_c can therefore be considered as the effective area for collision of all the atoms in a unit volume at unit pressure. This is a very convenient description of the probability of collision, but one is not justified in ascribing this area to any particular part of the atom. In the equation for the decrease in current in the beam of electrons, the probability of collision enters in exactly the same way that an absorption coefficient enters in the decrease in intensity of x-rays or of light in passing through matter. Lenard[1] called the coefficient P_c the absorbing power, and a large number of the workers in this field have used the designation absorption coefficient for this quantity. We know, however, that the electrons are for the most part scattered and that true absorption by attachment is a rare process.

[1] P. Lenard, Ann. d. Physik 12, 714 (1903).

Darrow[2] has preferred the designation "likelihood of interception," in place of absorption coefficient. The probability of ionization and the probability of excitation have been generally accepted as the nomenclature designating the number of ionizations and excitations. The nomenclature of the angular distribution of scattered electrons is commonly the expression, the probability of scattering. Consistent with this nomenclature we will use in this discussion probability of collision in place of absorption coefficient.

In discussing the characteristics of a single atom it is often convenient to use the designation, "*effective cross section for collision*," in place of "*probability of collision*." The effective area of a single atom q is found by dividing P_c by the number of atoms per unit volume, per unit pressure. If the unit of pressure is one mm of Hg at 0°C, and the unit of volume is one cm^3, then $q=0.281\times10^{-16}P_c$ cm^2. The radius r of a circle of this area may be described as the effective radius of the atom for collision and is given approximately by

$$r=0.3(P_c)^{\frac{1}{2}}\times10^{-8}\text{ cm}.$$

Many observers, especially in the measurement of the probability of excitation, express their results as the ratio of the effective cross section for excitation, $0.281\times10^{-16}\ P_x$, to some other cross section. Some use the mean radius of the atom, as observed by diffusion or other "kinetic theory" experiments, to compute a reference cross section P_{KT}. Others use the probability of collision and express their results as the ratio of P_x/P_c. This procedure has led to much confusion, since usually the value of the area is not given and different observers use different tables of atomic radii. The probabilities of excitation, ionization, and collision are all direct results of the experiments and should be stated explicitly. Occasionally a comparison with other cross sections is illuminating. Such comparisons should be accompanied by the specific value of the cross section used as a standard for comparison.

3. Experimental precautions

In many cases it will be found that these probabilities change rapidly with the velocity of the electron, and hence it is necessary to define sharply the velocity. Multiple collisions must be avoided since the velocity and direction of the electron are indefinite after the first collision. In the measurement of the probability of collision, Eq. (3), the limit of integration δ varies with the angle of the collecting aperture as seen from any point in the beam. The influence of this source of error will be discussed in Section 19.

The region in which the scattering takes place is assumed to be a field free space. It is therefore necessary to guard carefully against contact potentials and stray electric fields. The electron beam itself produces a disturbance of the electric field in the scattering region. Above the ionization potential the positive ions produced by the beam build up a potential gradient about the beam. Arnot[3] has measured the velocity of ejection of the positive ions at right angles to an intense beam of electrons in mercury vapor. The maximum velocity of the ejected positive ions corresponded to a potential drop of 2 or 3 volts. A radial potential of this order of magnitude would be very important in reducing the effect of small angle scattering.

At large current densities the probability of collision with a positive ion or excited atom along the path may become comparable with the probability of collision with an atom. The probability of collision with ions or excited atoms will be proportional to the current as the number of scattering centers increases with the current. These effects can be reduced by using small currents or by varying the current density and making corrections for the deviation from linearity introduced by the ions or excited atoms.

In the measurement of the probabilities of scattering, these space charge effects must also be avoided. The volume of the gas, effective in scattering, is often difficult to estimate, especially when collecting particles that were either scattered in nearly the same direction or backward to the direction of the initial beam. The efficiency of the collector is important, especially when retarding potentials are applied to separate out the number of elastic from inelastic particles. As will be seen later, these applied fields are liable to change the size of the aperture effective in collecting scattered electrons.

[2] K. K. Darrow, *Electrical Phenomena in Gases*, p. 136, (Williams and Wilkins, 1932).

[3] F. L. Arnot, Proc. Camb. Phil. Soc. **27**, 73 (1931).

The measurement of the probability of excitation by single impact is complicated by reabsorption of resonance radiation and second kind collisions of excited atoms with other atoms or with electrons which reduce the intensity of the emitted radiation. When excited by a high velocity electron, the atom may be raised to a state where several spectral lines are emitted and the radiation corresponding to the excitation of lower states will be enhanced by the radiation emitted as one step in the return of the atom from a higher state.

The production of a beam of electrons of nearly the same velocity is an important part of all of the experiments described in this paper. Causes of the wide spread of velocity are the thermal energy of the electrons emitted from the source, and the difference in potential of different parts of the emitting surface. A spread of velocity is also produced by the passage of the beam through narrow slits. Lehman and Osgood[4] have investigated this last factor and found it to be quite important. The spread of velocities can be reduced by several methods. An equipotential source of electrons can be used. Accelerating fields can be arranged so that the electrons are focussed towards the centers of the slits. If the electron beam is deflected by a magnetic or electric field, a series of slits can be arranged so that electrons of only a narrow velocity range will be selected.

4. Methods of measurement

The essential features of the experimental apparatus for the measurement of the probabilities of collision, excitation, and ionization, are indicated in Fig. 1. From a source F electrons are accelerated through an opening S_1 and travel as a beam along a path length x through a second opening S_2 and into a collector C. For the measurement of the probability of collision the volume bounded by S_1, A, S_2, and B is a field free space. If I_0 is the current entering S_1, and I the current entering the collector, then $I = kI_0e^{-P_c xp}$, where k is a factor representing the fraction of the initial beam that would have reached the collector if there had been no collisions with gas atoms. Taking the logarithm gives,

$$\log (I_0/I) + \log k = P_c xp. \tag{5}$$

If either x or p is varied and $\log (I_0/I)$ plotted as a function of xp, the slope of this line will be the probability of collision.

If a small potential is applied between A and B the positive ions formed by the electron beam in the region between S_1 and S_2 can be measured. By keeping the pressure low so that the probability of two collisions in the path length x is extremely small, the probability of ionization will be given by $I_p/I_0 = P_i xp$. For higher velocities the positive ion current, I_p, must be separated into the parts caused by singly charged ions, doubly charged, etc. The probability of excitation can be studied by focussing light from a definite volume of the beam on a thermopile, photo-cell or photographic plate and calculating the total number of quanta of radiation emitted in all directions per unit path light, per unit pressure at 0°C, per unit electron current.

The probability of scattering is measured by the arrangement of apparatus shown in Fig. 2. A beam of electrons from a source F is sent through the slit S_1 into a gas at low pressure. A small percentage of the electrons will have collisions with gas atoms in the region intercepted by the limiting lines drawn through the collector slits S_2 and S_3. The current to the collector measures

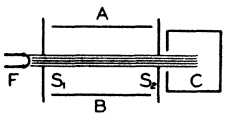

FIG. 1. Apparatus for the measurement of the probability of collision, excitation and ionization.

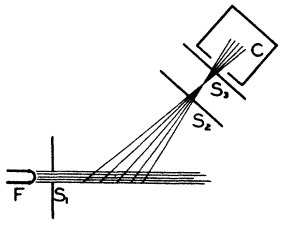

FIG. 2. Apparatus for the measurement of the probability of scattering.

[4] J. F. Lehman and T. H. Osgood, Proc. Roy. Soc. **A115**, 609 (1927).

the number of electrons scattered from this region. By applying a retarding potential between the collector C and the slit S_2 or by the use of some other velocity or energy analyzer the probability of scattering elastically, inelastically with excitation, and inelastically with ionization can be observed.

In addition to these experiments which give directly the values of the probabilities, there are a large number of physical phenomena which depend on these quantities. Where the dependence is simple, it is possible to get quantitative values for the probabilities. The most important of these indirect methods for the measurement of the probability of collision are the experiments of Townsend[5] on the diffusion of electrons in gases. An electron moves through a uniform potential gradient in a gas at relatively high pressure. It has many collisions and is deflected through various angles in each collision. Since it is accelerated in the direction of the electric field, its velocity varies throughout each free path. The results of the measurements of diffusion for low velocity electrons give values for a probability of collision that agree very well with those measured more directly. The chief advantage of the diffusion method is that it can be used to extend observations to very low velocities. Where the free path of the electrons changes rapidly within the range of speeds acquired by the electrons, and where the scattering on collision is far from uniform with angle, the diffusion experiments may give results that do not correctly represent the actual variation of probability of collision with velocity.

B. Probability of Collision

5. Lenard's measurements

The first quantitative study of the interaction of electrons with atoms was the measurement by Lenard[6] of the probability of collision (called by him absorbing power). The method devised by Lenard is that which already has been described in Section 4. The arrangement of Lenard's apparatus is shown in Fig. 3. Photoelectrons were liberated from a zinc plate Z. The electrons were accelerated to a grid N_1 and passed with uniform speed through the field free space between N_1 and N_2. Some of the electrons passed through the aperture A and were collected in the box C which was connected to an electrometer E. The total current G from the plate was measured by a galvanometer. The currents G_0 and E_0 were measured with only the pressure of the residual gas p_0. A small amount of gas at a pressure p_1, was admitted and the currents G_1 and E_1 measured. From Eq. (5), Section 4,

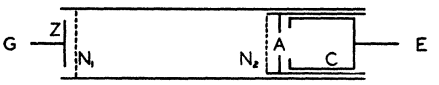

FIG. 3. Lenard's apparatus for the measurement of probability of collision.

$$P_c=[1/x(p_1-p_0)]\,[\log (G_0/E_0)-\log (G_1/E_1)].$$

In Lenard's apparatus the beam of electrons was much wider than the aperture A. As a consequence the effective aperture was increased as all electrons, scattered through a large enough angle to prevent them from going into A, are compensated for by electrons from further out in the beam which normally would not reach A but were scattered into the opening. This compensation extends as far as the dimensions of the beam. Lenard's measurements extended for 4.0 to 4000 volts. The gases He, A, H_2, CO_2, and air were studied. Lenard concluded that the probability of collision at higher velocities was proportional to the density of the gas. As the velocity decreased, the probability of collision increased, reaching an approximately constant value at low velocity. The probability of collision at low velocity was of the order of magnitude of the value deduced from the kinetic theory radius of an atom. The results of Lenard's measurements are shown in Fig. 4. In the original curve by Lenard the square root of the probability of collision was plotted. The previous summaries of this field by Brüche,[7] Darrow,[8] and Ramsauer and Kollath,[9] have reproduced Lenard's original

[5] J. S. Townsend, Phil. Mag. **42**, 873 (1921). J. S. Townsend and V. A. Bailey, Phil. Mag. **43**, 593 (1922); **44**, 1033 (1923); **46**, 657 (1923). H. L. Bröse and E. H. Saayman, Ann. d. Physik **5**, 797 (1930); **7**, 588 (1930).

[6] P. Lenard, Ann. d. Physik, **12**, 714 (1903).

[7] E. Brüche, Ergb. d. exakt Naturwiss. **8**, 185 (1929).

[8] K. K. Darrow, *Electrical Phenomena in Gases* (Williams and Wilkins, 1932).

[9] C. Ramsauer and R. Kollath, Handb. d. Physik **XXII**/2, 243 (1933).

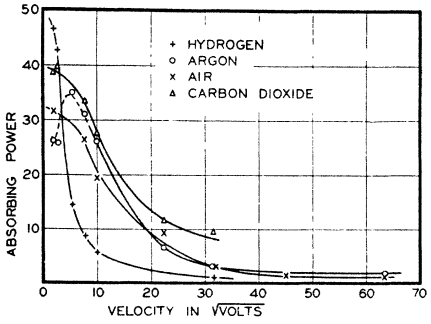

FIG. 4. Absorbing power or probability of collision as a function of electron velocity (Lenard).

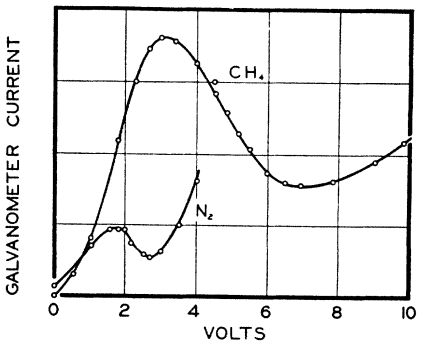

FIG. 5. Qualitative measurement of absorbing power by Akesson.

curve and incorrectly labeled it the probability of collision. Lenard drew his curve for argon at low velocities parallel to the curves for CO_2 and air. The dotted curve is drawn through his observed points and indicates a maximum in argon at low velocity. Lenard[10] in 1895 found that for high velocity electrons the effective cross section for collision of molecules was proportional to the sum of the cross sections of all of the atoms in the molecule. This conclusion of Lenard was further substantiated by the measurements in 1905 by Becker[11] and in 1910 by Silbermann.[12]

6. Åkesson's "selective absorption"

In 1916 Åkesson[13] discovered that the probability of collision did not increase uniformly to a limiting value at low velocities but that most elements showed maxima and minima. Åkesson's measurements were made with an apparatus practically identical with that of Lenard shown in Fig. 3. Åkesson measured the current to the electrometer E as a function of the galvanometer current G. In the absence of gas the current rose rapidly with increasing velocity, to a nearly constant value. If a small amount of gas whose collision cross section was independent of velocity had been introduced, the current to E would have been reduced nearly uniformly. Åkesson measured the current to E and found it to vary as shown in Fig. 5. Åkesson interpreted these minima in the current E as a "*selective absorption*" of the electrons. A maximum absorption or collision cross section would be found when the least current reached the collector, or at approximately 7 volts in CH_4 at 3 volts in N_2. These values have been confirmed by later quantitative measurements of the probability of collision. If Åkesson had compared his curves taken with gas in the apparatus, with curves taken in vacuum, he could have estimated the magnitude of the probability of collision. He was, however, able to make the observation from his data that in many cases "*the slower electrons were more penetrating than the faster.*"

Åkesson's work was criticized by Mayer,[14] who repeated the Lenard experiment and found for H_2, N_2, He, and CO_2 results that agreed with Lenard's conclusions, i.e., a uniform rise to a limiting value for the probability of collision as the velocity approaches zero. It is now known that Mayer's observations on these gases are unreliable, since maxima in the probability of collision curves are found in practically all of the cases indicated by Åkesson's curves.

7. Ramsauer effect

Working at the same time in the same laboratory with Mayer, C. Ramsauer[15] devised a method for measuring the probability of collision for slow electrons. The apparatus is shown in Fig. 6. Ultraviolet light falling on a zinc plate, Z,

[10] P. Lenard, Ann. d. Physik **56**, 274 (1895).
[11] A. Becker, Ann. d. Physik **17**, 381 (1905).
[12] L. Silbermann, Heidelberg Diss. (1910).
[13] N. Åkesson, Lunds. Årsskr N. F. 12, No. 11, p. 29 (1916).
[14] H. F. Mayer, Ann. d. Physik **64**, 451 (1921).
[15] C. Ramsauer, Ann. d. Physik **64**, 513 (1921).

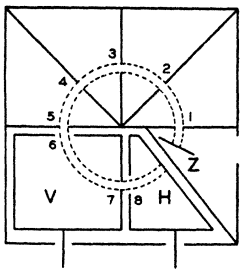

FIG. 6. Ramsauer's apparatus for the measurement of probability of collision.

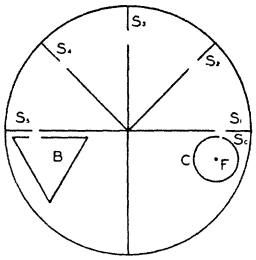

FIG. 7. Brode's apparatus for the measurement of probability of collision.

liberated electrons which were accelerated to the slit 1. A magnetic field normal to the plane of the paper deflected the electrons into a circular path after they had been accelerated. By adjusting the magnetic field the electrons could be sent through the slits 2 to 8. By measuring the current to H and the current to $V+H$, the loss in current in the path between slits 5 and 7 was found and from this the probability of collision was calculated. Electrons that have lost energy but have not had their directions changed are deflected by the magnetic field and do not reach H.

Ramsauer measured only velocities less than one volt and checked the values observed at about one volt by Mayer in H_2, N_2, and He. However in argon he found the remarkably small values of $P_c=2.6$ for 0.75 volt and $P_c=5.5$ for 1.1 volts. After Ramsauer's discovery of this small probability of collision for slow electrons in argon, Mayer measured argon with his apparatus and confirmed Ramsauer's discovery, finding a maximum of $P_c=73$ at 12 volts. Ramsauer[16] subsequently extended his measurements to He, Ne, A, Kr, and Xe. The extremely small probability of collision for slow speed electrons found in A, Kr, and Xe is known as the *Ramsauer effect.*

8. Relation to electronic structure

The close resemblance in shape, and regular variation in size, of the curves for A, Kr, and Xe (Fig. 8) suggested the existence of a relation

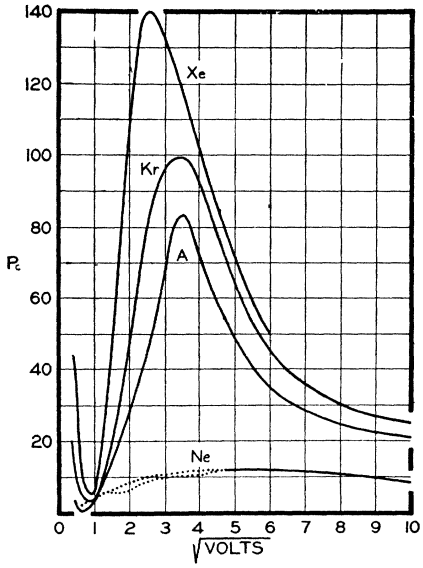

FIG. 8. Probability of collision in Ne, A, Kr and Xe.

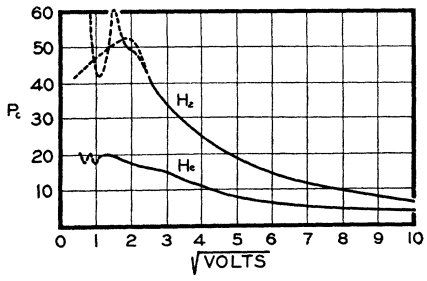

FIG. 9. Probability of collision in H_2 and He.

[16] C. Ramsauer, Ann. d. Physik **66**, 545 (1921); **72**, 345 (1923).

between electronic structure and the probability of collision. Measurements by Brode[17] extended this idea in two ways. The methane molecule, which has 8 external electrons and other properties resembling the noble gases, was found to have curves very much like the noble gas curves. Nitrogen and carbon monoxide, which are isoelectronic molecules, were found to give practically identical curves, a maximum at 19 volts a minimum at 9 volts and then a very rapid rise down to 3 volts. Brüche[18] extended the measurements from 3 volts to 1 volt and found a maximum for both of the gases at about 3 volts. More recent measurements of Normand[19] have shown even a closer identity between the two curves in their fine structure, Fig. 11. Brüche[20] has studied a large number of molecules with related electronic structure and has found consistently a similarity in curves of molecules with similar structure, Figs. 10, 11, and 14.

The remarkable decrease of the cross section for collision of the noble gas atoms as the velocity of the electrons approached zero, was a perplexing problem for the theoretical physicist (see Fig. 15). Rusch[21] was the first to observe a minimum in the curve for argon, at about 0.7 volt. Rusch's measurements were rather qualitative in nature.

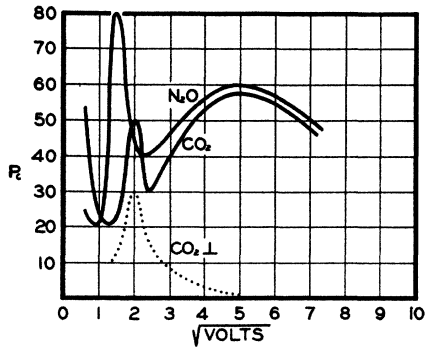

FIG. 10. Probability of collision in N_2O and CO_2. The dotted curve is the probability of scattering in CO_2 at right angles to the electron beam (see Section 17).

[17] R. B. Brode, Phys. Rev. **25**, 636 (1925).

[18] E. Brüche, Ann. d. Physik **81**, 537 (1926); **82**, 912 (1927).

[19] C. E. Normand, Phys. Rev. **35**, 1217 (1930).

[20] E. Brüche, Ergb. d. exakt. Naturwiss. **8**, 185 (1929).

[21] M. Rusch, Phys. Zeits. **26**, 748 (1925).

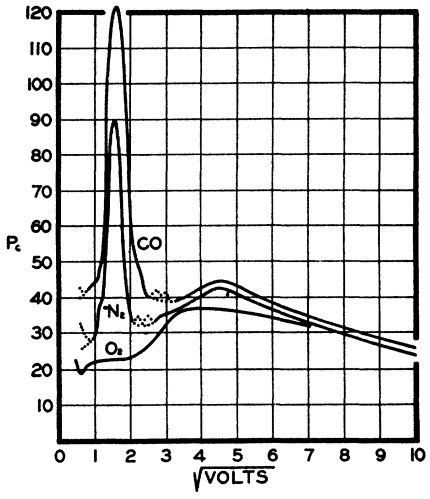

FIG. 11. Probability of collision in CO, N_2 and O_2.

The true course of the curve was found by Ramsauer and Kollath[22] who extended the previous measurements to 0.16 volt. There is a slight uncertainty in the lower voltage limit as measurements published at nearly the same time by Normand[19] give curves with practically identical shape but with a shift of the voltage scale of about 0.4 volt.

The extension of the observations to the monatomic metal vapors has been made largely by Brode.[23] The elements Cd, Zn, and Hg, Fig. 12, show a similarity of structure in their curves as would be expected from their electronic structure. The alkali metals, Fig. 13, are unusual in the large magnitude of the effective cross section. The effective cross section of a caesium atom for a two volt electron is 40 times as large as that of xenon, which is the next atom in the periodic table. The apparatus used for the measurements in metal vapors is shown in Fig. 7. Electrons from the filament F are accelerated to the cylinder C and a part of them go through the slit S_c. As in Ramsauer's arrangement, the electrons are bent by a magnetic field through a

[22] C. Ramsauer and R. Kollath, Ann. d. Physik **3**, 536 (1929).

[23] R. B. Brode, Phys. Rev. **34**, 673 (1929); **35**, 504 (1930); **37**, 570 (1931).

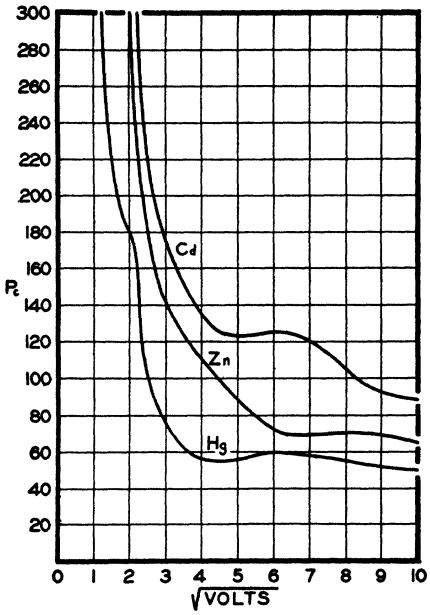

FIG. 12. Probability of collision in Zn, Cd and Hg.

series of slits and into a collector B. The current I_0 starting along the path is assumed to be proportional to the current G leaving the slit S_c; i.e., $I_0 = kG$. With Eq. (5) of Section 4, the probability of collision is found as the slope of $\log G/I$ plotted as a function of the path length x, times the pressure, p. The pressure of the metal vapors was varied by changing the temperature of the apparatus.

9. Summary of measurements

Figs. 8 to 14 give average curves for some of the more common substances. No attempt has been made to correct the observation for the effect of finite slit widths discussed in Section 19. The difference between the average curve and the measurements of individual observers is seldom as large as 10 percent.

For low velocity electrons the potential field of the external electrons is the determining factor for the probability of collision. The similarity of curves for atoms with similar external electron arrangements confirms this idea. The polarizability of the atom or the distortion of the

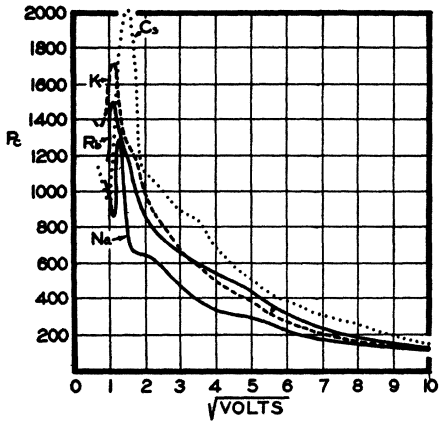

FIG. 13. Probability of collision in Na, K, Rb and Cs.

potential field by the scattered electron also is important. It is difficult to compare the relative magnitudes of the collision cross sections of the atoms when the curves have large variations in maximum and minimum values. At about 100 volts most of the curves are decreasing uniformly. A comparison of the magnitudes of the probability of collision at about 100 volts shows that the monatomic elements have values that are inversely proportional to their ionization potential and directly proportional to their polarizability.

The probability of collision has been studied for the atoms and molecules given in Table I.

TABLE I.

H_2[24, 25, 26]	CO[25, 26, 35]	Cd[31]	C_6H_{12}[40]
He[25, 27, 28]	CO_2[26, 35]	Hg[32]	CH_3OH[40]
Ne[25, 27, 28, 29]	CH_4[26, 36]	Tl[33]	C_2H_5OH[40]
A[25, 27, 28]	C_2H_6[36]	N_2[24, 25, 26]	CH_3F[40]
Kr[27, 28]	C_3H_8[36]	P_4[34]	CH_3NH_2[40]
Xe[27, 28]	C_4H_{10}[36]	As_4[34]	$(CH_3)_2NH$[40]
Na[30]	CH_3Cl[37]	O_2[26, 35]	$(CH_3)_2CH_2$[40]
K[30]	CH_2Cl_2[37]	NO[35]	$(CH_3)_3N$[40]
Rb[30]	$CHCl_3$[37]	N_2O[35, 38]	$(CH_3)_3CH$[40]
Cs[30]	CCl_4[37]	NH_3[39]	HCl[34]
Zn[31]	C_6H_6[37]	H_2O[39]	HCN[40]

[24] E. Brüche, Ann. d. Physik 82, 912 (1927).
[25] C. E. Normand, Phys. Rev. 35, 1217 (1930).
[26] C. Ramsauer and R. Kollath, Ann. d. Physik 4, 91 (1930).
[27] C. Ramsauer, Ann. d. Physik 66, 545 (1921).
[28] C. Ramsauer and R. Kollath, Ann. d. Physik 3, 536 (1929).

C. Probability of Excitation

10. Introduction

The excitation of atoms by electrons can be observed either by studying the energy distribution of the electrons after collision, or by observing the number of excited atoms. The existence of energy loss producing excitation has been known since the experiments of Franck and Hertz.[41] These initial experiments also indicated that some transitions were much easier to excite than others.

The probability of excitation to a particular state is not the same as the probability of emission of a particular spectral line produced by a transition from that excited state. The intensity of radiation corresponding to this transition will be proportional to the number of atoms in this particular state. Some atoms will reach this state by direct electron impart and this number can be calculated from the probability of excitation. Other atoms will reach this state as the result of transitions subsequent to excitation to higher energy states. It may also be possible for the atom to return to a lower state from this excited state by the emission of other spectral lines or by a collision of the second kind. In case the transition is to the normal state of the atom, the radiation that is emitted may be absorbed on its way out of the gas. Because of these complications the optical method does not give very good quantitative data on the probability of excitation.

The probability of excitation can be calculated by observing the number of electrons that have lost a certain amount of energy. This can be observed by applying a retarding potential to the collector and observing the number of electrons that have lost a definite energy. However, if the electrons are not moving normal to the retarding field, they will be kept from the collector by a potential less than that corresponding to their energy loss, and corrections must be made for this effect.

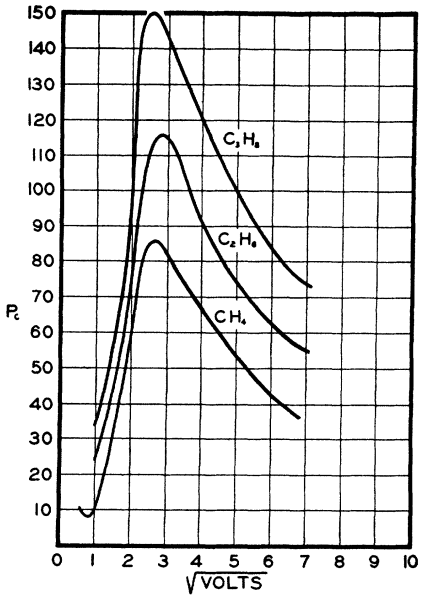

FIG. 14. Probability of collision in CH_4, C_2H_6 and C_3H_8.

As will be seen from the experimental data the probability of excitation may change very rapidly in a few tenths of a volt. For this reason special precautions should be taken to keep the spread of velocities in the beam of electrons as small as possible. A spread of 1.0 volt, as is not uncommon, would badly distort the curves showing changes that take place in a range of a few tenths of a volt.

11. Measurement by electron velocity distribution

As information can be satisfactorily interpreted only for those lines of the spectra which can be excited singly, the range of available material is

[29] E. Brüche, Ann. d. Physik **84**, 279 (1927).
[30] R. B. Brode, Phys. Rev. **34**, 673 (1929).
[31] R. B. Brode, Phys. Rev. **35**, 504 (1930).
[32] R. B. Brode, Proc. Roy. Soc. **A125**, 134 (1929).
[33] R. B. Brode, Phys. Rev. **37**, 570 (1931).
[34] R. B. Brode and M. C. Green, Phys. Rev. **37**, 1760 (1931).
[35] E. Brüche, Ann. d. Physik **83**, 1065 (1927).
[36] E. Brüche, Ann. d. Physik **4**, 387 (1930).
[37] W. Holst and J. Holtsmark, Kong. Norske. Vid. Selskab. 4, No. 25, p. 89 (1931).
[38] C. Ramsauer and R. Kollath, Ann. d. Physik **7**, 176 (1930).
[39] E. Brüche, Ann. d. Physik **1**, 93 (1929).
[40] F. Schmieder, Zeits. f. Elekrochemie **36**, 700 (1930).
[41] J. Franck and G. Hertz, Ber. d. D. Phys. Ges. **16**, 457 (1914).

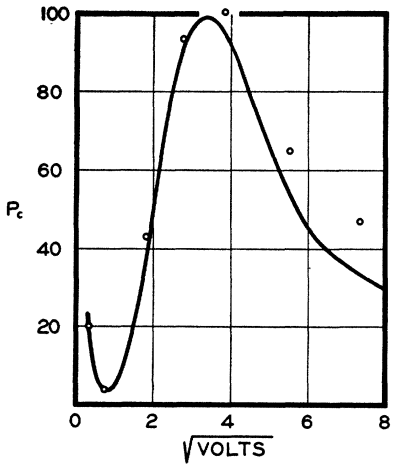

FIG. 15. Probability of collision in Kr (Ramsauer), with points from the theoretical calculations of Holtsmark. See reference 80.

not large. The excitation of mercury has been studied for transitions to the energy level 2^1P_1 and to the group $2^3P_{2,\,1,\,0}$; helium to the 2^3S_1 and potassium to the $2^2P_{\frac{1}{2},\,\frac{3}{2}}$ energy level.

The first measurements by Sponer[42] were made with a simple Franck and Hertz[41] apparatus. Electrons were accelerated through a uniform field to a grid with a plate directly behind the grid. A retarding potential applied between the grid and plate enabled one to measure the number of electrons that had had inelastic collisions. By varying the accelerating potential, the dependence on velocity of the number of inelastic collisions was estimated. From the pressure the number of atoms in the region between the filament and the grid was found and from this the probability of excitation was estimated. The observations of Sponer indicated a maximum probability of excitation at about 6 volts for the excitation to the $2^3P_{2,\,1,\,0}$ group (4.7, 4.9 and 5.4 volts). Because of velocity spread of the beam and other factors, Sponer concluded that the true excitation function may have its maximum at the critical potential and then decrease in an exponential fashion for higher velocities. The magnitude of the probability of excitation was recomputed from Sponer's data by Hertz[43] and found to be about 3 as compared with a probability of collision of 100.

Brattain[44] with an improved apparatus has measured the probability of excitation of the 2^1P_1 level and found a similar result to that of Sponer. The absolute magnitude of the scale shown in Fig. 16 is uncertain. The maximum probability of excitation may be anywhere from 20 to 3, probably between 5 and 15.

Measurements by Dymond[45] on the $1^1S_0-2^3S_1$ helium transition indicated a rise to a maximum P_e/P_{KT} of 0.001 at about 0.3 volt above the 19.77 volt excitation energy. The probability of excitation then dropped off rapidly with increasing voltage. Williamson[46] in studying the inelastic collision of electrons in potassium vapor found that his observations could be explained if one assumed a probability of excitation which rose abruptly to a maximum at the excitation potential and then decreased exponentially. The maximum probability of excitation was about 10 times the probability of collision computed from the kinetic theory. The ratio of the probability of

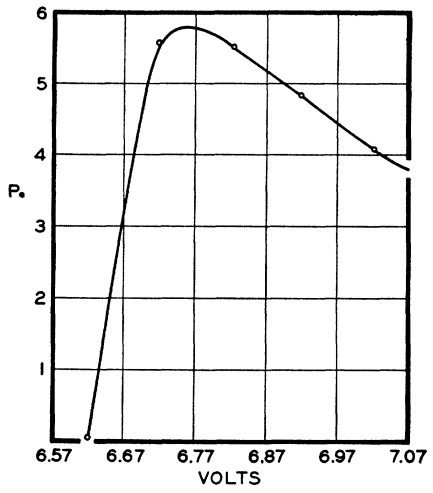

FIG. 16. Probability of excitation of the 2^1P_1 term in mercury (Brattain).

[42] H. Sponer, Zeits. f. Physik **7**, 185 (1921).

[43] G. Hertz, Zeits. f. Physik **32**, 298 (1925).

[44] W. H. Brattain, Phys. Rev. **34**, 474 (1929).

[45] E. G. Dymond, Proc. Roy. Soc. **A167**, 291 (1925).

[46] R. C. Williamson, Phys. Rev. **24**, 134 (1924).

excitation to the probability of collision gives $P_e/P_c=0.13$.

12. Measurement by intensity of spectral lines

The relative intensity of spectral lines excited by electron impact has been studied for a large number of gases and with a considerable range of electron energy. To give information about the probability of excitation, the gas pressure must be so low that the electron after collision will not strike another atom in the region from which light is observed. The velocity spread of the electrons must be as narrow as possible, and the energy of the electron must be less than the next excitation term which can emit the line being studied as a part of the transitions back to the normal state. These conditions limit the spectroscopic study, in general, to the first transitions from the normal state. Many of these transitions emit radiation that is strongly absorbed in the gas. The radiation excited by electron impact is sometimes partially polarized and the intensity is not distributed uniformly in all directions. Particular attention must be paid to the distribution of electron density in the beam if light from only a portion of the beam is focussed on the slit.[47] The intensity of light emitted should be a linear function of the electron current and of the gas pressure.

The experimental arrangement is that indicated in Fig. 1. The light from the beam is focussed on a photo-cell or on the slit of a spectrograph. Allowing for loss of light because of reflection and absorption in the apparatus, the intensity of light emitted by the gas under bombardment can be calculated, and from this can be deduced the number of atoms excited per unit electron current, per unit path length, per unit pressure at 0°C. This is the probability of excitation to the particular energy state being observed.

Fig. 17 shows the relative intensity of the first two lines of the cadmium spectrum as measured by Larché.[48] The line λ3261 rises rapidly and to a maximum and then decreases in much the same way as the measurements by electron energy loss

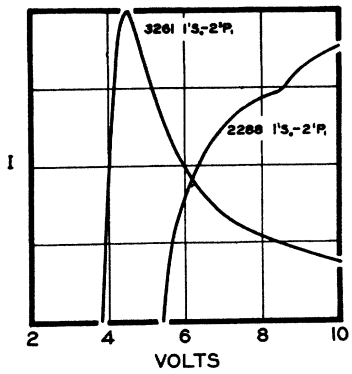

FIG. 17. Probability of excitation of the 2^3P_1 and 2^1P_1 terms in cadmium (Larché).

would indicate. The line λ2288, however, increases to a maximum at a voltage several times the excitation potential. At 6.2 volts the 2^3S_1 level is excited and in the return to the normal state the atom emits the radiation λ3261 so that above 6.2 volts the interpretation of the intensity of the line λ3261 as a measure of the probability of excitation to the state 2^3P_1, is no longer possible. At 6.6 volts the 2^1S_0 state is excited and it contributes to both the λ3261 line and the λ2288 line. At 7.1 and 7.2 volts additional energy states are excited which complicate still further the interpretation of the curves in Fig. 17.

The absolute magnitude of the probability of excitation has not been determined by the spectroscopic methods with any great accuracy. Bricout[49] has estimated that the maximum probability of excitation of the first resonance line in mercury is about 6. Loveridge[50] has measured the absolute magnitude of P_x for sodium and potassium and finds values of 12.5 and 15.6 for the maximum, which in each case is found to be about 1/2 volt above the excitation potential, when corrections have been made for electron velocity distribution. Loveridge's observations for sodium are shown in Fig. 18.

The order of absolute magnitude of the probability of excitation can be estimated from the probability of excitation of a particular spectral line, when it can be assumed that few

[47] J. H. Lees, Proc. Roy. Soc. **A137**, 173 (1932). J. H. Lees and H. W. B. Skinner, Proc. Roy. Soc. **A137**, 186 (1932).

[48] K. Larché, Zeits. f. Physik **67**, 440 (1931).

[49] P. Bricout, J. de Physique et le Radium 9, 88 (1928).

[50] L. E. Loveridge, *Thesis*, University of California, 1931.

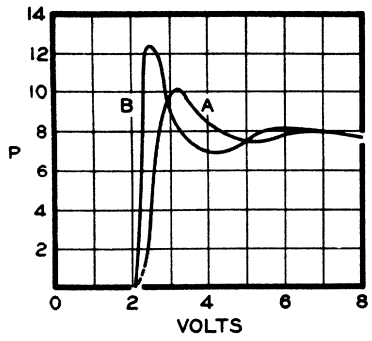

FIG. 18. Probability of excitation of the $2^2P_{\frac{1}{2}}$, $\frac{1}{2}$ terms in sodium (Loveridge). (Curve *A* uncorrected for electron velocity distribution; curve *B* corrected for electron velocity distribution.)

atoms arrive in the upper energy level of the transition except by direct electron impact, and that all or a known fraction of the atoms leave the upper state by emitting the spectral line that is being observed. The λ3889 line in the helium spectrum is such a line. Its excitation function has been studied by Lees and Skinner[47] who found that the probability of emission rose to a maximum a few volts beyond the initial appearance of the line and then fell rather rapidly with increasing voltage. The magnitude of the probability of emission at the maximum was found to be about 0.025 (P_e for the same energy being about 7.5). Hanle and Schaffernicht[51] have observed the probability of emission of a number of visible spectral lines from mercury vapor and found values from 0.054 to 1.800 (P_e for the same energy being about 50).

Michels[52] has found, for all spectral lines that he has studied, a sharp maximum within a volt of the excitation potential. He used an electron beam with a velocity spread of 10 volts and constructed an excitation curve from the observed curves by a process of differentiation. Michel's method assumes a definite maximum velocity in the electron velocity distribution. Actually there may be no definite maximum velocity in the electron distribution and his method of eliminating the velocity distribution may not be applicable.

13. Summary of measurements

The experimental difficulties encountered in the measurement of the probability of excitation have not been sufficiently overcome to make accurate measurements possible. The measurements that have been made indicate that the probability of excitation rises to a maximum either at or very close to the critical potential, and then decreases with increasing energy. The existence of further maxima in the curve is doubtful. The magnitude of the maxima is necessarily less than the probability of collision for the corresponding velocity and may be as small as one-thousandth of the probability of collision as found for the excitation of the 19.77 volt metastable state in helium.

D. Probability of Ionization

14. Measurement of efficiency of ionization

Of the collision phenomena discussed in this paper the probability of ionization P_i is the easiest to define and to measure experimentally. The experimental arrangement is given essentially in Fig. 1. To obtain quantitative results the pressure of gas must be so low that no electron will make a second collision after it has lost some of its energy. The electron beam density must be low enough to prevent space charge from altering the velocity of the electrons and to prevent ionization by processes involving more than one electron impact. The potential applied to remove the positive ions must be large enough to draw the positive ions to the collector before recombination or cumulative ionization takes place, but must be small enough so that it will not appreciably disturb the electron beam. The current to the positive ion collector is primarily a measure of the total positive charge liberated by the electrons. However, electrons released by photoelectric action of radiation from the beam will be measured as positive current. Electrons may also be released by the action of metastable atoms in giving up their energy to the surface of the collector. Electrons scattered in the gas may also reach the collector and neutralize some of the positive ion current.

[51] W. Hanle and W. Schaffernicht, Ann. d. Physik **6**, 905 (1930).

[52] W. C. Michels, Phys. Rev. **36**, 1362 (1930); **38**, 712 (1931).

Compton and Van Voorhis[53] used a system of fine wires on which to collect the positive ions, Fig. 19. The small area of the collector reduced greatly the effect of photo-emission, metastable atoms, etc. The electric field in the ionizing

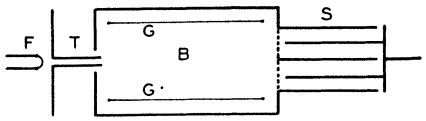

FIG. 19. Apparatus for the measurement of efficiency of ionization (Compton and Van Voorhis).

chamber was distorted by the collector wires and its effect on the velocity of the electrons was included as a correction to the measurements.

The use of a magnetic field parallel to the electron beam was suggested by Tate.[54] A sufficiently strong magnetic field will keep all scattered electrons concentrated in spirals around the original beam and will prevent the emission of slow electrons from the metal collector. The heavier positive ions will not be appreciably affected by the magnetic field and will be drawn to the collecting electrode by a small electric field.

In general the results of the different observers are in fair agreement (Fig. 20). The early observations and those indicated in Figs. 20 and 21 represent the efficiency of ionization, i.e., total positive ion current, rather than the probability of ionization. Exceptions to the general agreement are the measurements of von Hippel[55] and of Funk.[56] Both of these observers find a sharp maximum in the curve at about twice the ionization potential.

15. Measurement of probability of ionization

It is only possible to compute the probability of ionization when the relative number of multiply charged ions is known. The efficiency of ionization, E_i, is related to the probabilities of single and multiple ionizations, P_{1i}, P_{2i}, P_{3i}, etc., by the relation $E_i = 1P_{1i} + 2P_{2i} + 3P_{3i} \cdots$. Bleakney[57] has measured the relative abundance

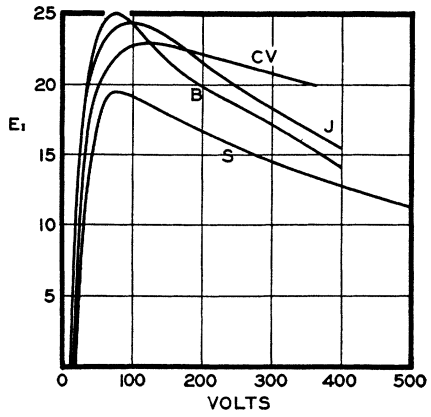

FIG. 20. Efficiency of ionization in mercury (*CV*, Compton and Van Voorhis; *J*, Jones; *B*, Bleakney; and *S*, Smith).

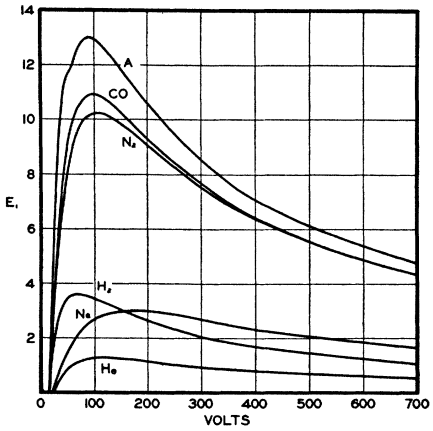

FIG. 21. Efficiency of ionization in He, Ne, A, N_2, CO and H_2 (Smith).

of ions of multiple charge. A cross section of his apparatus is shown in Fig. 22. In principle the ionization chamber is the same as in Fig. 1. Some of the ions, however, pass through the slot in the plate *B*, and are acted on by the field of the condenser *C–D* and by the magnetic field which is parallel to the electron stream and normal to the plane of the figure. By adjustment of the electric field in the condenser *C–D* ions of different charge can be directed through the slot in *L* to the collector *K*.

[53] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925); **27**, 724 (1926).
[54] T. J. Jones, Phys. Rev. **29**, 822 (1927).
[55] A. von Hippel, Ann. d. Physik **87**, 1035 (1928).
[56] H. Funk, Ann. d. Physik **4**, 149 (1930).

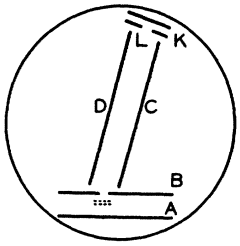

FIG. 22. Cross section of Bleakney's apparatus for the measurement of probability of ionization.

The percent of the total positive ion current due to the different ions in mercury is shown in Fig. 23. From the total positive ion current the probability of ionization of different degrees can

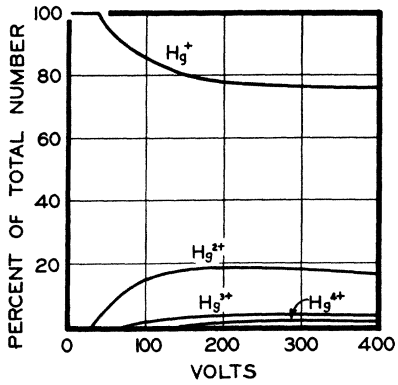

FIG. 23. Percent of Hg^+, Hg^{2+}, Hg^{3+}, and Hg^{4+} ions in mercury (Bleakney).

be calculated as shown in Fig. 24. The efficiency of ionization has been measured in

H_2[61, 59, 53]	N_2[61, 63]	C_2H_2[61]
He[60, 53, 62]	CO[61, 63]	HCl[53]
Ne[60, 53, 62]	O_2[61]	Hg[53, 54, 57, 58, 62]
A[60, 53, 62]	NO[61]	

[57] W. Bleakney, Phys. Rev. **34**. 157 (1929); **35**, 139 (1930); **36**, 1303 (1930).
[58] P. T. Smith, Phys. Rev. **37**, 808 (1931).
[59] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[60] P. T. Smith, Phys. Rev. **36**, 1293 (1930).
[61] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).
[62] A. L. Hughes and E. Klein, Phys. Rev. **23**, 450 (1924).
[63] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

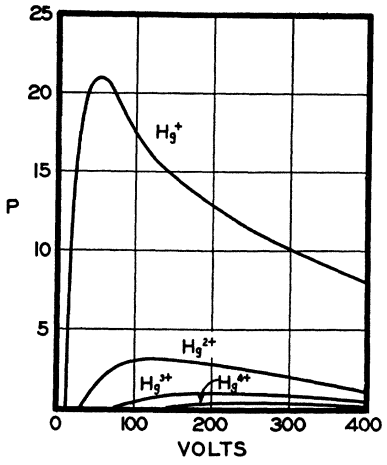

FIG. 24. Probability of ionization in mercury (Bleakney). If the data of Smith for the efficiency of ionization are used, these values should be reduced about 25 percent.

The information necessary for the calculation of the probability of ionization has been observed for

Hg^{57}	Ne^{64}
He^{64}	A^{64}

In the study of diatomic or polyatomic molecules the process of ionization is complicated by the possibility of dissociation. The process of the dissociation has been shown to impart to the ions an appreciable kinetic energy.[65, 66] In addition the ion or the atom (or both) may be either excited or ionized in various degrees.

16. Fine structure and magnitude of probability of ionization

As in the study of the probability of excitation, it is only possible to observe the true variation of the probability, in the immediate neighborhood of the critical potential, when the velocity distribution in the electron beam is made very small. Lawrence[67] used a magnetic resolution of electron velocities before the beam entered the ionizing chamber. He found that the relative

[64] W. Bleakney, Phys. Rev. **36**, 1303 (1930).
[65] W. Bleakney, Phys. Rev. **35**, 1180 (1930); **40**, 496 (1932).
[66] W. W. Lozier, Phys. Rev. **36**, 1285 (1930).
[67] E. O. Lawrence, Phys. Rev. **28**, 947 (1926).

probability of ionization that would explain his observations was a curve of the type shown in Fig. 25, a sudden rise at the critical potential to the maximum probability followed by an exponential decrease. Lawrence also found that

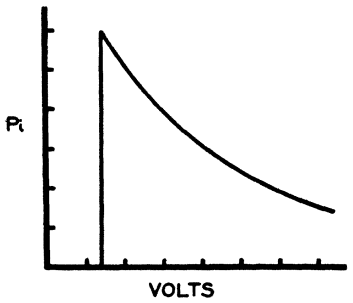

FIG. 25. Probability of ionization near the ionization potential (Lawrence).

there were a number of critical potentials above the 10.4 ionization potential. Smith[58] found 12 critical potentials in the first two volts above the ionization potential. With a very homogeneous electron beam the probability of ionization would appear as in Fig. 26, while with a broad velocity

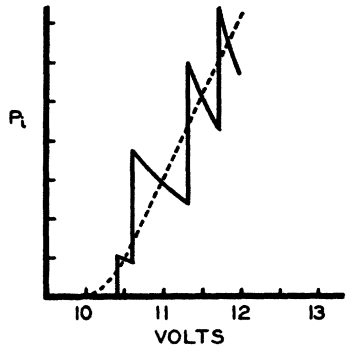

FIG. 26. Ultra-ionization potentials of mercury (Lawrence). The dotted curve shows the results to be expected from measurements with a broad velocity distribution.

distribution the dotted curve would be observed. Moderate distribution would give evidence of the ultra-ionization potentials by changes in the slope of the curve.

The magnitude of the probability of ionization agrees with the probability of collision. Fig. 27 shows the probability of collision and the probability of ionization for mercury. The probability of collision has not been corrected for the finite slit widths of the measuring apparatus and therefore may be from 10 to 20 percent too small. The maximum in the curve is apparently due to the contribution of increased probability of ionization. A large proportion of the collisions of high velocity electrons result in ionization of the mercury atom.

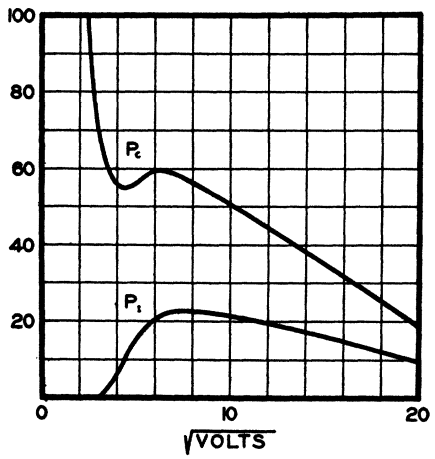

FIG. 27. Probability of collision and ionization in mercury (Brode and Bleakney).

E. PROBABILITY OF SCATTERING

17. Measurement of scattering

The existence of elastic reflection of electrons from atoms of a gas with a change of direction but negligible loss of energy was established as early as 1913 by Franck and Hertz.[68] The direction of reflection and the volume of gas effective in scattering were not sharply defined in this experiment. A more quantitative study of the scattering at right angles to the original electron beam was made by Kollath,[69] whose apparatus is shown in Fig. 28. A beam of electrons

[68] J. Franck and G. Hertz, Ber. d. D. Phys. Ges. 15, 373 (1913).

[69] R. Kollath, Ann. d. Physik 87, 259 (1928).

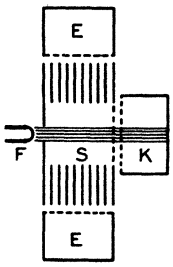

FIG. 28. Kollath's apparatus for the measurement of right-angle scattering.

passes through the space S into the collector K. Those electrons that are scattered through 90 degrees may pass between the plates and reach the collector E. Fig. 10 shows the comparison between the current scattered through right angles and the total scattered current in CO_2. At higher velocities the intensity of the right angle scattered current dropped rapidly to a very small fraction of the total scattered current. Werner[70] has also used a similar arrangement for the study of right angle scattering.

The most important measurements of the scattering of slow electrons have been made with an apparatus first used by Dymond,[71] Fig. 2. A beam of electrons from a source F passes through a space filled with gas at a low pressure. A set of slits S_2 and S_3 in front of the collecting cylinder, C, define a volume in space in which electrons can be scattered into the collector, provided their direction of motion is through the slits S_2, S_3. The velocity distribution of the electrons entering C can be analyzed by either a magnetic field, an electrostatic field, or a retarding potential.

The principal difficulty with this apparatus is the proper determination of the effective volume of scattering and the effective solid angle of the aperture defined by S_2 and S_3 as seen from various points in the beam. As pointed out by Tate and Palmer[72] retarding potentials that penetrate into the region of the defining slits, will have a large influence on the effective dimensions of the apparatus.

Let A be the distance of the slit S_2 from the center of intersection of the axis of the collecting slit system and the axis of the parallel electron beam; B the distance of the slit S_3; a and b the widths of the slits S_2 and S_3, respectively; h the height of the slit S_2; and θ the angle between the slit axis and the electron beam. If ω is the solid angle of the aperture as measured from any point in the electron beam, and dx is an element of length along the electron beam, then[73]

$$\int \omega dx = abh/[A(A-B)\sin\theta].$$

This expression assumes that the height of the first slit determines the limiting deflection in the direction perpendicular to the plane of the paper. If the rear slit is the limiting factor, the equation is slightly different. This equation also breaks down at small angles as will be seen from the complications arising when one of the limiting lines drawn through the slits S_2, S_3, becomes parallel to the electron beam. Throughout most of the angle range used in the experiments the approximation is sufficiently exact. If the apparatus is not properly centered so that the distances A and B are also functions of the angle θ, further complications will be introduced. The scattered current per unit current, per unit path length, per unit pressure at 0°C, per unit solid angle in the direction θ, is the probability of scattering, S, or $S=I_\theta/(I_0 p\int\omega dx)$. Because of these difficulties in determining the geometrical constants, many of the experimenters have simply divided their observed current by the initial current times the pressure, times the sine of the angle, and taken this as a measure of S in arbitrary units. Arnot[74] reduced his observations to absolute units by estimating his solid angles, but seems to have made a slight mistake in the definition of his effective scattering region. Tate and Palmer[72] used the relation, Eq. (3), between the probability of scattering and the probability of collision to evaluate the arbitrary constant. Figs. 29, 30, and 31 give some of the experimental results by this method.

[70] S. Werner, Proc. Roy. Soc. **A134**, 202 (1931).
[71] E. G. Dymond, Phys. Rev. **29**, 433 (1927).
[72] J. T. Tate and R. R. Palmer, Phys. Rev. **40**, 731 (1932).
[73] E. B. Jordan and R. B. Brode, Phys. Rev. **43**, 112 (1933).

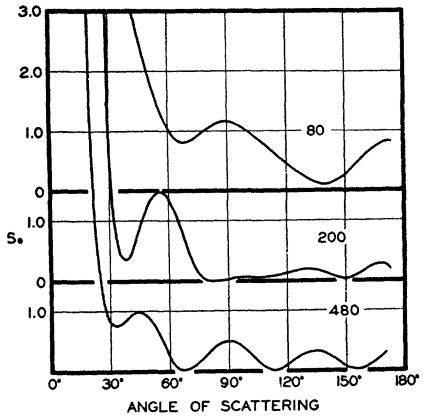

FIG. 29. Probability of elastic scattering in mercury. (Average curves from data of Arnot,[74, 75] Pearson and Arnquist,[76] Tate and Palmer[72] and Jordan and Brode.[73])

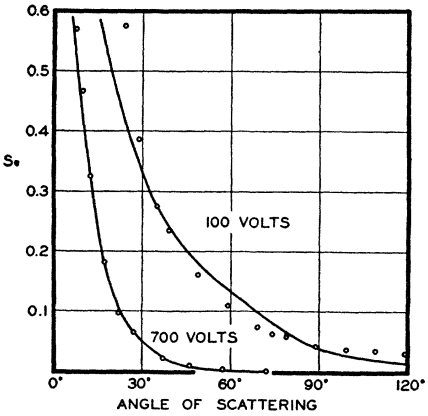

FIG. 30. Probability of elastic scattering in helium. The observed points are shown together with the theoretical curves calculated from the theory of Mott[78] (Hughes, McMillen and Webb[77]).

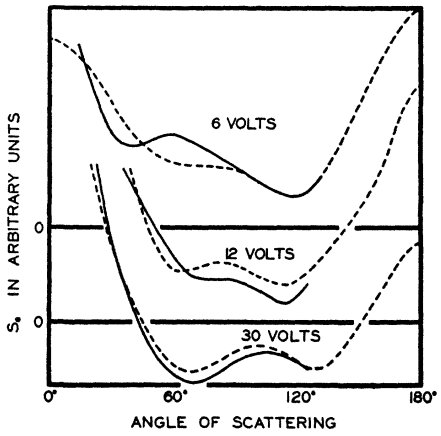

FIG. 31. Probability of scattering in argon. The dashed curve is the theoretical calculation after the method of Holtsmark[80] (Bullard and Massey[79]).

Ramsauer and Kollath[81] devised a system of zonal collectors for the study of the scattering at low velocities, Fig. 32. With this apparatus they have obtained measurements at velocities below one volt. The evaluation of the effective scattering region for each zone was estimated graphically. A typical curve is shown in Fig. 33 for elastic scattering.

For many studies the scattering in small angles from the original direction of the beam is quite

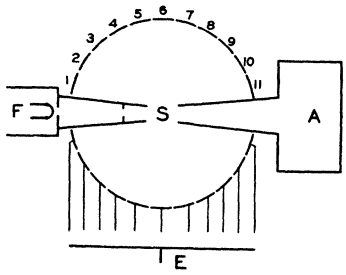

FIG. 32. Zonal apparatus for the measurement of probability of scattering (Ramsauer and Kollath).

[74] F. L. Arnot, Proc. Roy. Soc. **A125**, 660 (1929); **A130**, 655 (1931).

[75] F. L. Arnot, Proc. Roy. Soc. **A140**, 334 (1933).

[76] J. M. Pearson and W. N. Arnquist, Phys. Rev. **37**, 970 (1931).

[77] A. L. Hughes, J. H. McMillen and G. M. Webb, Phys. Rev. **41**, 154 (1932).

[78] N. F. Mott, Proc. Roy. Soc. **A125**, 222 (1929).

[79] E. C. Bullard and H. S. W. Massey, Proc. Roy. Soc. **A133**, 647 (1931).

[80] J. Holtsmark, Zeits. f. Physik **55**, 437 (1929); **66**, 49 (1930).

[81] C. Ramsauer and R. Kollath, Ann. d. Physik **12**, 529 and 837 (1932).

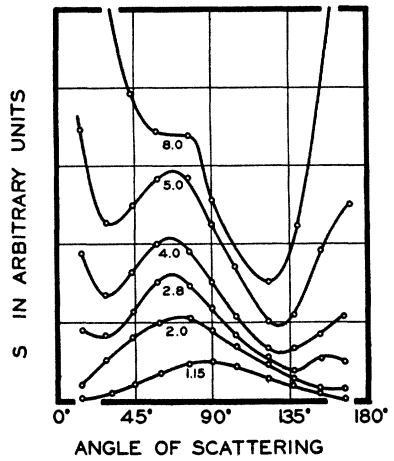

FIG. 33. Probability of scattering in argon (Ramsauer and Kollath).

important. The scattering of high speed electrons in small angles gives sufficient information to estimate the potential field or the form factor of the scattering atom. By choosing a suitable form factor for the scattering atom, the curve for the electron scattering obtained agrees with the experimental observations. Figs. 30 and 31 show the results of such calculations. The theoretical study of this problem has been reviewed by Morse[82] and by Condon[83] in a recent number of this journal. The maximum and minimum are explained as the diffraction of the electron waves by the potential field of the atom.

18. Inelastic scattering

By applying a retarding potential between the collector and a slit or grid in front of it, or by other electric or magnetic velocity analyzers, the apparatus for the study of the scattering of electrons, Fig. 2, can be used to investigate the probability of excitation. Eq. (1) gives the relation between the probability of excitation and the observed scattered currents. This method has been used by Tate and Palmer,[72] Fig. 34, for the measurement of the excitation of mercury vapor with electrons of from 80 to 700 volts. Most of the losses of energy, counted as producing excitation, corresponded to the 6.7 volt excitation. The value of P_x is found to be a little large, compared with Brattain's[44] observations. However, Brattain's measurements are somewhat uncertain, and Tate and Palmer's values of the probability of ionization are a little large when compared with the more direct measurements of Smith[58] and Bleakney.[57]

A number of observers[71, 72, 77, 84, 85, 86] have studied the angular distribution of inelastically scattered electrons, but have either covered only a small angle range or have given their data in arbitrary units, so that Eq. (3) cannot be used to calculate the probability of excitation.

Mohr and Nicoll[86] have recently shown that the angular distribution curves of the inelastically scattered electrons in H_2, CO_2, N_2, Ne, He, A, and Hg for velocities of about 50 volts show the same type of maxima and minima in their distribution as the elastically scattered electrons, Fig. 35.

19. Correction of probability of collision for finite aperture

The influence of the size of the defining apertures on the value of the probability of

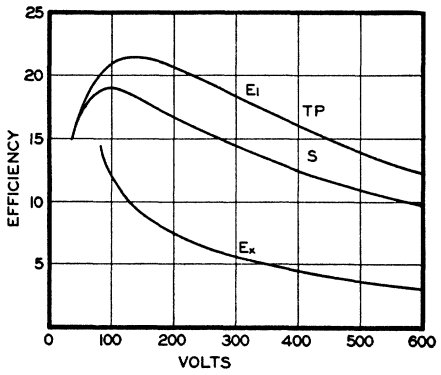

FIG. 34. Efficiency of excitation and ionization in mercury (*TP*, Tate and Palmer; *S*, Smith).

[82] P. Morse, Rev. Mod. Phys. **4**, 577 (1932).
[83] E. U. Condon, Rev. Mod. Phys. **3**, 43 (1931).
[84] A. L. Hughes and J. H. McMillen, Phys. Rev. **39**, 585 (1932); **41**, 39 (1932). J. H. McMillen, Phys. Rev. **36**, 1034 (1930).
[85] G. P. Harnwell, Phys. Rev. **34**, 661 (1929).
[86] C. B. O. Mohr and F. H. Nicoll, Proc. Roy. Soc. **A138**, 229 and 469 (1932).

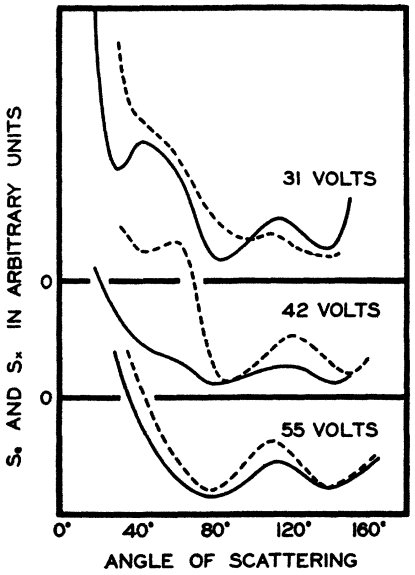

FIG. 35. Probability of elastic scattering (solid curves) and probability of scattering with excitation (dashed curves) in mercury (Mohr and Nicoll).

collision has been investigated by Green[87] and by Palmer.[88] Green's measurements gave practically no variation in the probability of collision with the size of aperture. These measurements were shown to be unreliable by Palmer, who pointed out the importance of the ionization in the region where retarding potentials were applied. Palmer's measurements indicated a variation with effective aperture which he has subsequently checked with calculations from angular distribution curves.

The apparatus used by Palmer is shown in Fig. 36. The distance between S_1 and S_2 is l, the path length; r is the radius of the circular aperture S_2. The limiting angle for a deflection along the axis is given by $\tan\theta_0=r/l$. If I_0 is the current entering S_1, I the current entering S_2, and I' the difference between I_0 and I, at low pressures $P_c'lp=I'/I_0$ where P_c' is the observed probability of collision.

The number of electrons scattered to the collector A is given by the equation

$$I'=I_0\left(\int_{\theta_0}^{\pi}2\pi(l-r/\tan\theta)S\sin\theta d\theta-lE_i\right).$$

The term, $-lE_i$, is due to the positive ions formed in the gas and assumes that the number of ions leaving A for B is the same as the number leaving B for A. If a retarding potential is applied between B and A this will not be true. The effect of the aperture on the value of P_c is shown in Fig. 37. The influence is more marked at high electron velocities. Moreover mercury shows a greater change with angle than helium. The crosses indicate the values calculated from the data of Tate and Palmer[89] and of Smith.[90] The values of the probability of collision calculated by Palmer for an apparatus with negligibly small limiting angle θ_0 are about 40 percent greater than the values obtained by Brode with finite slits. The efficiency of ionization E_i obtained by Palmer is about 20 percent higher than that observed by Smith.

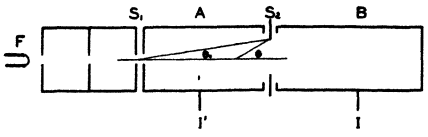

FIG. 36. Palmer's apparatus for the measurement of the influence of the size of the collecting aperture on the probability of collision.

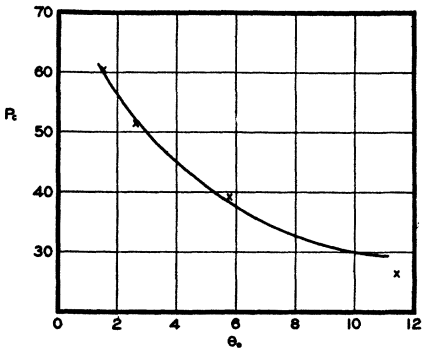

FIG. 37. Probability of collision as a function of the limiting angle, θ_0 (Palmer).

[87] M. C. Green, Phys. Rev. 36, 239 (1930).
[88] R. R. Palmer, Phys. Rev. 37, 70 (1931).
[89] J. T. Tate and R. R. Palmer, Phys. Rev. 40, 731 (1932).
[90] P. T. Smith, Phys. Rev. 37, 808 (1931).

If two collecting chambers are placed in series as shown in Ramsauer's apparatus, Fig. 6, the influence of the aperture openings will be reduced. If the geometry of the defining slits at the opening to the two chambers is the same and if the current entering each slit is the same, then, due to the finite slit width, as many electrons will be scattered into the collector as are scattered out from it at the other end, and the probability of collision will be observed as for infinitesimal slit widths. In the actual experiment, however, the accuracy of the measurement depends on an appreciable loss of electrons in the first chamber. It is not infrequent that ½ to ¾ of the electrons entering the first chamber are collected by it and in this case a correction for the finite slit width must be applied. For a loss of ¾ of the electrons to the first chamber, the correction would be about ¾ of the correction to be applied to the single chamber measurements, Fig. 37.

F. Theoretical Interpretation

The theoretical calculation of the probability of scattering, collision, ionization or excitation is a very difficult problem. A considerable amount of information about the atom is needed before the problem can be set up. The potential field of the atom in the normal and excited states and the orientation of the field must be known. The potential field is a function of the disturbance or polarization caused by the colliding electron. This polarization is a function of the time and not readily calculable for even the simplest atoms. For the range of velocities used in the experiments of this summary, the wave-length associated with the electron varies from 0.5 to 20×10^{-8} cm. This is just the order of magnitude of atomic dimensions so that only a wave mechanical treatment can be expected to give the correct solution. Another effect that must also be taken into account arises from the identity of all electrons. The electron sent at the atom may not be the same as the one leaving the atom. If ionization takes place the impacting electron and the emitted electron cannot be distinguished from each other.

An exact solution of the collision problem for even the simplest atom, monatomic hydrogen, is not possible at present. An approximate solution for an idealized atom can be obtained by a method given by Born.[91] The amplitude of the electron wave scattered from any volume element is proportional to the amplitude of the electron wave incident on the volume element and to the potential of the volume element. The scattered wave consists of a system of spherical waves sent out from the volume element. In Born's calculation, and in the work of Mensing,[92] Elsasser,[93] and Wentzel,[94] the subsequent scattering of the scattered wave on other elements of volume has been neglected. In the calculations of Faxen and Holtzmark,[95] Allis and Morse,[96] and Massey and Mohr,[97] this subsequent scattering has not been neglected. The intensity of the scattered electrons at any point in space is obtained by integrating the amplitude of the scattered wave arriving at that point from all the elements of volume of the scattering atom, and then multiplying this by its conjugate value. Because the amplitude is a complex function of the distance and angle from the scattering atom, this calculation brings in the effects of interference.

The incident electron beam can be considered as a plane wave whose amplitude is given by the equation $\psi=e^{ikz}$; where $k=2\pi/\lambda$. The time dependence, $e^{2\pi i\nu t}$ has here been separated from the part dependent on the space coordinates. In a potential field the amplitude of the electron waves must satisfy the equation $\nabla^2\psi+(8\pi^2m/h^2)\times(E-V)=0$. If the potential is zero the solution of this equation is e^{ikz}, where $k^2=8\pi^2mE/h^2=4\pi^2/\lambda^2$ (m is the mass of the electron, E is its kinetic energy, V is its potential energy and λ the de Broglie wave-length associated with the electron). This is the equation for the amplitude of a plane wave propagated in the direction z. The existence of a potential due to the scattering center requires a solution that can be approximated by a system of spherical waves sent out

[91] M. Born, Gött. Nach. p. 146 (1926); Zeits. f. Physik 38, 803 (1926).
[92] L. Mensing, Zeits. f. Physik 45, 603 (1927).
[93] W. Elsasser, Zeits. f. Physik 45, 522 (1927).
[94] G. Wentzel, Zeits. f. Physik 40, 590 (1926).
[95] H. Faxen and J. Holtsmark, Zeits. f. Physik 45, 307 (1927).
[96] W. P. Allis and P. M. Morse, Zeits. f. Physik 70, 567 (1931).
[97] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A132, 605 (1931).

from all parts of the scattering atom, and a plane wave moving in the direction of the original electron beam. This solution of the wave equation can be written in the form

$$\psi = e^{ikz} + \int f(e^{ikr}/r)dv + \int g(e^{ikr}/r)dv.$$

Here f is a function of the angle of scattering and depends on the potential field of the atom and on the amplitude of the electron beam at the point of scattering. g is a similar function that represents electrons originally a part of the atom which, through an exchange of energy with an electron in the initial beam, are knocked out of the atom. These functions f and g are also functions of the state of excitation or ionization of the atom. Due to the antisymmetrical nature of the electrons the scattered intensity is not given by the magnitude $|f|^2+|g|^2$, but as Oppenheimer[98] has shown, by the expression $\frac{1}{4}(3|f-g|^2+|f+g|^2)$.

For the collisions of high velocity electrons this exchange phenomenon, and the distortion of the potential field by polarization, are less important. A good approximation can be obtained by assuming a potential field for the atom and by neglecting polarization and exchange. Mott,[99] using the method of Born, has derived a general scattering formula for electrons that is valid for electrons with energies above 15 Z^2 volts. Z is the nuclear charge of the scattering atom. A comparison between Mott's theoretical curve and the experimental scattering data is shown in Fig. 30. The magnitudes of the theoretical curves have arbitrarily been adjusted so as to agree with the experimental data at one point.

By modifying the potential field assumed for the atom one can introduce a correction for the polarization of the atom. Holtzmark[100] has done this for argon and krypton and by numerical integration obtained curves for the probability of collision of these atoms that agree remarkably well with the observed curves (Fig. 15). These calculations show that the Ramsauer effect can be explained as a natural physical phenomenon due to the wave properties of the electrons. Bullard and Massey[101] have used the data of Holtzmark to calculate the angular distribution of the scattered electrons in argon and have found quite good agreement as shown in Fig. 31. Henneberg[102] has calculated the angular distribution of the electrons scattered by mercury and has also obtained quite good agreement with the observed scattering.

The method of numerical integration is very laborious. By assuming a potential field for the atom that is a simple function of the atomic radius, it is possible to solve the wave equation and get a more analytic expression for the probability of collision. This method has been used by Mensing[92] and by Allis and Morse.[96] The calculations by the latter give surprisingly good agreement in shape and magnitude for the curves of the probability of collision of a large number of elements. The calculation of the probability of ionization and excitation is more difficult than the calculation of the probability of elastic collision. Massey and Mohr[97] have, however, calculated the probability of excitation of hydrogen and helium and have obtained curves that are in quantitative agreement with the experimental curves.

G. Summary

In this survey the more direct experiments that give us quantitative information about the probabilities of collision, excitation, ionization and scattering, have been described. The probability of collision was found to depend on the velocity of the electron and on the potential field of the atom. The probability of collision for high velocity electrons decreases uniformly with increasing velocity. The magnitude of the probability of collision with different atoms is proportional to the atomic number of the element for high velocity electrons. For slow electrons, similar curves for the variation of the probability of collision with electron velocity were obtained, when atoms or molecules with similar external electronic structure were studied. The probability of collision for slow electrons is often found to

[98] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[99] N. F. Mott, Proc. Roy. Soc. **A124**, 425 (1929); **A125**, 222 (1929); **A127**, 658 (1930). Proc. Camb. Phil. Soc. **24**, 304 (1929).

[100] J. Holtsmark, Zeits. f. Physik **48**, 231 (1928); **52**, 485 (1928); **55**, 437 (1929); **66**, 49 (1930).

[101] E. C. Bullard and H. S. W. Massey, Proc. Roy. Soc. **A133**, 647 (1931).

[102] W. Henneberg, Zeits. f. Physik **83**, 555 (1933)

change by a factor of from 2 to 10 in the range of a few volts. The theoretical solution of the problem has been obtained by considering the diffraction of the electron wave by the potential field of the atom. The theoretical calculations are in good agreement with the experimental results.

When an elastic sphere is bombarded by particles, the intensity of scattering per unit solid angle is equal in all directions. This simple model is quite insufficient to explain the many maxima and minima found in the observed scattering curves. However, the wave mechanics has been able to explain quite completely the observed curves. The scattering can be considered to be somewhat similar to the diffraction of light by particles that are of the same order of magnitude as the wave-length of the light.

The probability of ionization can be considered as a probability of excitation to a state where one of the electrons of the atom acquires sufficient energy to escape from the potential field of the atom. The shape of the probability of excitation and the probability of ionization curves is similar. They indicate a rapid rise to a maximum at or near the critical potential, followed by a more gradual decrease. If there are a large number of critical potentials close together, and if there is a spread in the electron velocities in the exciting beam, the curve will rise more gradually to a maximum. The observed curves can be explained in this way.

More extensive surveys have been published for some of the fields discussed in this paper. Additional experimental details and results of measurements can be obtained from the following surveys:

E. Brüche, Ergb. d. exakt. Naturwiss. **8**, 185 (1929). (*Probability of collision.*)

K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930); **3**, 191 (1931). (*Probability of collision, excitation, ionization and scattering.*)

E. U. Condon, Rev. Mod. Phys. **3**, 43 (1931).

K. K. Darrow, "*Electrical Phenomena in Gases*" (Williams and Wilkins, 1932). (*Probability of collision, excitation, ionization and scattering.*)

W. de Groot and F. M. Penning, Handb. d. Physik **XXIII**/1, 23 (1933). (*Probability of excitation and ionization.*)

W. Hanle and K. Larché, Ergb. d. exakt. Naturwiss. **10**, 285 (1931). (*Probability of excitation.*)

P. M. Morse, Rev. Mod. Phys. **4**, 577 (1932). (*Theoretical.*)

C. Ramsauer and R. Kollath, Handb. d. Physik **XXII**/2, 243 (1933). (*Probability of collision and scattering.*)

H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931). (*Probability of ionization.*)