which, for our purposes, is more conveniently expressed as

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{L^2}{r^2}+k^2\right)\mathbf{\Phi}=0,$$

employing Eq. (40a) of the text. All three possible types of radial functions associated with a given orbital angular momentum l thus satisfy the differential equation

$$\left\{\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+k^2-\frac{l(l+1)}{r^2}\right\}f_l(r)=0. \tag{A18}$$

The solution $\mathbf{\Phi}_j$ for $l=j$ (or more exactly the real part of $\mathbf{\Phi}_j e^{-ikct}$):

$$\mathbf{\Phi}_j=\mathbf{L}f_j(r)P_j{}^m$$

represents a transverse wave field ($\nabla\cdot\mathbf{\Phi}_j=0$) which is to be identified as the vector potential describing the radiation emitted by a magnetic multipole of order $2j$. Appropriate linear combinations of the solutions for $l=j\pm1$

$$\mathbf{\Phi}_{j+1}=\{(j+1)(\mathbf{r}/r)+i((\mathbf{r}/r)\times\mathbf{L})\}f_{j+1}P_j{}^m,$$
$$\mathbf{\Phi}_{j-1}=\{-j(\mathbf{r}/r)+i((\mathbf{r}/r)\times\mathbf{L})\}f_{j-1}P_j{}^m,$$

may be found to represent the longitudinal and transverse parts of the vector potential associated with an electric multipole of order $2j$. Using the recursion relations

$$f_{j+1}+f_{j-1}=(2j+1/kr)f_j, \tag{A19}$$
$$(j+1)f_{j+1}-jf_{j-1}=-(2j+1/k)(d/dr)f_j,$$

one may verify that

$$\mathbf{\Phi}_1=\mathbf{\Phi}_{j+1}+\mathbf{\Phi}_{j-1}=-\frac{2j+1}{k}\left\{\frac{\mathbf{r}}{r}\frac{d}{dr}f_j-i\frac{\mathbf{r}\times\mathbf{L}}{r^2}f_j\right\}P_j{}^m \tag{A20}$$
$$=-(2j+1/k)\nabla f_jP_j{}^m,$$

by Eq. (40) of the text. Similarly

$$\mathbf{\Phi}_2=\frac{j}{2j+1}\mathbf{\Phi}_{j+1}-\frac{j+1}{2j+1}\mathbf{\Phi}_{j-1}$$
$$=\left\{\frac{j(j+1)}{kr}\frac{\mathbf{r}}{r}f_j-i\frac{\mathbf{r}\times\mathbf{L}}{r}\frac{1}{kr}\frac{d}{dr}(rf_j)\right\}P_j{}^m \tag{A21}$$
$$=-(i/k)\nabla\times(\mathbf{L}f_jP_j{}^m).$$

These functions therefore satisfy

$$\nabla\times\mathbf{\Phi}_1=0,\quad \nabla\cdot\mathbf{\Phi}_2=0,$$

and are thus to be identified as the longitudinal and transverse fields of an electric $2j$-pole.

DECEMBER 1, 1940 PHYSICAL REVIEW VOLUME 58

On the Theory of Recombination

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(Received October 5, 1940)

In Section I a general formula for α, the coefficient of recombination of ions in gases, is developed. It covers all ranges of pressures and temperatures and can be made to include all types of recombination (preferential, initial and volume ionization). The evaluation of the general formula, (1.1), depends on the relative values of three linear quantities: the mean free path of the ions λ, the mean distance between ions of different signs $\bar{r}$ and the well-known parameter $a_0=e^2/(kKT)$. In Section II the case $\lambda\ll a_0$ is treated. The mechanism of recombination then depends on the ratio $a_0/\bar{r}$. If $a_0/\bar{r}$ is large the migration of the ions under their mutual attraction prevails and (1.1) leads to Langevin's formula; in the opposite case, $a_0/\bar{r}\ll1$, diffusion is the decisive feature and 1.1 leads to a formula which is practically identical with that of Harper. In Section III the case $\lambda\gg a_0$ is treated by a method previously developed by the author. Under certain restrictions (1.1) reduces to Thomson's formula, but in general α depends on the concentration of the ions. In Section IV it is shown that (1.1) is in fair agreement with such experimental data as are available for the region of transition between the cases treated in Sections II and III.

THE problem of recombination of ions in gases under varying conditions of ionization, pressure and temperature has proved to be much more complex than was originally anticipated. Various types, such as preferential, initial and volume recombination are involved.[1] It has been recognized in recent years that the two most important theoretical formulae for the coefficient of recombination, that of Langevin and that of Thomson, have separate domains of applicability. Harper[2] and Loeb[3] have given formulae which bridge the expressions of Langevin and Thomson in a formal way, but it

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[1] For the definition of these types and a survey of the whole subject see the excellent treatment in: L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, New York, 1939).

[2] W. R. Harper, Phil. Mag. **18**, 97 (1934); **20**, 740 (1935).

[3] L. B. Loeb, Phys. Rev. **51**, 1110 (1937).

seems desirable to establish a general theoretical expression from which either of them, and eventually others, can be derived. It is the object of the following paper to give a theory that covers the whole range of physical conditions and that can be made to include the various types of recombination.

I. The General Formula

We start by defining three probabilities. Let n_+ and n_- be the instantaneous average volume densities of positive and negative ions, respectively. The ionization is considered to be homogeneous in a macroscopic sense and no preferential directions are assumed to exist. Still, in order to include preferential and initial recombination, we shall admit microscopic inhomogeneities. Then let $p_1(r)n_-d\tau$ be the probable number of negative ions which are located in an element of volume $d\tau$ at a distance r (irrespective of direction) from a positive ion.

By $p_2(r)dr$ we define the probability that the nearest neighbor to a positive ion is to be found at distances between r and $r+dr$. Evidently we have to have

$$\int_{r_m}^{\infty} p_2(r)dr=1,$$

if r_m is the nearest distance of approach for two ions of different signs.

Further, let $p_3(r)$ signify the probability of recombination. That is, of dN_r pairs of nearest neighbors of different signs which are at distances between r and $r+dr$, $p_3(r)dN_r$ are supposed to recombine on the average. This probability concept replaces the strict criterion for recombination which other authors[4] have tried to establish.

Finally, we have to define the velocity of approach of two nearest neighbors of different signs. If they are at a distance r apart, $u(r)$ is to signify the average component, in the direction of r (from the negative to the positive ion), of the relative velocity. This is supposed to be the resultant of all acting influences, i.e., diffusion and electrostatic attraction. It might also be made to include the action of an external field, but we limit ourselves to the case where there is no such external field.

The expressions of n_+, n_-, p_1 and p_2 will, in general, be functions of the time, as it is our object only to calculate the instantaneous coefficient of recombination, α.

With these definitions it is easy to write down a general expression for α by generalizing Langevin's argument. In doing so we first fix our attention on such positive ions as have their nearest negative neighbors at distances between r and $r+dr$. There are $p_2(r)n_+dr$ positive ions of this class per cc. We consider each of them surrounded by a sphere of radius r. The number of negative ions crossing one of these spheres during a time interval Δt will be given by $4\pi r^2p_1(r)n_-u(r)\Delta t$. But not all these ions will ultimately move up to the positive center and recombine, but only the fraction $p_8(r)$ of them. Hence

$$4\pi r^2n_+n_-p_1(r)p_2(r)p_3(r)u(r)dr\Delta t$$

is the number of pairs (per cc) of the specified class which are to be considered as lost by recombination during Δt. Adding over all distances r and dividing by $n_+n_-\Delta t$ we obtain

$$\alpha=4\pi\int_{r_m}^{\infty} p_1(r)p_2(r)p_3(r)u(r)r^2dr \qquad (1.1)$$

as our general expression for the coefficient of recombination.

Before we try to evaluate (1.1) for special cases, a few words must be said regarding the physical significance of the various functions of r. First of all, the probabilities $p_1(r)$ and $p_2(r)$ determine the particular type of recombination. They are not independent of each other.

If the distribution is homogeneous also in the microscopic sense, i.e. if $p_1(r)=1$, and, furthermore, if the diameter of the ions can be neglected, the probability $p_2(r)$ is known. P. Hertz[5] has shown that, in a random distribution of points without extension (n per cc), $p_2(r)$ is given by

$$p_2(r)dr=4\pi nr^2 \exp\,(-4\pi nr^3/3)dr. \qquad (1.2)$$

This law is modified, though only slightly, if, instead of points without extension, ions of

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[4] (*a*) J. J. Thomson, Phil. Mag. **47**, 337 (1924); (*b*) L. B. Loeb and L. C. Marshall, J. Frank. Inst. **208**, 371 (1929); W. R. Harper, Proc. Camb. Phil. Soc. **28**, 219 (1932); **31**, 430 (1935).

[5] P. Hertz, Math. Ann. **67**, 387 (1909).

finite diameter have to be considered. It is, however, evident that this modification will be insignificant if the average separation of the ions is very large compared with their diameter, as in all cases of gaseous ionization. Then, also, r_m can be replaced by 0.

If $p_1(r)$ is a given variable function of r, it can be shown by an argument which is exactly analogous to that of Hertz that $p_2(r)$ will be determined by

$$p_2(r)dr = 4\pi r^2 n_- p_1(r) \exp\left(-n_- P(r)\right)dr, \tag{1.3}$$

where

$$P(r) = \int_{r_m}^{r} 4\pi r^2 p_1(r)dr. \tag{1.4}$$

Thus when $p_1(r)$ is determined the probability $p_2(r)$ may be calculated. Bradbury[6] has recently determined $p_1(r)$ for the cases of preferential and initial recombination and, therefore, it would not be difficult to evaluate α for these types of recombination. However, we shall limit ourselves to the fundamental case of volume ionization with $n_+ = n_- = n$. Not even then is it permissible, in the strict sense, to replace $p_1(r)$ by 1. Owing to the electrostatic attraction there is a greater probability of finding a negative ion in an element $d\tau$ near a positive ion than in an equal element at a greater distance. This is conclusively shown by the theory of ionic atmospheres as developed by Debye and Hückel.[7] This theory is applicable to our case, but for all cases of gaseous ionization the characteristic distance of the Debye theory is so large in comparison with the mean distance between two ions that this inhomogeneity may be disregarded.

For these reasons we shall, in all that follows, take $p_1(r) = 1$ and shall also replace r_m by 0 which amounts to determining $p_2(r)$ by (1.2).

The functions $p_3(r)$ and $u(r)$ depend on the mechanism of recombination which is effective under given circumstances. Their determination constitutes the specific difficulty of the problem. Before starting to effectuate this determination for particular cases we wish to emphasize that these evaluations are only approximate. Whereas our formula (1.1) claims to be exact and to cover the whole ground, the following calculations are only intended to give a survey of possible cases.

II. SPECIAL CASE: λ SMALL IN COMPARISON WITH a_0

The mechanism of recombination depends upon the relative importance of Brownian movement and migration under the mutual attraction of the ions. Whether the one or the other process is prevalent can be inferred from the ratio of two linear quantities: $\bar{r}$, the mean distance between an ion and its nearest neighbor of opposite sign, and a characteristic length defined by

$$a_0 = e^2/(KkT), \tag{2.1}$$

where e is the elementary charge, K the dielectric coefficient and k the Boltzmann constant. If $a_0/\bar{r}$ is large, migration is decisive, while, if $a_0/\bar{r}$ is small, Brownian movement predominates. This fact has been pointed out by Loeb and Harper and will be shown by our treatment in a somewhat different way.

A further distinction has to be introduced according to whether Brownian movement can be adequately described by the differential equation of diffusion or not, and this distinction depends upon whether the mean free path of the ions, λ, is small or large in comparison with a_0.

Boltzmann's fundamental equation must be considered the basis for every rigorous kinetic deduction. The author[8] has shown that the solution of Boltzmann's equation has to proceed along entirely different lines if the mean free path λ is small and if it is large compared with the linear dimensions concerned in the problem. The decisive length, in our case, is a_0. If, then, λ is small compared with a_0 the usual treatment by the differential equations of transport is adequate, though it represents only a first approximation.

From the study of the differential equation of *relative* Brownian movement Onsager[9] has deduced the following expression for the probability $p_3(r)$:

$$p_3(r) = 1 - \exp(-a_0/r). \tag{2.2}$$

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[6] N. E. Bradbury, J. App. Phys. **11**, 267 (1940).

[7] P. Debye and E. Hückel, Physik. Zeits. **24**, 185 (1923).

[8] G. Jaffé, Ann. d. Physik **6**, 195 (1930).

[9] L. Onsager, Phys. Rev. **54**, 554 (1938).

It follows that a_0 is, in a certain way, the length which decides the fate of a pair of ions. Though there is no definite critical distance, the pair will recombine if $a_0/r \gg 1$ and will not recombine if $a_0/r \ll 1$.

To these two limiting cases correspond two entirely different mechanisms of motion. To show this we shall calculate the time which the one ion takes to travel the distance $\bar{r}$ relative to the other, upon the assumption that either migration in their mutual field or diffusion alone is effective.

If k_+ and k_- are the mobilities of the ions and if $r_m \ll \bar{r}$, the time required under the mutual attraction alone will be[10]

$$t_k = \bar{r}^3 K / [3e(k_+ + k_-)]. \tag{2.3}$$

If, on the other hand, diffusion alone were effective the corresponding time would be[11]

$$t_D = \bar{r}^2 / [2(D_+ + D_-)], \tag{2.4}$$

D_+ and D_- being the coefficients of diffusion.

If t_D is very much shorter than t_k diffusion will be prevalent and vice versa. Hence the ratio

$$t_D/t_k = 3a_0/2\bar{r} \quad \text{(by 2.17)} \tag{2.5}$$

is decisive, as stated above.

The probability function (1.2) has a strong maximum for

$$r_0 = [1/(2\pi n)]^{\frac{1}{3}}. \tag{2.6}$$

Hertz has pointed out that this "most probable value" is numerically very little different from the "mean value"

$$\bar{r} = \Gamma(4/3) \cdot [3/(4\pi n)]^{\frac{1}{3}}, \tag{2.7}$$

and that both are well approximated by the value $5/9n^{\frac{1}{3}}$ which ought to replace the value $(1/n)^{\frac{1}{3}}$ usually adopted. For reasons which will become evident we shall use r_0 instead of $\bar{r}$.

Now we are prepared to treat the subsidiary limiting cases. If, besides $\lambda \ll a_0$, the ratio a_0/r_0 is large, migration will be prevalent. Then we have

$$u_k(r) = e(k_+ + k_-)/(Kr^2), \tag{2.8}$$

and for all significant values of r, namely those in the neighborhood of the maximum r_0, (2.2) yields

$$p_3(r) = 1. \tag{2.9}$$

Inserting these expressions into (1.1) and making use of (1.2), we find

$$\alpha_k = 4\pi e(k_+ + k_-)/K, \quad \lambda \ll a_0, \quad r_0 \ll a_0, \tag{2.10}$$

which is Langevin's formula.

If, on the other hand, a_0/r_0 is small diffusion prevails and we find from (2.2)

$$p_3(r) = a_0/r. \tag{2.11}$$

We still have to calculate $u(r)$ and it is this calculation which introduces a certain ambiguity. Because, according to the usual treatment of Brownian movement, a velocity in the proper sense does not exist, we must define $u(r)$ by some mean value. In doing so we start from the point-source solution for relative Brownian movement, i.e.,[12]

$$p(r, t) = \frac{1}{[4\pi(D_+ + D_-)t]^{\frac{3}{2}}} \times \exp\left(-\frac{r^2}{4(D_+ + D_-)t}\right). \tag{2.12}$$

Arguing in the usual way we might deduce from (2.12) the relation

$$\langle r^2 \rangle_{\text{Av}} = 6(D_+ + D_-)t, \tag{2.13}$$

but it must be remembered that this is the mean square of the distance traveled in time t. What is required in our case is the mean time required for a given displacement. This is found from (2.12) to be

$$\bar{t} = r^2 / [2(D_+ + D_-)]. \tag{2.14}$$

By differentiating this expression we obtain an approximative value for $u(r)$. As, however, there remains a certain ambiguity regarding the numerical coefficient, we shall write

$$u_D(r) = f_1(D_+ + D_-)/r, \tag{2.15}$$

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[10] In deducing (2.3) we have tacitly assumed that the mobilities are not affected by the very intense fields in the immediate neighborhood of the ions, but it must be remembered that we are only making an estimate.

[11] For an explanation of the numerical factor see paragraph containing Eq. (2.14).

[12] We have normalized (2.12) in such a way that $\int_0^\infty 4\pi r^2 p dr = 1$, i.e., $4\pi r^2 p$ represents the probability of finding two ions at time t at a distance r if, at time $t=0$, they are both at $r=0$. The solution (2.12) can be verified either directly as the point-source solution of the differential equation of *relative* Brownian movement (see for instance L. Onsager, J. Chem. Phys. **2**, 599 (1934)), or it can be derived by multiplying the point-source solutions for a positive and a negative ion (relative to a fixed system of coordinates) and subsequent suitable transformation and integration.

where f_1 represents a numerical factor which is likely to be equal to 1 and certainly is of the order 1.

Introducing (2.11) and (2.15) into (1.1) we obtain

$$\alpha_D = f_1 4\pi(D_+ + D_-)a_0, \quad \lambda \ll a_0, \quad r_0 \gg a_0, \tag{2.16}$$

which is, but for the numerical factor, an equation previously deduced by Harper.[13]

Making use of Townsend's relation in the form

$$(D_+ + D_-)/(k_+ + k_-) = kT/e, \tag{2.17}$$

the expression (2.17) can be transformed into

$$\alpha_D = f_1 \alpha_k. \tag{2.18}$$

This shows the remarkable fact, previously observed by Harper, that the coefficient of recombination is practically (exactly, for $f_1 = 1$) the same, whether migration in the field or diffusion is alone effective, though, of course, the mechanisms are far different.

We shall see in Section IV that the case where r_0 and a_0 are comparable is of no practical significance. It is, however, easy to obtain an approximate solution which bridges the two limiting cases treated so far. As a first, rough, approximation it will be legitimate to assume that $u(r)$ will then be a simple superposition of the expressions (2.8) and (2.15). Introducing this superposition and the general expression (2.2) into (1.1) we obtain

$$\alpha = 4\pi \int_0^\infty (1 - e^{-a_0/r}) \times (e(k_+ + k_-)/K + f_1(D_+ + D_-)r) p_2(r) dr, \tag{2.19}$$

where $p_2(r)$ is given by (1.2). As the function (1.2) has a strong maximum for $r = r_0$ we obtain a good approximation for (2.19) by using the saddle-value method. Remembering (2.17) we can write the result in the form:

$$\alpha = 4\pi(D_+ + D_-)a_0(1 - e^{-z})(1 + f_1/z), \quad \lambda \ll a_0, \tag{2.20}$$

where we have put

$$z = a_0/r_0. \tag{2.21}$$

It will be noticed that in the limiting cases $z \gg 1$ and $z \ll 1$ formula (2.20) leads back to (2.10) and (2.16), but that in all other cases α is dependent on z, i.e., on the concentration of the ions.

III. SPECIAL CASE: λ LARGE IN COMPARISON WITH a_0

With this restriction conditions are analogous to those prevailing in "molecular flow." The solution of problems of this type can be developed[8] into a series which progresses with powers of λ^{-1}.

We shall split the probability $p_3(r)$ into two factors, the probability $p_3'(r)$ that two neighboring opposite ions which are at a distance r will be caught into related closed orbits, and the probability p_3'' that, subsequently, actual recombination takes place. The probability $p_3'(r)$ could be calculated rigorously by successive approximations and even the curvature of the paths could be taken into account (reference 8, §4). The problem offers a comparatively simple application of the method developed by the author since no boundaries have to be considered. Still, some law of interaction between the ions and the neutral molecules would have to be accepted and the evaluations would be very involved.

For these reasons we shall adopt an approximative procedure which is based on the analogy with the theory of heat radiation. In the zero approximation collisions are altogether disregarded and the ions are considered to be "emitted" from each element of volume isotropically with their mean velocity.

We start again by considering a positive ion A which is supposed to be at rest and has its nearest negative neighbor B at a distance between r and $r + dr$. The two ions will, on the average, form closed orbits if B approaches A within a distance less than[4]

$$d = 2e^2/(3KkT) = 2a_0/3. \tag{3.1}$$

We are only interested in the case $d \ll r$. Then we shall have in our present approximation

$$p_3'(r) = (1/4\pi)(d^2\pi/r^2) = d^2/4r^2 \tag{3.2}$$

and

$$u(r) = c_{12}, \tag{3.3}$$

where c_{12} is the average relative velocity.

Assuming provisionally $p_3'(r) = p_3(r)$ and inserting (3.2) and (3.3) into (1.1) we find as zero

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[13] W. R. Harper, reference 4(*b*).

approximation

$$\alpha_\lambda^{(0)}=\pi d^2 c_{12}. \tag{3.4}$$

This is, of course, the usual formula of the kinetic theory (for a cross section of radius d), and it becomes identical with the limiting value of Thomson's theory if we take

$$c_{12}=(\bar{c}_+^2+\bar{c}_-^2)^{\frac{1}{2}}. \tag{3.5}$$

If, now, collisions occur, each of them is considered an act of "absorption" and "re-emission," the re-emission being equally probable in all directions and the velocity remaining, on the average, unaltered. Since the probability of a collision along an element of path ds is given by ds/λ, the reciprocal of the mean free path must be considered the "coefficient of absorption."

Let us again assume that a negative ion B is emitted at a distance r from its nearest positive neighbor A at an angle ϑ_1 with the line joining them. We obtain a first approximation by assuming that one, and only one, collision occurs outside the sphere of radius d around A. If the collision occurs at a distance r_1 from the starting point of B, at a point which is at a distance ρ_1 from A, B will have to travel a distance $r_1+\rho_1-d \sim r_1+\rho_1$ before being caught, and its average radial velocity (as required for (1.1)) will be $u(r)=c_{12}r/(r_1+\rho_1)$.

It simplifies matters to calculate in one step $\langle u(r)p_3'(r)\rangle_{\mathrm{Av}}$, i.e., the average of the product for all possible loci of the collision. We obtain[14]

$$\langle u(r)p_3'(r)\rangle_{\mathrm{Av}} =\frac{c_{12}d^2}{8\lambda}\int_0^\infty \frac{e^{-r_1/\lambda}dr_1}{r_1}\int_{\rho_{10}}^{\rho_{11}}\frac{d\rho_1}{\rho_1(r_1+\rho_1)}, \tag{3.6}$$

where

$$\rho_{11}=r+r_1,\quad \rho_{10}=[(r'-r_1)^2+d^2]^{\frac{1}{2}},\quad r'=(r^2-d^2)^{\frac{1}{2}}. \tag{3.7}$$

The first integration in (3.6) is immediate, the second can be carried out to a good approximation since the function $r_1^2 \exp(-r_1/\lambda)$ has a pronounced maximum for $r_1=\lambda$. We thus find

$$\langle u(r)p_3'(r)\rangle_{\mathrm{Av}} =\frac{c_{12}d^2}{8\lambda^2}\left\{\log\frac{r+\lambda}{r+2\lambda}-\log\frac{[(r'-\lambda)^2+d^2]^{\frac{1}{2}}}{[(r'-\lambda)^2+d^2]^{\frac{1}{2}}+\lambda}\right\} \tag{3.8}$$

$$=\frac{c_{12}d^2}{8\lambda^2}\varphi_1\left(\frac{d}{\lambda},\frac{d}{r}\right).$$

In order to calculate α, we must remember that it consists now of two parts, the one being due to ions which are caught without having undergone a collision, and the second to ions which have made one collision. The first part we obtain by multiplying (3.4) by $\exp(-r_0/\lambda)$, the second by inserting (3.8) and (1.2) into (1.1) and evaluating by the saddle-value method. Thus we finally obtain

$$\alpha_\lambda^{(1)}=\pi d^2 c_{12}\left\{e^{-r_0/\lambda}+\frac{r_0^2}{2\lambda^2}\varphi_1\left(\frac{d}{\lambda},\frac{d}{r_0}\right)\right\}$$

$$=\pi d^2 c_{12}\psi_1\left(\frac{d}{\lambda},\frac{d}{r_0}\right). \tag{3.9}$$

The function ψ_1 approaches unity for small and large values of λ/r_0. Neglecting terms of the order $(d/r_0)^2$ we find

$$\alpha_\lambda^{(1)}=\pi d^2 c_{12}\left\{e^{-r_0/\lambda}+\frac{1}{2}\left(\frac{r_0}{\lambda}\right)^3+\cdots\right\},\qquad \lambda/r_0\gg 1, \tag{3.10}$$

and

$$\alpha_\lambda^{(1)}=\pi d^2 c_{12}\left\{1-\frac{\lambda}{r_0}+\cdots\right\},\quad \lambda/r_0\ll 1. \tag{3.11}$$

For the latter case, however, our present approximation is not adequate. The author, therefore, has carried through the next approximation taking account of those ions B which reach A after two collisions. The result is too lengthy to be quoted *in extenso*. In the limiting case $\lambda/r_0\ll 1$

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[14] It must be pointed out that, in establishing (3.6), we have made use of (3.2) (with ρ_1 replacing r) for the probability of capture after the collision. However, this is not quite correct because it is not true that $d\ll\rho_1$ in the whole space of integration. The correct value of the solid angle determining capture would be $\Omega=2\pi[1-(1-d^2/\rho_1^2)^{\frac{1}{2}}]$ rather than $\pi d^2/\rho_1^2$. We have carried out the calculations with this value and verified that the result is not noticeably different from (3.6).

In determining the region of integration we have omitted the whole solid angle Ω' subtended at B by the sphere of radius d. This means omitting the negligible probability of cases in which the ion remains inside Ω' in spite of a collision. The space inside Ω' behind the sphere has to be omitted.

Finally it must be remarked that (3.6) is not a symmetrical function of the ions A and B unless λ is taken as the average value for positive and negative ions. In a somewhat more rigorous deduction (3.6) would have to be replaced by its arithmetic mean for λ_+ and λ_-.

it is found

$$\alpha_\lambda^{(2)}=\pi d^2 c_{12}\left\{1-\frac{2\lambda}{r_0}+6\left(\frac{\lambda}{r_0}\right)^2+\cdots\right\},\qquad \lambda/r_0\ll 1. \quad (3.12)$$

The comparison with (3.11) shows that the convergence of our procedure for this limiting case may be slow, though the essential feature, convergence towards $\pi d^2 c_{12}$ for $\lambda/r_0\rightarrow 0$, is preserved.

So far we have identified $p_3'(r)$ with $p_3(r)$, i.e., we have assumed that each pair of ions which is caught into closed orbits will ultimately recombine. It is, however, evident from J. J. Thomson's well-known argument that this need not be the case. Therefore the α so far calculated has still to be multiplied by the probability p_3'' as defined above.

A rigorous calculation of this p_3'' would have to be based on a quantum-mechanical study of the interaction between ions and neutral molecules on the one hand and ions of different signs on the other. Such a study does not seem feasible at the present time. We may, however, accept Thomson's treatment as a first approximation, though it cannot hold down to zero pressure, as was pointed out by Loeb.[15]

The probability p_3'' as calculated by Thomson is given with sufficient accuracy by [16]

$$p_3''=\varphi_2(d/\lambda)=2\omega-\omega^2, \quad (3.13)$$

where

$$\omega=\left[1-\frac{\lambda^2}{2d^2}\left\{1-e^{-2d/\lambda}\left(\frac{2d}{\lambda}+1\right)\right\}\right]. \quad (3.14)$$

Hence our final expression for α_λ becomes

$$\alpha_\lambda=\pi d^2 c_{12}\psi_1(d/\lambda,\ d/r_0)\varphi_2(d/\lambda),\qquad \lambda\gg d. \quad (3.15)$$

This result, though intimately connected with Thomson's, is distinguished from it by two essential features: It depends upon d/r_0, i.e., upon the concentration of the ions, and it gives a marked maximum for α_λ at $r_0=\lambda$, as can be shown from the form of $\varphi_1(d/\lambda,\ d/r_0)$. Sufficiently above pressures where $r_0\sim\lambda$, and for ionizations sufficiently weak to make d/r_0 a small number, ψ_1 can be approximated by 1 (see (3.11) and (3.12)) and our formula reduces to Thomson's

$$\alpha_\lambda=\pi d^2 c_{12}\varphi_2(d/\lambda),\qquad \lambda\gg d,\quad d\ll r_0. \quad (3.16)$$

IV. Discussion and Comparison with Experiment

We have seen that our general expression (1.1) reduces, for well-defined special conditions, to the formulae of Langevin, Harper and Thomson. However, it must be emphasized that only under the restrictions specified by (2.10), (2.16), and (3.16) does the coefficient of recombination become independent of the ionic density, n. The transitional formulae, (2.20) and (3.15), involve the parameter

$$q=d/r_0=2a_0/3r_0=d(2\pi n)^{\frac{1}{3}}. \quad (4.1)$$

It seems to be generally accepted that the Langevin formula holds with adequate accuracy for sufficiently high pressures. As pointed out by Harper, this does not prove the correctness of the mechanism by which Langevin deduced his formula, as shown by the formal similarity between the expressions for α_k and α_D (see (2.18)).

It is pretty certain that in no direct experiments on volume recombination is the migration of the ions under their mutual attraction the predominant feature. The highest observed values of n are of the order 10^7 ions per cc. Even in liquid dielectrics (which behave in this regard like very dense gases) n never rises above 2×10^8. The corresponding values of r_0 are 2.5×10^{-3} and 0.92×10^{-3}. As $d=4.05\times 10^{-6}273/T$, q is never larger than about 4×10^{-3} and in most cases is considerably smaller. Under these circumstances diffusion prevails and the agreement of experimental data with Langevin's formula really proves the diffusion formula (2.16).

There is, however, indirect evidence for the correctness of Langevin's formula, including its mechanism. The theory of columnar ionization, as developed by the author, seems to be generally accepted for the ionization with heavy particles. The fundamental concept of this theory is that, inside the columns, recombination (and diffusion) take place according to the usual laws and with the same coefficients as in cases of more homogeneous ionization.

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[15] See reference 1, p. 130.

[16] See reference 1, p. 119. The function φ_2 is found tabulated there.

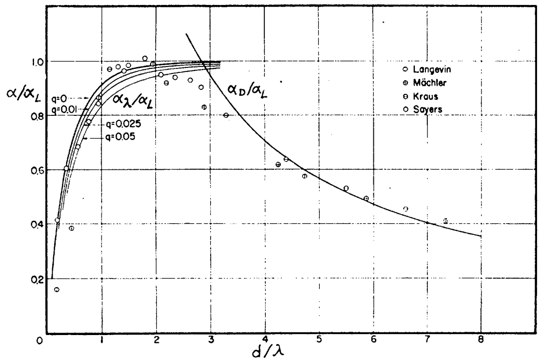

FIG. 1. The diagram represents α/α_L as a function of d/λ. The curves for α_λ/α_L are calculated from (3.16) and (3.12) for various values of q, and the curve for α_D/α_L is calculated from (4.3) with $f_1=f_2=1$. The observational points are reduced values.

The initial concentration in the axis of a column[17] is of the order of 5×10^9 in air of atmospheric pressure and rises in liquid hexane to 2.50×10^{18}, giving values of q from 1.2×10^{-2} to 9.5. This brings columnar ionization in dense gases within the scope of formula (2.20)[18] and for liquid dielectrics even of (2.10). Thus the agreement of the columnar theory with experimental facts indirectly confirms Langevin's theory.

At low pressures, say up to 1 atmos., Thomson's theory seems to give an adequate representation of experimental facts. That is to be expected from our theory as long as λ is somewhat larger than d and, at the same time the pressure is sufficiently high to make λ smaller than r_0.

In the region where λ becomes comparable with d neither the formula for α_D nor that for α_λ is a sufficiently good approximation for our general formula (1.1), as they are only first steps in the evaluation for $\lambda/d\ll1$ and $\lambda/d\gg1$, respectively. Theoretically, it would be possible to carry the two approximations on until they meet, but practically, that is out of the question. The failure is, however, not due to a breakdown of the fundamental concepts (as in the case of Langevin's or Thomson's theory beyond their domains of applicability) but to our inability to evaluate the general formula (1.1). Conditions are thus exactly the same as in the transition from Poiseuille's "frictional flow" to Knudsen's "molecular flow."

As is well known, the critical region is in the neighborhood of atmospheric pressure, since $\lambda=1\times10^{-5}\,(760/p)(\lambda/\lambda_a)$ where λ/λ_a is the ratio of the mean free path of the ion to that of a molecule in air at NTP.[19] For this region of transition it must be tested whether the two approximations approach each other sufficiently to make a graphical interpolation possible.

According to (3.16) α_λ is given as a function of d/λ, whereas α_D is represented by (2.16) as a function of $(D_+ + D_-)$. To reduce the two representations to common terms we must represent D_+ and D_- by atomic data and this reduction introduces a further ambiguity. For our purpose it will suffice to introduce a mean coefficient of diffusion, defined by $D=(D_+ + D_-)/2$, a mean velocity $\bar{c}=(\bar{c}_+ + \bar{c})/2$, and write

$$D=f_2\bar{c}\lambda/3, \qquad (4.2)$$

where λ is also the average value for positive and negative ions and f_2 a numerical factor. According to the usual elementary theory f_2 is unity, but we insert the factor f_2 of order 1 to leave room for the improvements of the more elaborate theories.

Making use of (4.2) and (3.1) and remembering that $c_{12}=2^{\frac{1}{2}}\bar{c}$, we find

$$\alpha_D=\pi d^2c_{12}\cdot f_1f_2 2^{\frac{3}{2}}\lambda/d. \qquad (4.3)$$

If we introduce the limiting value $\alpha_L=\pi d^2c_{12}$ we see that both α_D/α_L and α_λ/α_L, the latter given by (3.16), are universal functions of d/λ. We have represented these two functions by the heavy lines of Fig. 1, choosing $f_1=f_2=1$. It will be seen that a fair representation of α/α_L for all values of d/λ can be gained by the two approximations from either side, though, of course, we have no quantitative criterion to show at which particular values of d/λ the deviations become noticeable.

As to the agreement with empirical data we are of the opinion that neither the present state of experimental research nor our evaluations of Sections II and III would justify a comparison of absolute values. Therefore we have adopted a procedure of testing relative values. As α/α_L

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[17] G. Jaffé, Ann. d. Physik **32**, 152 (1910); H. J. van der Byl, Ann. d. Physik **39**, 170 (1912).

[18] According to (2.20) the coeff. of rec. does not vary much with q. Assuming $f_1=1$, α has a maximum, for $a_0/r_0\sim2$, which is about 30 percent higher than the values at the extremes.

[19] L. B. Loeb, reference 1, p. 118.

should be a universal function of d/λ, we have tried to reduce the α-scale, as well as the p scale, in such a way that the experimental values fit the theoretical curves. This, of course, amounts to taking c_{12} (or the mass of the ion) and λ as two constants which are to be determined experimentally.

All measurements of α in air in the interval between 1 and 8 atmos. have been included. These are the measurements of Langevin, Mächler, Kraus and Sayers.[20] The values adopted for $\alpha_L \cdot 10^6$ are, respectively, 1.83, 1.71, 1.70 and 2.35 and the values for λ/λ_a 0.40, 0.41, 0.33, 0.26, respectively.[21]

It will be seen that the points thus determined seem to confirm the theoretical curve, but we do not want to stress this kind of agreement. Measurements in the indicated interval which include the determination of α and the mobilities in the same sample of gas are an urgent desideratum. The differences among the values of α_L and of λ/λ_a, as assumed above, are probably due to the fact that different observers have been dealing with ions of different age and nature.

So far we have limited our discussion to the case where the parameter q is very small, which reduces the more general expressions (2.20) and (3.15) to the simple forms (2.16) and (3.16). To illustrate the influence of q we have calculated α_λ/α_L from (3.12) for the values $q=0.01$, 0.025 and 0.05 and inserted the curves into the diagram.

It will be seen that α_λ/α_L decreases with increasing q and that means with increasing n.[22] A dependence of α on the concentration of the ions signifies that the simple law $dn/dt=-\alpha n^2$ ceases to hold, but the change of α predicted by theory is so slow that it seems adequate to retain the formal law and to speak of a variation of α with concentration. This procedure has always been adopted by experimenters.

It is well known that the coefficient of recombination, as determined experimentally, is not constant. Even after the stage of initial recombination is over, α goes on changing for a considerable time. This lack of constancy has been explained[23] by a gradual change in the nature of the ions and there can hardly be a doubt that this is the correct interpretation. The aging of ions will generally tend to decrease α with time and, therefore, with decreasing ionic density, as is also confirmed by the corresponding effect on the mobilities. Apart from this aging effect, however, all recent observers[23] have noticed that α is *larger* for lower values of the ionic concentration. The author is of the opinion that this dependence, which coincides in direction with that predicted by the present theory, is a genuine effect not due to secondary causes. The few quantitative data which are available indicate that the observed effect is considerably larger than the effect foreseen by our theory. This, however, is only true as long as the ionization is supposed to be homogeneous in all cases. The effect would be much stronger if, for the lower ionic densities, the initial inhomogeneity became more marked, an effect for which there are distinct indications.[24] The dependence of α on ionic density is the second point where an extension of experimental evidence is desirable.

We do not want to dwell here on the question of recombination at very low pressures. We have observed (p. 974), however, that, under conditions where $\lambda \sim r_0$, something like selective recombination should occur according to Eq. (3.15).[25] This fact shows how careful one ought to be in extending Thomson's formula to very low pressures, whether in the atmosphere or the discharge tube. This point requires further study, but the study will, no doubt, be complicated by the fact that in the same interval of pressures the carriers of electricity change character.

The author wishes to express his gratitude to the Department of Physics of the University of Colorado for courtesies extended.

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[20] P. Langevin, Ann. Chim. Phys. **28**, 289, 433 (1903); W. Mächler, Zeits. f. Physik **104**, 1 (1936); P. Kraus, Ann. d. Physik **29**, 449 (1937); J. Sayers, Proc. Roy. Soc. **A169**, 83 (1938).

[21] All measurements refer to "room-temperature," but the exact values are not given in some cases. As d depends on the temperature this ought to be known for a more exact evaluation. We have chosen $t=18°$. Furthermore, Sayers' values had to be taken from his diagram.

[22] A change for α_D is hardly to be expected for realizable values of n, as long as volume ionization only is considered.

[23] L. C. Marshall, Phys. Rev. **34**, 618 (1929); O. Luhr, Phys. Rev. **35**, 1394 (1930); M. E. Gardner, Phys. Rev. **53**, 75 (1938); J. Sayers, reference 20.

[24] A. D. Power, J. Frank. Inst. **196**, 327 (1923).

[25] The maximum indicated by 3.15 is *not* erased by the next approximation, but a second minor maximum is added for $r_0=2\lambda$.