are counted, but the thickness of the photographic plane favors small angles.

If one considers the experimental difficulties, the values of 48° and 20° for 360 kev and 650 kev radiation are in reasonably good agreement with theory.

The Klein-Nishina formula

The present experimental data offer no conclusive evidence in regard to the exactness of the Klein-Nishina formula. Read and Lauritsen found that for a range of 50 to 20 x-units (the wave-length of 500 kev radiation is 24.7 x-units) the *total* absorption coefficients of carbon and aluminum are within 1 percent of the Klein-Nishina value, and they state that their maximum likely error is 3 percent. Since a measure of the total absorption is a measure of the total number of photons removed from the incident beam, it is also a measure of the total number of electrons taking part in the interaction (if one assumes no coherent scattering). Thus, if only recoil electrons are emitted and the Klein-Nishina formula is correct, a measure of the total absorption should check the Klein-Nishina formula exactly. However, if the error in this experiment were as much as 3 percent, three photoelectrons in a total of 100 could be present and still not be detected. This corresponds to a σ/τ value of about 30. Consequently an experiment of this type cannot distinguish between the theoretical value of σ/τ of about 5000 which one gets from Eq. (9), and a value as low as 30. According to the present results, the value of σ/τ for 500 kev x-rays in nitrogen is of the order of 100 and is probably less than this; however, just how much less cannot be determined with the present data. If σ/τ is less than 30, the Klein-Nishina value may be too high.

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Initial Recombination of Ions

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The probability that a pair of ions of given initial separation will recombine with each other is computed from the laws of Brownian motion, which is the proper procedure whenever the Langevin factor equals unity, as in gases at high pressures. In the absence of forces other than the Coulomb attraction, the probability of escape equals the reciprocal of the Boltzmann factor. This result includes the correlation between temperature and pressure coefficients of the ionization by light particles previously predicted by Compton, Bennett and Stearns, if one allows their basic hypothesis about the laws which govern the initial separation of the ions. The effect of an electric field is to increase the fraction of escaping ions by a factor which in the incipient stage of the effect is proportional to the field intensity and independent of the initial distance, although it depends on the orientation of an ion pair. The predicted increase of the ionization current is a little more than one percent for every 100 volts/cm, which accounts for the observed effects of fields exceeding 1500 volts/cm. A reasonable amount of columnar recombination would help to explain the proportionately greater effects of weak fields. The inferred initial separations of the ions are apparently compatible with present knowledge of electron scattering and attachment.

It stands to reason that an electron, ejected by a photon or by collision with a charged particle, if not removed too far before it becomes attached to a molecule or otherwise slowed down to thermal velocities, may recombine with its parent ion. The possibility of such *initial recombination* was pointed out long ago by Rutherford.[1] In recent years particular attention has been paid to the possible effect of this process upon the ionization of air by particles of low ionizing power (cosmic rays, β-(γ-) rays).

[1] E. Rutherford, *Radioactivity* (1904), p. 33.

Compton, Bennett and Stearns[2] were indeed able to correlate the effect of temperature with that of pressure; but the observed increase of the ionization with the collecting field belies their prediction that fields of much less than 40,000 volts/cm would hardly interfere with the initial recombination. From a rigorous analysis of the Brownian motion problem involved, I have been led to a different conclusion.

At present, initial recombination is not as confidently assumed as *columnar recombination* ("en colonnes"), which involves all the ions in the track left by one ionizing particle. Jaffé,[3] who carried out an approximate computation of the latter effect, found that it accounts very well for the much less complete collection of ions in the case of α-rays, as compared with β-rays at the same gas pressure. He was not, however, entirely satisfied with his attempts to correlate the collected amounts of ionization caused by β-rays for different gas pressures. While the discrepancies which aroused his suspicion have only been confirmed by subsequent experiments, recent authors have at times given less weight to them.[4]

The theories of initial and columnar recombination are related, for both processes depend on the initial distances of separation of ions of opposite sign. As yet, our best information about this question is inference from the collection of ions. However, granted a good guess about the distribution of initial distances, the extent of recombination can be computed from the laws of diffusion and migration.

The theory of columnar recombination leads to a nonlinear system of differential equations, and Jaffé's approximate solution is not easily improved.

The theory of initial recombination reduces to a problem of Brownian motion of *one particle* under the action of the collecting field together with the Coulomb attraction, with the combined potential (in polar coordinates r, Θ)

$$w = -\epsilon X r \cos\Theta - (\epsilon^2/Dr) = kT(-2\beta r\cos\Theta - (2q/r)). \quad (1)$$

The equation of Brownian motion

$$\partial f/\partial t = kT(\omega_1+\omega_2)\times \times \operatorname{div}(\exp(-w/kT)\operatorname{grad} f\exp(w/kT)), \quad (2)$$

with the potential w of Eq. (1), I have studied before in order to compute the ionization of weak electrolytes in strong fields,[5, 6] and I have shown that velocity of ionization is increased by an external field, in the ratio:

$$K(X)/K(0) = F(2\beta q) = J_1(4(-\beta q)^{\frac{1}{2}})/2(-\beta q)^{\frac{1}{2}}. \quad (3)$$

The theory of (general) recombination on the basis of Eq. (2) is equivalent to Langevin's well-known treatment,[7] and leads to his formula for the coefficient of recombination in terms of the mobilities of the ions,

$$\alpha = 4\pi\epsilon^2(\omega_1+\omega_2)/D, \quad (4)$$

independent of the field. The verification of Eq. (4) affords a general criterion for the applicability of Eq. (2); thus it is indicated that our considerations will be valid in gases for pressures above a few atmospheres.

The derivation of Eq. (3) involved the solution of Eq. (2) for the case stationary flow with a source at the origin and a sink for $r=\infty$. The problem of initial recombination involves the case of a source at a general point (r, Θ) with sinks at origin and infinity:

$$f(\infty, \Theta) = 0, \quad f(0, \Theta) < \infty. \quad (5)$$

The solution to this problem—the Green function of Eq. (2)—is rather complicated.[6] Fortunately, as an equation for $f\exp(w/kT)$, Eq. (2) is self-adjoint in 3 dimensions, and considering the symmetry of its Green function, one can show that the chance φ for any ultimate fate of the ion must itself satisfy the differential equation

$$\operatorname{div}(\exp(-w/kT)\operatorname{grad}\varphi) = 0, \quad (6)$$

which admits the trivial solution $\varphi = 1$ (certainty). In the following, we shall understand by $\varphi(r, \Theta)$ the probability that an ion pair of initial separation r at an angle Θ with the "downstream" direction of the field will escape initial recombi-

[2] A. H. Compton, R. D. Bennett and J. C. Stearns, Phys. Rev. **39**, 873 (1932).
[3] G. Jaffé, Ann. d. Physik IV, **42**, 303 (1913).
[4] H. Zanstra, Physica **2**, 817 (1935).
[5] L. Onsager, J. Chem. Phys. **2**, 599 (1934).
[6] L. Onsager, Diss. Yale, 1935.
[7] P. Langevin, Ann. chim. phys. VII, **28**, 433 (1903).

nation. Obviously, the boundary conditions are

$$\begin{aligned}\varphi(0,\ \Theta)&=0,\\ \varphi(\infty,\ \Theta)&=1.\end{aligned}\tag{7}$$

In the absence of a collecting field ($\beta=0$), the required solution is simply the reciprocal of the Boltzmann factor:

$$\varphi=e^{w/kT}=e^{-2q/r}.\tag{8}$$

At the corresponding stage of their considerations, Compton, Bennett and Stearns[2] introduced the assumption that the effect of the density ρ upon the distribution $f_0(r)$ of initial displacements can be described by a simple scale-factor:

$$f(\rho,\ r)=\rho^3F(\rho r).\tag{9}$$

Combining this hypothesis with Eq. (8) we obtain for the total current of escaping ions

$$I=I_0\int_0^\infty e^{-2q/r}F(\rho r)4\pi\rho^2r^2d(\rho r)=I_0g(2q\rho).\tag{10}$$

As reasonable as Eq. (9) is the assumption that the temperature does not enter as an independent parameter in the function F. On this basis, one obtains a correlation between pressure and temperature coefficients of the ionization current, identical with that previously derived by Compton, Bennett and Stearns. The result expressed by Eq. (10) differs from theirs in certain restrictions imposed on the type of function g, so as to prevent negative values of the corresponding range-function $F(t)$. Thus their suggestion

$$g(z)=a(a^2+z^2)^{-\frac{1}{2}},$$

is not admissible because it would imply

$$4\pi F(t)=at^{-4}J_0(a/t).$$

However, it seems possible to describe the available data by reasonable image-functions $F(t)$. The simple pair

$$F(t)=(\kappa^3/4\pi t^3)^{\frac{1}{2}}e^{-\kappa t},$$

$$g(2q\rho)=(1+(8\kappa q\rho)^{\frac{1}{2}})e^{-(8\kappa q\rho)^{\frac{1}{2}}},$$

might be of some interest, although the maximum of this g is not quite flat enough.

While Eq. (9) is probably a good approximation to the truth, it is hard to believe that the effect of the Coulomb field on the diffusion of the electrons before their attachment to molecules would be altogether negligible, and if not, the simple relations given here would seem to require corrections.

Our results so far contain little that is new, and involve assumptions about the initial separations of ions—for without such assumptions, Eq. (8) is rather barren of predictions. Our predictions about the effect of the collecting field will be more independent in this regard, and to the same extent, their experimental verification will test only our reasoning and general picture.

A solution of Eq. (6) with boundary conditions given by Eq. (7) is now required for the general case $\beta>0$. We are fortunate enough to find the labor all done. It turns out that a previously published solution[5] of Eq. (2), when divided by the Boltzmann factor, satisfies the boundary conditions for $1-\varphi$. Thus we obtain

$$\begin{aligned}\varphi(r,\ \Theta)&=e^{-\beta r(1+\cos\Theta)}\\ &\quad\times\int_{s=2q/r}^\infty J_0(2(-\beta r(1+\cos\theta)s)^{\frac{1}{2}})e^{-s}ds\\ &=e^{-(2q/r)-\beta r(1+\cos\Theta)}\sum_{m,\ n=0}^\infty\beta^{n+m}\\ &\quad\times(1+\cos\Theta)^{n+m}(2q)^mr^n/m!(m+n)!.\end{aligned}\tag{11}$$

The double series can be obtained by omitting all negative powers of r from the complete Laurent expansion of $\exp((2q/r)+\beta r(1+\cos\Theta))$. The corresponding representation of φ by a contour integral might be useful in connection with analytic range-functions $F(\rho r)$.

According to Eq. (11), the *relative* effect of the collecting field reaches its maximum for *small* initial separations r, in which case

$$e^{2q/r}\varphi(r,\ \Theta)\rightarrow J_0(4(-\beta q)^{\frac{1}{2}}\cos\tfrac{1}{2}\Theta).\tag{12}$$

The variation of φ with r is best brought out by expansion in powers of q as follows

$$e^{2q/r}\varphi(r,\ \Theta)=1+(2q/r)(1-e^{-\beta r(1+\cos\Theta)})+O(\beta^2),\tag{13}$$

where the factor implied by $O(\beta^2)$ has an upper bound independent of r and Θ. Expansion in power series of the field intensity yields

$$e^{2q/r}\varphi = 1 + 2\beta q(1+\cos\Theta) + O(\beta^2), \qquad (14)$$

where the approximation is no longer uniform in r;—naturally $\varphi < 1$. Even with this reservation, it is remarkable enough that in the limit represented by Eq. (14), the relative effect of the field is independent of the distance r, although it depends on the direction Θ.

In comparing these predictions with experience, we may rely on the diffusion of the electrons before capture to produce a practically isotropic distribution of directions. Hence, in the approximation expressed by Eq. (14), the yield of ions escaping initial recombination will be

$$I(X)/I(0) = 1 + 2\beta q = 1 + 9.64|X|/DT^2. \qquad (15)$$

For $D=1$, $T=300$ we get

$$2\beta q = 1.07\times 10^{-4}|X|.$$

The predicted effects are somewhat larger than those recently observed by Broxon and Merideth[8] for field intensities from 1500 to 4500 volts/cm in air at pressures of 20–200 atmospheres. The deficiency is greater the lower the pressure, and might well be ascribed to saturation in the sense of Eq. (13). On the other hand, the field effects observed by Broxon and Merideth for the range 10–1000 volts/cm are substantially greater than those expected for initial recombination alone. It should be observed that the theory permits but little leeway in this direction, dependent on the greater values of q and β for ions carrying more than a single charge,[5] and allowance for a reasonable proportion of these hardly makes a difference. The discrepancy varies about linearly with the logarithm of the field intensity, which is precisely what one should expect if *some columnar recombination takes place*. For pressures of 100–200 atmospheres and electric fields of the order 1000 volts/cm, the number of ions thus removed would amount to 20 ± 10 percent of those which escape initial recombination. Attractive though this explanation is, I hesitate to accept it as final because the expected variation with the lineal density of ions in the "columns" (for which the total current is an independent measure) refuses to appear in the data. The latter circumstance might perhaps be better explained by simultaneous ejection of several electrons to form a cluster of ions; but I am not ready to support this hypothesis either without more direct evidence.

This and some other puzzling details will hardly affect the conclusion that initial recombination is the most important process which interferes with the collection of ions at high pressures, except in the case of heavy ionizing particles. The theory developed here is of course widely applicable to phenomena of ionization, whether by α-rays, β-rays, other ionizing particles, or ordinary photons, wherever this type of recombination occurs as a prominent or minor factor. The agent which liberates the original electrons is not as important as their opportunity for subsequent energy losses and attachment to molecules; in this respect, different types of environment offer enormous variations.

In the particular case of air, it is known that the oxygen molecules are responsible for the attachment of the electrons. It is gratifying that the median diffusion range of the ejected electrons before attachment, as inferred from the observations in connection with the present theory,—of the order 5×10^{-6} cm at 100 atmospheres pressure—seems compatible with our knowledge about the interaction between electrons and oxygen molecules.[9]

[8] J. W. Broxon and G. T. Merideth, Phys. Rev. **54**, 1 (1938).

[9] F. Bloch and N. E. Bradbury, Phys. Rev. **48**, 689 (1935).