

tude of the binding can be determined by a consideration of the oxides, which are isoelectronic with the ions. For example, the vibration frequency of the normal state of CaO is  $843\text{ cm}^{-1}$ .<sup>12</sup> A correction for the difference of reduced mass gives  $790\text{ cm}^{-1}$  as an approximate estimate of the vibration frequency of CaF<sup>+</sup>, indicating considerably stronger binding than in the CaF normal state ( $\omega_e'' = 587\text{ cm}^{-1}$ ). SrF and BaF give similar results. It seems reasonable, then, on the hypothesis that the excitation of the  $x\sigma$  electron alone determines the higher energy states of this group of molecules, that those states should be more firmly bound than the normal state configuration.

<sup>12</sup> P. H. Brodersen, *Zeits. f. Physik* **104**, 135 (1936).

The continua that appear at the ultraviolet limit of the spectrum in the case of every molecule investigated can be reasonably attributed each to its specific molecule. Some repulsive excited states of relatively high energy are theoretically predicted for most molecules, and only in absorption at high temperature can transitions involving such states be observed in many cases. Although the possibility exists that all the continua are due to some persistent impurity, the appearance of the  $\lambda 2180$  continuum of CaF is certainly characteristic, and probably the others are also.

In conclusion the writer wishes to thank Professor F. A. Jenkins, whose direction and criticism were of considerable assistance in this investigation.

## On the Joint Action of Diffusion and Recombination of Ions

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The differential equation which describes the joint action of diffusion and recombination of ions is solved, for the one-dimensional case, by a method previously developed by the author. In Section I, the decay of a given initial distribution of ions is treated. The observable coefficient of recombination, as modified by diffusion, depends strongly in the initial stage on the given distribution. For later times it depends in a simple way on the density of ionization and the distance between the collecting plates.

### INTRODUCTION

**I**N all measurements on recombination of ions diffusion plays a noticeable and often an important part. This holds whether the ionized volume extends to the collecting electrodes or not. For, in the former case, ions are lost to the electrodes and, in the latter case, the ionized volume increases by diffusion, thus affecting the apparent coefficient of recombination.

Langevin<sup>1</sup> was the first to recognize the importance of diffusion in measurements on recombination. As early as 1905 he solved the problem of the steady state created by a constant pro-

In Section II, the establishment of the steady state, with constant production of ions, is calculated. Diffusion introduces a linear term which may, for sufficiently small values of the ionic density and the electrode distance, mask the usual quadratic term. In Section III, it is shown that anomalies observed by Gardner in the recombination coefficient of oxygen and by Power in the establishment of the steady state in air are explained, without further assumptions, by diffusion to the walls.

duction of ions between parallel plates under the joint action of recombination and diffusion. His results do not seem to have found the attention which they deserve. In quite a number of cases where their application would have been of value they were replaced by less accurate computations. In more recent measurements on recombination, all observers had to correct their results for diffusion and did it somehow or other,<sup>2</sup> but none of the formulae used are adequate.

<sup>1</sup> A. D. Power, *J. Frank. Inst.* **196**, 327 (1923); L. C. Marshall, *Phys. Rev.* **34**, 618 (1929); O. Luhr, *Phys. Rev.* **35**, 1394 (1930); **36**, 24 (1930); P. Kraus, *Ann. d. Physik* **29**, 449 (1937); M. E. Gardner, *Phys. Rev.* **53**, 75 (1938); J. Sayers, *Proc. Roy. Soc.* **A169**, 83 (1938).

<sup>1</sup> P. Langevin, *J. de phys.* (4) **4**, 322 (1905).

Under these circumstances it seemed desirable to the author to develop formulae for the non-steady state, because Langevin's results are of no avail in cases where the change of ionization with time is observed. The following calculations refer to the case where the problem depends only on one local coordinate,  $x$ .

I. DECAY OF A GIVEN INITIAL DISTRIBUTION

We shall disregard the difference in mobility of positive and negative ions. Let  $n$  signify, under these conditions, their common density,  $D$  their coefficient of diffusion and  $\alpha$  the coefficient of recombination. Then the problem to be solved will be given by

$$\partial n / \partial t = D \partial^2 n / \partial x^2 - \alpha n^2 \tag{1.01}$$

with suitable boundary and initial conditions. We shall assume that the volume under consideration extends from  $x=0$  to  $x=l$ . Then it will be required that

$$n=0 \text{ for } x=0 \text{ and } x=l, \tag{1.02}$$

and that  $n$  reduces to a given initial distribution

$$n=n_0(x) \text{ for } t=0. \tag{1.03}$$

The nonlinear partial differential equation (1.01) can be solved by a rigorous method developed by Lichtenstein,<sup>3</sup> but the results are involved and hold only for sufficiently small values of  $t$ . The author, therefore, has preferred to use an approximate method which was introduced by him into the theory of columnar ionization and which has been used since in various cases.<sup>4</sup> Its usefulness lies in the fact that it is applicable to all values of  $t$  and all values of the involved parameters.

The method is as follows. Let  $n'(x, t)$  be the exact solution of (1.01) in the case where recombination is disregarded ( $\alpha=0$ ). Then it is assumed that the solution of the complete Eq. (1.01) is of the form

$$n(x, t) = N(t)n'(x, t). \tag{1.04}$$

<sup>3</sup> L. Lichtenstein, *J. f. d. reine u. angew. Math.* **158**, 80 (1927).

<sup>4</sup> G. Jaffé, *Ann. d. Physik* **42**, 303 (1913); **1**, 977 (1929); D. E. Lea, *Proc. Camb. Phil. Soc.* **30**, 80 (1934); L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, New York, 1939), p. 134 and following.

The function  $N(t)$  is determined by introducing (1.04) into (1.01), integrating with regard to  $x$  from  $x=0$  to  $x=l$  and thus transforming (1.01) into an ordinary differential equation for  $N(t)$ , namely

$$dN/dt = -\alpha f(t)N^2, \tag{1.05}$$

where

$$f(t) = \int_0^l n'^2 dx / \int_0^l n' dx. \tag{1.06}$$

We shall normalize  $n'$  by the condition

$$\int_0^l n'(x, 0) dx = 1. \tag{1.07}$$

Then  $N$  will represent the total ionization per cm<sup>2</sup> section and  $N_0$  the respective initial value.

The solution  $n'(x, t)$  is easily found by known methods. If the initial distribution is supposed to be given in the form of a Fourier series

$$n'(x, 0) = \sum_{m=1}^{\infty} A_m \sin(m\pi x/l) \tag{1.08}$$

(where the  $A_m$ 's have to be subjected to the condition resulting from (1.07)) we shall have

$$n'(x, t) = \sum_{m=1}^{\infty} A_m e^{-m^2 \tau} \sin(m\pi x/l), \tag{1.09}$$

where

$$\tau = D\pi^2 t/l^2. \tag{1.10}$$

Making use of (1.09) we can evaluate (1.06) and then solve (1.05) by separation of the variables. For our purposes, however, it is preferable to introduce first the "mean ionic density" defined by

$$\bar{n}(t) = (N(t)/l) \int_0^l n'(x, t) dx. \tag{1.11}$$

Differentiating Eq. (1.04) with regard to  $t$  we find after some transformations

$$d\bar{n}/dt = -\bar{\alpha}\bar{n}^2 - \bar{D}\bar{n}, \tag{1.12}$$

where

$$\bar{\alpha} = \alpha l \left[ \int_0^l n'^2 dx / \left( \int_0^l n' dx \right)^2 \right] \tag{1.13}$$

and

$$\bar{D} = D \left[ \left( \left( \frac{\partial n'}{\partial x} \right)_0 - \left( \frac{\partial n'}{\partial x} \right)_l \right) / \int_0^l n' dx \right]. \tag{1.14}$$

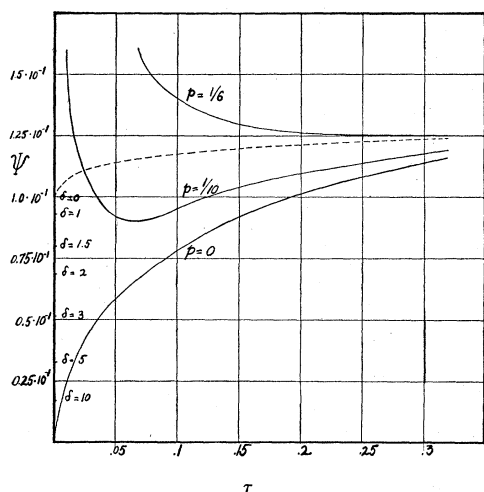


FIG. 1. Representation of  $\Psi$  as a function of  $\tau$ . The three full curves correspond to constant initial ionization of different breadth, the parameter  $p=a/l$  being given by 0,  $1/10$ ,  $1/6$  respectively. The broken line corresponds to the parabolic initial distribution which results from diffusion alone (see (1.26)).

Equation (1.09) then yields

$$\bar{\alpha} = \alpha \pi^2 S_1 / 8 S_3^2, \quad (1.15)$$

$$\bar{D} = D \pi^2 S_2 / l^2 S_3, \quad (1.16)$$

where  $S_1, S_2, S_3$  represent the sums

$$S_1 = \sum_{m=1}^{\infty} A_m^2 \exp(-2m^2\tau), \quad (1.17)$$

$$S_2 = \sum_{\mu=0}^{\infty} (2\mu+1) A_{2\mu+1} \exp(-(2\mu+1)^2\tau), \quad (1.18)$$

$$S_3 = \sum_{\mu=0}^{\infty} (2\mu+1)^{-1} A_{2\mu+1} \exp(-(2\mu+1)^2\tau). \quad (1.19)$$

Thus the mean ionic density decreases according to a law involving a quadratic and a linear term, and the respective coefficients,  $\bar{\alpha}$  and  $\bar{D}$ , are average values depending on the initial distribution (the  $A_m$ 's) and the time ( $\tau$ ).

For comparison with experimental data (1.12) can be written in the form

$$d\bar{n}/dt = -\alpha^* \bar{n}^2, \quad (1.20)$$

where

$$\alpha^* = \bar{\alpha} (1 + \bar{D} / \bar{\alpha} \bar{n}). \quad (1.21)$$

This  $\alpha^*$  can be interpreted as the "instantaneous coefficient of recombination" which varies with time owing to diffusion.

The quotient

$$\bar{\alpha} \bar{n}^2 / \bar{D} \bar{n} = (\alpha/D) \bar{n} l^2 \psi, \quad (1.22)$$

where

$$\psi = S_1 / 8 S_2 S_3 \quad (1.23)$$

represents the ratio of the loss by recombination to that by diffusion.

Let us now evaluate  $\bar{\alpha}$  and  $\psi$  in two special cases.

### (a) First case

The initial distribution is given by the following:

$$\begin{aligned} n_0(x) &= 0 & \text{for } 0 < x < a, \\ n_0(x) &= \text{const.} & \text{for } a < x < (1-a), \\ n_0(x) &= 0 & \text{for } (1-a) < x < 1. \end{aligned}$$

The constant is determined by the normalizing equation (1.07). We obtain

$$\begin{aligned} A_{2\mu+1} &= [4 / (\pi(l-2\alpha)(2\mu+1))] \\ &\times \cos((2\mu+1)\pi a/l), \quad \mu=0, 1, 2, \dots \end{aligned} \quad (1.24)$$

and this solution includes the limiting case  $a=0$  where the initial ionization extends to the collecting plates. Upon introducing (1.24) into (1.15) and (1.23) it is seen that  $\bar{\alpha}$  and  $\psi$  depend only on  $\tau$  and the parameter

$$p = a/l. \quad (1.25)$$

They are represented in Figs. 1 and 2 for the three values  $p=0, \frac{1}{10}, \frac{1}{6}$  as functions of  $\tau$ .

### (b) Second case

The initial distribution is assumed to be

$$n_0(x) = qx(l-x)/2D, \quad (1.26)$$

where  $q$  is a constant. This assumption leads to

$$N_0 = ql^3/12D \quad (1.27)$$

and

$$A_{2\mu+1} = 48 / (l\pi^3(2\mu+1)^3), \quad \mu=0, 1, 2, \dots \quad (1.28)$$

The corresponding curves for  $\bar{\alpha}$  and  $\psi$  are drawn by broken lines in the Figs. 1 and 2.

The significance of (1.26) is that it represents the steady state distribution if there is a constant production of  $q$  pairs of ions per sec. and  $\text{cm}^3$  and if conditions are such that recombination can be disregarded.

In the more general case where diffusion and recombination must be considered the steady

state distribution depends, according to Langevin,<sup>1</sup> on a "reduced distance" for which we choose<sup>5</sup>

$$\delta = l(q\alpha/36D^2)^{1/2}. \quad (1.29)$$

The steady state distribution is then given by an elliptic function and the coefficients  $A_m$  can be evaluated, even in this case, by harmonic analysis. However, this necessity will rarely occur. The above calculations give  $\bar{\alpha}$  and  $\psi$  in the limiting case  $\delta \ll 1$ . In the other limiting case,  $\delta \gg 1$ , the distribution will approach  $n_0 = \text{const.}$ , i.e., case (a) with  $p=0$ . Thus the curves for variable  $\delta$  will lie between those limiting cases. Furthermore, the points from which they start at  $\tau=0$ , can be determined from calculations which the author has made in another connection.<sup>6</sup> Some such points are indicated in Fig. 1 and it will be seen that a fair estimate of  $\psi$  can be made for all values of  $\delta$  and  $\tau$  by graphical interpolation. The changes of  $\bar{\alpha}$  are unimportant.

Our Fig. 1 shows that, for small values of  $\tau$ , there are significant changes of  $\psi$  with  $\tau$ , depending on the initial distribution. For values  $\tau > 0.2$  all curves approach the asymptotic value  $\psi = 0.125$  which holds for all distributions (see (1.23)).

The initial stage of rapid changes does not extend much beyond the period of initial recombination which our theory does not include. Therefore, for small values of  $\tau$ , our calculations are not applicable and for larger values it will, in most cases, be sufficient to give  $\psi$  its asymptotic value. The relative influence of diffusion can then easily be deduced from (1.22). This formula brings out the influence of  $l$  and the ionic density. For sufficiently large values of the time diffusion will always be predominant owing to the decrease of  $\bar{n}$ .

The changes in  $\bar{\alpha}$  are far less important, as is seen from Fig. 2. The larger the parameter  $p$ , the more marked is the initial decrease of the apparent coefficient of recombination. This increase is due to the broadening of the ionized volume. It must be stressed that our calculations

(according to (1.11)) refer  $\bar{\alpha}$  to the total volume extending from  $x=0$  to  $x=l$ . If the volume is referred to the part initially ionized, as is generally done by experimenters, our values of  $\bar{\alpha}$  have to be multiplied by  $(l-2a)/l$  which makes them start with the normal value  $\bar{\alpha} = \alpha$  and then decrease. The asymptotic value of  $\bar{\alpha}$  is given by  $\bar{\alpha} = \alpha\pi^2/8$  for all initial distributions.

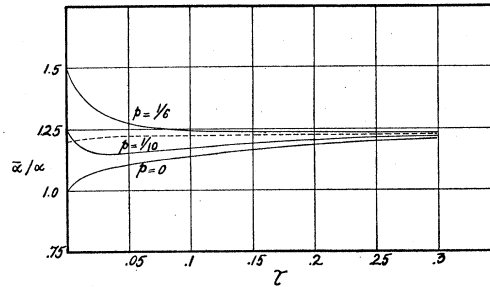


FIG. 2. Representation of  $\bar{\alpha}/\alpha$  as a function of  $\tau$ . The three full curves correspond to constant initial ionization of different breadth, the parameter  $p = a/l$  being given by 0, 1/10, 1/6 respectively. The broken line corresponds to the parabolic initial distribution which results from diffusion alone (see (1.26)).

## II. ESTABLISHMENT OF THE STEADY STATE

We will assume that there is no ionization up to  $t=0$  and that, from  $t=0$  on, there is a constant production, of  $q$  pairs of ions per sec. and  $\text{cm}^3$ , in the whole volume. The differential equation then becomes

$$\partial n / \partial t = q + D \partial^2 n / \partial x^2 - \alpha n^2, \quad (2.01)$$

with the same boundary conditions as in Section I.

Let us assume

$$n_\infty(x) = \sum_{m=1}^{\infty} B_m \sin(m\pi x/l) \quad (2.02)$$

as the solution for the steady state. Then we attempt to solve (2.01) by putting

$$n(x, t) = n_\infty(x) - N_1(t)n'_1(x, t). \quad (2.03)$$

Here  $N_1(t)$ , a function of time only, is normalized by

$$N_1(0) = 1 \quad (2.04)$$

and

$$n'_1(x, t) = \sum_{m=1}^{\infty} B_m e^{-m^2\tau} \sin(m\pi x/l) \quad (2.05)$$

<sup>5</sup> G. Jaffé, Ann. d. Physik **43**, 249 (1914).

<sup>6</sup> Reference 5, p. 267 and following. Table I on p. 270 may be used but it must be mentioned that the indications of this table are not sufficiently accurate for the present purpose for values of  $\delta < 0.4$ . Also the expansions (52) and (56) must be carried further.

is that solution of

$$\partial n_1'/\partial t = D\partial^2 n_1'/\partial x^2, \quad (2.06)$$

which reduces, for  $t=0$ , to  $n(x)$ .

It is evident that (2.03) satisfies the initial and boundary conditions. To determine  $N_1(t)$  we use the same procedure as in Section I and find the ordinary differential equation

$$dN_1/dt = -2\alpha f_1(t)N_1 + \alpha f_2(t)N_1^2, \quad (2.07)$$

where

$$f_1(t) = \int_0^l n_\infty n_1' dx / \int_0^l n_1' dx \quad (2.08)$$

and

$$f_2(t) = \int_0^l n_1'^2 dx / \int_0^l n_1' dx. \quad (2.09)$$

Introducing again the "mean ionic density"

$$\bar{n}_1 = (N_1(t)/l) \int_0^l n_1' dx \quad (2.10)$$

we find

$$d\bar{n}_1/dt = -(2\bar{\alpha}_1\bar{n}_\infty + \bar{D})\bar{n}_1 + \bar{\alpha}\bar{n}_1^2. \quad (2.11)$$

Here  $\bar{\alpha}$  and  $\bar{D}$  are defined as in (1.13), (1.14) ( $n_1'$  replacing  $n'$ ) and  $\bar{\alpha}_1$  is given by

$$\bar{\alpha}_1 = \alpha l \left[ \int_0^l n_\infty n_1' dx / \left( \int_0^l n_\infty dx \cdot \int_0^l n_1' dx \right) \right]. \quad (2.12)$$

To compare conditions with those prevailing in the absence of diffusion we solve the differential equation

$$dn/dt = q - \alpha n^2 \quad (2.13)$$

by

$$n = n_\infty - n_i. \quad (2.14)$$

Here  $n_\infty$  represents the solution for the steady state

$$n_\infty = (q/\alpha)^{1/2}, \quad (2.15)$$

and  $n_i$  is subject to the condition:

$$n_i = n_\infty \quad \text{for } t=0.$$

Substituting (2.14) into (2.13) we find

$$dn_i/dt = -2\alpha n_\infty n_i + \alpha n_i^2, \quad (2.16)$$

and this equation has to be compared with (2.11).

From (2.16) we see that, even in the absence of diffusion, the rate of change  $dn_i/dt$  ( $= -dn/dt$ ) can be represented by the sum of a linear and a

quadratic term. If, now, diffusion is taken into account comparison with (2.11) shows that the linear term is increased by a term involving  $\bar{D}$ . Thus the establishment of the steady state will tend to deviate from the quadratic law towards a linear law. The larger  $\bar{D}$  is in comparison with  $2\bar{\alpha}_1\bar{n}_\infty$  the more the linear term will prevail. The conditions of experiment will then determine whether we obtain a better representation by a quadratic law

$$d\bar{n}_1/dt = -\alpha^*\bar{n}_1^2 \quad (2.17)$$

using the time-dependent coefficient of recombination

$$\alpha^* = (2\bar{\alpha}_1\bar{n}_\infty + \bar{D})/\bar{n}_1 - \bar{\alpha}, \quad (2.18)$$

or by a linear law

$$d\bar{n}_1/dt = -\beta^*\bar{n}_1, \quad (2.19)$$

where

$$\beta^* = 2\bar{\alpha}_1\bar{n}_\infty - \bar{\alpha}\bar{n}_1 + \bar{D}. \quad (2.20)$$

For large values of  $\delta$ , only thin layers near the plates are affected by diffusion. For  $\delta$  larger than 2 or 3,  $n_\infty$  in (2.02) can be replaced by its limiting value (2.15). Under these conditions we have, from (2.12)

$$\bar{\alpha}_1 = \alpha. \quad (2.21)$$

### III. COMPARISON WITH EXPERIMENT

The preceding formulae were developed to yield adequate corrections for measurements on recombination. Their application clarifies anomalies in previous measurements.

#### (a) Experiments on decay

The most accurate measurements of  $\alpha$  concerning a well-defined pure gas are presumably those of Gardner<sup>7</sup> on oxygen. These measurements show the striking fact that the observed values of  $\alpha$  depend strongly on the time of exposure,  $t'$ , and on the ionic density. After the first large drop (due to initial recombination) the observed values become practically constant, but the apparently constant value decreases as  $t'$  increases. Furthermore, the values belonging to different  $t'$ 's move apart if the pressure, or the distance between the plates, is decreased. Loeb<sup>8</sup> has shown that these phenomena cannot be explained by his theory of initial recombination

<sup>7</sup> M. E. Gardner, reference 2.

<sup>8</sup> L. B. Loeb, reference 4, p. 136 and following.

TABLE I. The values of  $\alpha$  observed by Gardner are compared with values calculated from formula (1.21).

|  | $t'$   | $n_0$              | $\alpha^* \times 10^6$ CALC. |                 | $\alpha \times 10^6$ OBS. |
|--|--------|--------------------|------------------------------|-----------------|---------------------------|
|  |        |                    | $t=0.1$<br>SEC.              | $t=0.3$<br>SEC. | $t=0.1$<br>SEC.           |
| $V=190 \text{ cm}^3$<br>$l=3 \text{ cm}$<br>$a=0.3 \text{ cm}$<br>$P=76 \text{ cm Hg}$<br>$\alpha=1.98 \times 10^{-6}$<br>$D=4.7 \times 10^{-2}$ | 0.5    | $1.00 \times 10^6$ | 2.00                         | 2.03            | 1.99                      |
|  | 0.25   | $6.45 \times 10^5$ | 2.03                         | 2.06            | 2.12                      |
|  | 0.0625 | $1.79 \times 10^5$ | 2.20                         | 2.22            | 2.25                      |
|  | 0.0313 | $0.90 \times 10^5$ | 2.42                         | 2.45            | —                         |
| $V=190 \text{ cm}^3$<br>$l=3 \text{ cm}$<br>$a=0.3 \text{ cm}$<br>$P=38 \text{ cm Hg}$<br>$\alpha=1.48 \times 10^{-6}$<br>$D=9.4 \times 10^{-2}$ | 0.5    | $6.07 \times 10^5$ | 1.61                         | 1.65            | 1.58                      |
|  | 0.25   | $3.45 \times 10^5$ | 1.72                         | 1.75            | 1.64                      |
|  | 0.0625 | $8.93 \times 10^4$ | 2.41                         | 2.44            | 2.07                      |
|  | 0.0313 | $4.46 \times 10^4$ | 3.32                         | 3.37            | —                         |
| $V=700 \text{ cm}^3$<br>$l=7 \text{ cm}$<br>$a=1 \text{ cm}$<br>$P=10 \text{ cm Hg}$<br>$\alpha=0.85 \times 10^{-6}$<br>$D=3.57 \times 10^{-1}$  | 0.5    | $1.84 \times 10^5$ | 1.05                         | 1.06            | 1.04                      |
|  | 0.25   | $9.42 \times 10^4$ | 1.32                         | 1.33            | 1.56                      |
|  | 0.125  | $4.72 \times 10^4$ | 1.87                         | 1.88            | 2.55                      |
|  | 0.0625 | $2.37 \times 10^4$ | 2.96                         | 2.98            | 4.86                      |

unless improbable values for the coefficient of diffusion are assumed.

Our formulae show that the observed phenomena are due, at least to a considerable part, to diffusion to the walls. In order to apply our exact formula (1.21) we should know accurately the initial distribution of the ions. Now, this initial distribution depends strongly on the time of exposure  $t'$ . It would be possible to calculate the distribution of the ions as a function of  $t'$  by the method of Section II. Such a calculation, however, would hardly be worth while because the initial distribution affects mainly the changes in  $\alpha$  for those intervals of time where initial recombination is prevalent and masks the changes foreseen by our theory. We have, therefore, applied the approximate asymptotic formulae.

Some of the results of our calculations are compared, in Table I, with the observed values as taken from Gardner's diagrams. As the exact values of the ionic densities were not known, they were calculated under the assumption that  $n_0 = 1 \times 10^6$  for atmospheric pressure and that  $q$  is proportional to the pressure. For this purpose the observed *apparent* values of  $\alpha$  were substituted into the simple law (2.13).<sup>9</sup>

<sup>9</sup> The author is very much indebted to Professor Loeb and Professor Gardner for furnishing him information concerning the measurements.

The values of  $D$  used and the true values of  $\alpha$ , as corrected for diffusion, are also indicated in the table. From the calculated values it will be seen that diffusion, under the conditions of Gardner's experiments, has a very marked influence on the coefficient of recombination. It will be noticed that the values of  $\alpha^*$  may appear to be constant over a considerable interval of time though they are different from the true value  $\alpha$ . Furthermore, the apparent values move apart with decreasing  $t'$  and  $n_0$ , as observed.

The numerical agreement is about as good as might be expected from the approximate nature of the calculations. The theoretical deviations are too large for the pressure  $P=38 \text{ cm Hg}$  and too small for  $P=10 \text{ cm Hg}$ . The former deviation is probably due to the fact that the assumed values of  $n_0$  are too small, the latter deviation to the fact that initial recombination (at  $P=10 \text{ cm Hg}$ ) is not yet quite over at  $t=0.1 \text{ sec}$ .

It must be emphasized that the only numerical values assumed arbitrarily in the preceding calculations are the true values of  $\alpha$  which are to be determined. The apparent increase in the observed values is due to the fact that, at the time when the initial recombination is over, diffusion to the walls has become important. Because of the decrease of  $\bar{n}$ , the observable  $\alpha^*$  ought to increase slowly afterwards (see (1.21)) and should pass through a very flat minimum. This mini-

TABLE II. The values of  $\alpha$  and  $\beta$  observed by Power are compared with values calculated from formulae (2.18) and (2.20). The value underlying the calculations is  $\alpha = 1.6 \times 10^{-6}$ .

| GROUP | $n_{\infty}$ | $q$  | $\alpha \times 10^6$<br>OBS. | $\beta \times 10^3$<br>OBS. | $\alpha^* \times 10^6$ CALC. |                 | $\beta^* \times 10^3$ CALC. |                 |
|-------|--------------|------|------------------------------|-----------------------------|------------------------------|-----------------|-----------------------------|-----------------|
|       |              |      |                              |                             | $t=0$                        | $t=120$<br>SEC. | $t=0$                       | $t=120$<br>SEC. |
| I     | 1070         | 11.8 | 4.53                         | 6.61                        | 5.05                         | 13.3            | 5.40                        | 5.70            |
| II    | 1620         | 21.9 | 3.65                         | 8.00                        | 4.13                         | 11.6            | 6.70                        | 7.52            |
| III   | 2680         | 33.8 | 2.12                         | 8.46                        | 3.31                         | 10.3            | 8.85                        | 11.0            |

mum has been observed by Gardner with his smaller condenser ( $l=3$  cm) at  $P=76$  cm Hg. In all other cases it should have occurred at times  $t$  larger than those observed.

Concerning the influence of the initial density,  $n_0$ , our formula predicts a change of 3.5, 17, 272 percent for 76, 38, 10 cm Hg, respectively, if  $n_0$  is changed from  $10^6$  to  $10^5$  at atmospheric pressure. These numbers refer to conditions in Gardner's larger vessel ( $l=7$  cm) where the influence of diffusion is less marked. They agree, approximately, with the observed changes except at  $P=76$  cm Hg where a discrepancy remains, the theoretical change being too small (3.5 percent as against about 20 percent).

#### (b) Establishment of the steady state

It was first pointed out by von Schweidler<sup>10</sup> that the establishment of the steady state is, in cases of weak ionization, described more accurately by a linear law than by the usual quadratic law. This fact has been confirmed by Power<sup>11</sup> and suggests strongly that diffusion is active.<sup>12</sup>

As Power's values show considerable fluctuations we have formed three groups out of the data contained in his Table VII. The first group with 6 observations where  $n_{\infty}$  (as corrected by Power for diffusion) ranges from 1480 to 1780, the second includes 6 values from 2130 to 2720 and the last group 5 values from 3490 to 4560.

<sup>10</sup> E. von Schweidler, Akad. Wiss. Wien **127**, (2a), 953-967 (1918); **128**, (2a), 947-955 (1919).

<sup>11</sup> A. D. Power, J. Frank. Inst. **196**, 327 (1923).

<sup>12</sup> The author is indebted to Professor J. W. Broxon for making accessible to him, at the University of Colorado, a Doctor's thesis by G. T. Merideth on recombination at high pressures. In the measurements of Dr. Merideth the same fact was observed.

The calculations are based on the exact formulae (2.18) and (2.20), respectively, and on the normal values  $D=0.035$ ,  $\alpha=1.6 \times 10^{-6}$ . The geometrical conditions required  $l=12.6$  cm,  $a=0$ ;  $\alpha^*$  and  $\beta^*$  were calculated for  $t=0$  and  $t=120$  sec.<sup>13</sup>

It will be seen from Table II that the calculated values of  $\beta^*$  are much more nearly constant than those of  $\alpha^*$  and that they agree within reasonable limits with the observed values though no constant has been chosen so as to obtain agreement. A better agreement might be attained by making  $\alpha$  different from  $1.6 \times 10^{-6}$  but there can scarcely be a doubt that the apparent high values of  $\alpha$  in Power's experiments are largely due to diffusion, in spite of the relatively large distance between the plates.

However, it must be pointed out that von Schweidler and Power report measurements with very much larger condensers in which the value of  $\alpha$  appears to be as high as  $1 \times 10^{-4}$ . Under these conditions the observed values cannot be explained by diffusion to the walls alone. These discrepancies at large volumes, as well as the discrepancy mentioned above, indicate that some other influence is active. It seems reasonable to assume that besides diffusion in molecular dimensions (initial recombination) and diffusion in macroscopic dimensions (the factor studied here) some intermediate inhomogeneity in the initial distribution may play a part. It is, however, premature to assert such an influence before further measurements in this direction have been carried out.

<sup>13</sup> For  $t=120$  sec. asymptotic values and the legitimate approximation (2.21) were introduced.