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XXI. *On the Rate of Recombination of Ions in Gases.* By GEORGE W. WALKER, M.A., A.R.C.Sc.; *Fellow of Trinity College, Cambridge, and Lecturer in Physics in the University of Glasgow* *.

THE importance of this subject, at which Mr. McClung has been an enthusiastic worker for some time, will hardly be questioned.

In examining carefully his papers † I have observed what appear to me to be somewhat serious discrepancies in the results, which require explanation before one can accept the conclusions at which he arrives.

The following criticisms are not made from lack of appreciation of the enormous experimental difficulties; for I was working in the same laboratory when the later experiments were made, and saw Mr. McClung very frequently. At the same time, the important generalizations made from the experiments demand for proof substantial agreement between theory and experiment, whatever the difficulties may be.

We shall first recapitulate the fundamental assumptions, but shall assume that the reader has the papers at hand.

If q is the rate of production of ions (in this case by Röntgen rays) per unit volume, and n is the number of ions per unit volume; then, when a steady state is reached,

$$q = \alpha n^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α is the coefficient of recombination.

Again, when the rays are cut off,

$$\frac{1}{n_t} - \frac{1}{n_0} = \alpha t, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n_0 is the number of ions per unit volume when the rays cease, and n_t is the number per unit volume which remain after a time t .

It is shown that

$$\alpha = K \cdot Q/N^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Q is the total rate of production in the given volume, and N is the total number in the given volume when the steady state is reached, and therefore at the instant the rays cease.

K is a constant depending on the dimensions of the apparatus.

We may call N_t the number of ions existing in the given volume after a time t .

* Communicated by the Author.

† Phil. Mag. vol. iii. pp. 283-305 (1902), vol. vi. pp. 655-666 (Dec. 1903), vol. vii. pp. 81-95 (Feb. 1904).

In the experiments N_t and N were measured. It is further assumed that the saturation current gives a measure of Q .

The absorption of the rays is neglected as small.

From the measurements of Q and N , McClung concludes that α as given by the formula (3) is independent of the pressure from $\frac{1}{4}$ atmosphere to 3 atmospheres. He also concludes that Q is proportional to the pressure, the intensity of the rays remaining constant. If this is so, then N^2 should be proportional to the pressure, the intensity of the rays being constant.

In testing the formula (1), it appears to me that he assumes the relation between N_t , N , and t to be of the same form as (1). This, as I shall show, is not the case in his experiments. It would be true if the beam of rays were cylindrical.

He does not think the measurements of N_t , N , and t at different pressures can be relied on to find how α depends on the pressure, urging that the intensity of the rays may vary between the experiments at different pressures. I am unable to follow this argument. α is a property of the gas, and must be independent of the means by which the N ions are produced. It is quite true that both Q and N depend on the intensity of the rays; but if the theory as proposed is correct, the values of α , whether obtained from (3) or from the relation between N_t and N , must be the same, and quite independent of the intensity of the rays, provided that the intensity is the same for any one determination of N and Q .

We shall now establish the relation between N_t , N , and t . Using the same notation as McClung, we have

$$q_0 = \frac{Q}{A_1 l} = \frac{\alpha N^2}{l^2 A_1^2 \left(1 + \frac{l}{2d}\right)^2},$$

$$n_t = \frac{n_0}{1 + n_0 \alpha t},$$

and

$$n_0 = \frac{d}{x} \sqrt{\frac{q_0}{\alpha}}.$$

Hence the total number in the given conical volume after a time t is

$$\begin{aligned} N_t &= \int_d^{d+l} n_t \frac{A_1 x^2}{d^2} dx \\ &= N \left\{ 1 - \frac{\mu}{\left(d + \frac{l}{2}\right)} + \frac{\mu^2}{l \left(d + \frac{l}{2}\right)} \log_e \left(1 + \frac{l}{d + \mu}\right) \right\} \end{aligned}$$

where

$$\mu = \lambda t,$$

and

$$\lambda = d \sqrt{q_0 \alpha}.$$

Hence

$$\alpha = \frac{\lambda}{N} \frac{l \left(1 + \frac{l}{2d}\right) A_1}{d}, \quad \dots \dots \dots (4)$$

or

$$\alpha = \frac{\lambda^2}{Q} \cdot \frac{A_1 l}{d^2}, \quad \dots \dots \dots (5)$$

or

$$\alpha = \frac{Q}{N^2} l A_1 \left(1 + \frac{l}{2d}\right)^2. \quad \dots \dots \dots (6)$$

If we use the values of l and d given in the paper, we get

$$\frac{N_t}{N} = 1 - \frac{\mu}{35 \cdot 07} + \frac{\mu^2}{701 \cdot 4} \log_e \left(1 + \frac{20}{25 \cdot 07 + \mu}\right). \quad \dots \dots (7)$$

It is quite easy to test the results. We have only to substitute a value of μ , and calculate the value of the expression on the right-hand side. Then, since we know N , we can calculate the value of N_t ; and hence from the experimental curve we get the value of t , and hence of λ . The values of λ for a given pressure should agree. Having obtained λ , we may get the absolute value of α by any of the three formulæ (4), (5), and (6); and the values so obtained should be the same. As I have already pointed out, these values cannot be affected by the intensity of radiation.

With a view to testing these points, the following table was prepared from the results given in McClung's paper (Phil. Mag. March 1902, pp. 293-296). In preparing it the values of μ were substituted in the expression on the right-hand side of (7), and then the values of t obtained from the experimental curves.

Pressure in Atmospheres.	μ .	$\frac{N_t}{N}$.	t .	$\lambda = \frac{\mu}{t}$.	Deflexion for N.	$\frac{\lambda}{N}$.
3	100	·266	·41	244	236	
3	50	·417	·20	250	236	1·06
2	100	·266	·47	212	196	
2	50	·417	·23	217	196	1·10
1	100	·266	·54	185	181	
1	50	·417	·28	178	181	·98
·5	100	·266				
·5	50	·417	·34	147	154	·95
·25	100	·266				
·25	50	·417	·53	94	136	·69
·125	100	·266				
·125	50	·417	·47	106	124	·83

The agreement between the values of λ for any one pressure is very satisfactory. But if α is independent of pressure, $\frac{\lambda}{N}$ should be constant. There is considerable deviation at the lower pressures. It cannot be held to be due to experimental error without detracting seriously from the value of the conclusion. It may be due to a difference in the sensibility of the electrometer; and if so, Mr. McClung may be able to explain the deviation if he has a record of the sensibility.

The next table is prepared from the same experimental results, and gives the values of α calculated by the three formulæ (4), (5), and (6). The values are expressed as multiples of e , the charge on an ion.

Pressure in Atmospheres.	λ .	Defl. for N.	α_N .	Defl. for Q.	α_Q .	$\frac{N^2}{Q}$.	$\alpha_Q \cdot \frac{Q}{N^2}$.
3	250	236	1916 e	143	974 e	389	3940 e
2	217	196	2060 e	112	937 e	343	4466 e
1	178	181	1829 e	51	1384 e	642	2387 e
.5	147	154	1776 e	41	1170 e	578	2652 e
.25	94	136	1286 e	26	757 e	711	2156 e

The numbers are reduced by the data given on p. 300 of the same paper; and we may note that the values of N and Q given there give $N^2/Q=453$.

In the table the values of α for any given pressure are quite discordant, and the values of α calculated by any one method cannot be said to be independent of pressure.

It may be argued, since the values of N^2/Q differ, that this is due to a change of sensibility of the electrometer. If so, the values of N , Q , and $\frac{N^2}{Q}$ would have to be changed in the same proportion for any one pressure. This, however, would not improve the relative values of α_N and α_Q at that pressure. For example, at 3 atmospheres α_{Q/N^2} would have to be reduced while α_N and α_Q would have to be increased in the same proportion, and thus α_{N/Q^2} would be brought nearer α_N or α_Q , but α_N and α_Q would not be brought nearer. Again, at .5 atmos. α_{N/Q^2} would have to be increased and α_N and α_Q diminished in the same proportion. Thus I do not think that a change of sensibility would improve matters.

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The discordance seems to me to be very serious, and requires explanation before we can accept either the theory or the conclusions.

The following table was prepared from the numbers on p. 298 of the paper, from which Mr. McClung showed that $\frac{Q}{N^2}$ was independent of pressure.

P. Pressure in Atmospheres.		Defl. for N.	Defl. for Q.	$\frac{N^2}{P} \times 10^{-2}$.	$\frac{Q}{P}$.	$\frac{N^2}{Q}$.
A.	1	121	34.4	146	34.4	425
	3	193	79.7	124	26.5	467
B.	1	67.9	16.6	46.1	16.6	278
	2.5	103.2	35.5	42.6	14.2	300
C.	1	70.4	15.2	49.5	15.2	326
	2	96.0	26.5	46.1	13.2	348
D.	1	128.6	38.2	165	38.2	433
	1.5	148.7	49.4	147	32.9	448
E.	1	110	29.3	121	29.3	413
	.5	93.5	20.7	174	41.4	422
F.	1	70	23.5	49.0	23.5	208
	.25	43.5	9	75.7	36	210
G.	1	61.9	22.7	38.3	22.7	168
	.125 ...	29.9	5.1	71.5	40.8	175

If α is independent of pressure and Q is proportional to the pressure, then N^2 is proportional to the pressure.

It would be unfair to compare values of N^2/P from different sets, say A and F, as the intensity of the rays might be very different. This, however, does not apply to the values of N^2/Q , which must be independent of the intensity. Nor does it apply to observations of any one set, *e. g.* F, where the intensity must be approximately constant if the numbers are to mean anything at all.

Was there, then, any difference in sensibility of the electrometer in A, B, F, and G?

The agreement between the values of N^2/P or Q/P in A, B, C or D, although not very good, may be accepted as approximately proved. But in E, F, or G there cannot be said to be substantial agreement.

The questions which naturally arise are : (1) Is the proposed theory correct? For the experiments cannot be held to support it. And (2) Do the measurements actually give the values of N , N_0 , and Q ?

In connexion with the second question, I have considerable

doubt whether the saturation current gives a measure of Q . I think it gives a measure of the excess of the rate of production of ions over the rate of recombination; and I see no reason for assuming that the latter is negligible. It is equal to αN_s^2 , where N_s is the number of ions per unit volume when the steady state, with the saturation current passing, is reached. It certainly cannot be zero, and may be comparable with Q .

In conclusion I should like to express my great obligation to my colleague Mr. James Gray, for his kindness in revising the tedious arithmetical calculations.

Physical Laboratory,
The University, Glasgow.
25th March, 1904.

XXII. *Reply to Mr. G. W. Walker's Paper on the "Rate of Recombination of Ions in Gases."* By R. K. McCLUNG, M.A., Trinity College, Cambridge*.

THROUGH the courtesy of Mr. Walker I am enabled to make a reply to the criticisms of my experiments on the rate of recombination of ions contained in his paper, which appears in the present number of this Magazine. These criticisms are evidently due to a want of knowledge of the exact conditions under which the experiments, described in my paper, were made, and the relation of the different experiments to one another. I am very sorry that Mr. Walker has wasted so much valuable time in making what must have been such very tedious arithmetical calculations, for the numbers obtained by him are quite valueless, and consequently the criticisms based upon these numbers are quite beside the mark.

Although at the beginning of his paper he mentions three of my papers which have appeared in the Philosophical Magazine, yet he confines his criticisms to the one on the effect of pressure on the rate of recombination of ions. I shall therefore also confine my remarks to the experiments described in that paper.

In the first place, Mr. Walker makes the following statement in the first part of his paper:—"In testing the formula (1) it appears to me that he assumes the relation between N_t , N , and t to be of the same form as (1). This, as I shall show, is not the case in his experiments. It would be true if the beam of rays were cylindrical." In deriving formulæ (1) and (2) no assumption whatever is made as to the shape of the beam of

* Communicated by the Author.