

## LXXXIII. The relation between the rate of recombination of ions in air and the temperature of the air

R.K. McClung M.A. B.A.

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LXXXII. *The Relation between the Rate of Recombination of Ions in Air and the Temperature of the Air.* By R. K. McCLUNG, M.A. (McGill), B.A. (Cantab.), Trinity College, Cambridge, 1851 Exhibition Scholar\*.

**I**N a previous paper (Phil. Mag. March 1902) I gave the results of an investigation of the relation between the pressure of the air and the rate of recombination of the ions in the air which had been ionized by Röntgen rays. The experiments described in that paper were performed at the ordinary temperature of the room. It was thought that it would be of interest to pursue this investigation further, and ascertain what effect a change of temperature of the air would have upon the rate at which the ions recombine.

Prof. Rutherford investigated experimentally the rate of recombination of ions in gases at the ordinary temperature and pressure of the surrounding air (Phil. Mag. Nov. 1897), and he verified the equation

$$\frac{dn}{dt} = -\alpha n^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which represents the law of recombination of the gaseous ions.

It was shown by the author, in the paper referred to above, that over a considerable range of pressures, both above and below atmospheric pressure, the same law holds true. The present series of experiments were therefore undertaken with the object of ascertaining, in the first place, whether this same law of recombination holds at various temperatures of the air, and, secondly, what effect a change of temperature of the gas has upon the value of the coefficient of recombination  $\alpha$ .

The method employed in the previous investigation was adopted in the present instance. It was necessary, however, to modify the apparatus somewhat in certain details, as in this case it was to be subjected to fairly high temperatures in the course of the experiments. The following apparatus was therefore employed.

#### *Description of Apparatus.*

The general arrangement of the apparatus is shown in fig. 1. The Röntgen-ray bulb and the induction-coil which run it were, as usual, inclosed in a lead-covered box as a shield, and the rays were allowed to emerge through a

\* Communicated by Prof. J. J. Thomson.

well-defined circular opening, A, in the lead. The cylinder in which the air was ionized is shown more in detail in

Fig. 1.

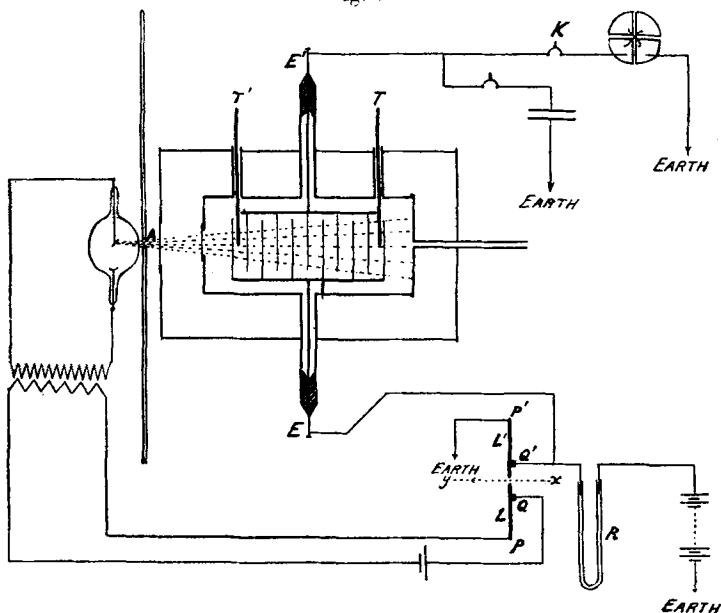


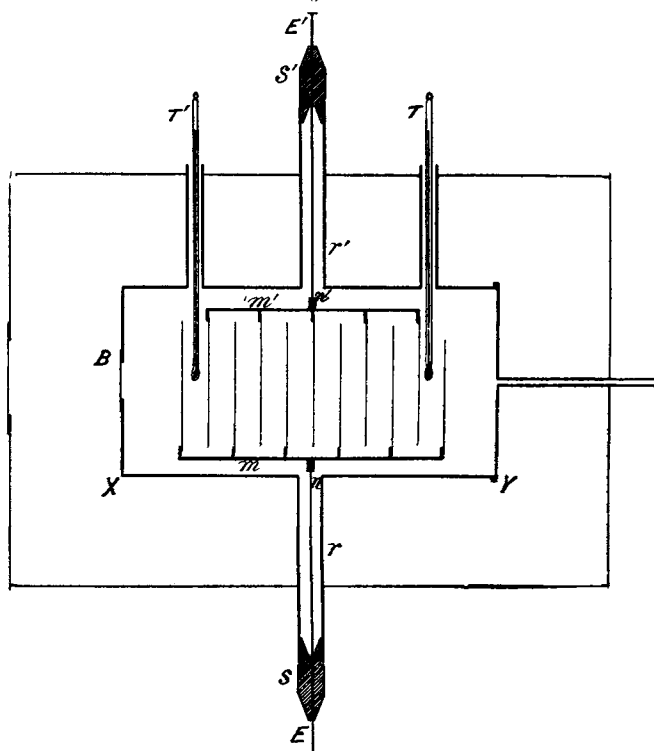
fig. 2. XY was a circular brass cylinder about 34 cms. long and 14 cms. diameter. The end Y was closed by a brass cap which screwed on to the end of the cylinder, while at the other end was a thin aluminium window, B, through which the rays were allowed to pass into the cylinder.

The arrangement of electrodes inside the cylinder was similar to that used in the previous experiments, for the same reasons as were explained in that instance, but the method of supports and insulation had to be modified somewhat on account of the higher temperatures which were to be used. The electrodes consisted of extremely thin aluminium foil which was stretched on brass annular rings for support. These rings were 9.1 cms. inside and 10 cms. outside diameter, and were grooved round the outside edge, and the aluminium foil was folded over this edge and then bound tightly round with thin copper wire. These rings were eleven in number, and were placed about 2 cms. apart, so that there was a length of about 20 cms. of air on which the measurements were made. Six of these alternate rings were

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fastened to a heavy brass rod,  $m$ , thus forming one electrode, while the other five were attached to the rod  $m'$ , forming the

Fig. 2.



second electrode. These rods were supported by the rods  $n$  and  $n'$ , which passed out through the brass tubes  $r$  and  $r'$ , and were supported by the insulating ebonite plugs  $S$  and  $S'$ .

The brass cylinder was surrounded by a sheet-iron cylinder, separated from it by a uniform air-space of about 10 cms. The ends of this iron cylinder were also closed, as shown in the diagram. The cylinder and inclosed air were heated by means of a long bunsen-burner which was placed underneath the iron cylinder, and ran nearly the full length of the cylinder. The iron cylinder was covered with sheet asbestos to prevent as far as possible the heat from radiating. The air between the two cylinders became heated and formed a hot air-jacket round the brass cylinder, and the air inside it could thus be kept at a fairly constant temperature by regulating the supply of gas to the bunsen-burner. The

regulation of the temperature was a comparatively simple matter. The temperature of the air which was being experimented upon in the cylinder was measured by the two mercury thermometers, T and T', shown in the diagram; and the mean of the temperatures indicated by these two thermometers was taken as the average temperature of the air which was being experimented upon.

The electrode E' was connected to one pair of quadrants of the electrometer, the other pair being connected to earth. The electrometer used throughout these experiments was one of the Dolazalek type, and gave a deflexion of about 2000 scale-divisions for a difference of potential of one volt between the quadrants when the needle was charged to 120 volts.

The arrangement for making and breaking contacts by means of a pendulum and levers was similar to that used in the previous experiments, and has been fully described in the former paper. In the present instance the contacts were broken by means of a heavy steel-ball pendulum, the ball being suspended by two thin steel wires about three metres long. A pointer on the bottom of the ball struck the ends of the levers as it swung along the path  $xy$ . The levers L and L' were held in contact with Q and Q' by means of springs. The electrode E was connected through a large liquid resistance R, consisting of a solution of cadmium iodide in alcohol, to one pole of a battery of accumulators, the other pole of the battery being connected to earth.

At the beginning of the investigation a Röntgen-ray bulb was used of the ordinary form, without any vacuum regulator of any sort attached. This, however, did not prove satisfactory, for it was inclined to run hard with use, and the intensity of the rays was therefore apt to change during the course of a series of experiments, making it difficult to obtain consistent results. This bulb was therefore abandoned, and a focus-tube with an automatic vacuum-regulator attached was obtained. This bulb proved much more satisfactory, and was employed throughout the remainder of the investigation. All the results given in this paper were obtained with this bulb.

#### *Test of the Law of Recombination at Various Temperatures.*

When equation (1) is integrated it becomes

$$\frac{1}{n} - \frac{1}{N} = at, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where N is the maximum number of ions per c.c. at the

instant the rays cease, and  $n$  is the number per c.c. remaining at the end of a time  $t$  after the cessation of the rays, while  $\alpha$  is the coefficient of recombination. Now one of the objects of this investigation was to test whether this equation represents the law of recombination at various temperatures of the gas. To test this the three quantities to be measured are  $n$ ,  $\bar{N}$ , and  $t$ .

When the levers  $L$  and  $L'$  were placed directly opposite each other, as in the diagram (fig. 1), then the pendulum in swinging along the path  $xy$  struck the two levers at the same instant, and thus the rays were stopped and the electromotive force applied to the electrode  $E$  at the same instant. Now if, when the ionization in the cylinder has reached a steady state, the source of ionization be suddenly cut off and a large electromotive force be applied to one of the electrodes, the other electrode will receive a charge proportional to the number of ions existing in the gas between the electrodes. Also if the electromotive force be applied to the electrode at a given interval after the cessation of the rays, the other electrode will receive a charge proportional to the number of ions which are left in the gas.

In the actual experiments, the observations were taken as follows :—When the gas had reached the temperature to be investigated, and the temperature had become steady, the rays were started and allowed to run for an interval of ten or fifteen seconds, so that the ionization might reach a steady state. During this time both the electrodes  $E$  and  $E'$ , as well as the electrometer-quadrants, were connected to earth. At the end of that time the electrode  $E'$  was insulated by opening the key  $K$ , and the pendulum was released, which broke the contacts, stopping the rays and applying the electromotive force to  $E$  at the same instant. In order to avoid the violent kick of the electrometer-needle which would occur, due to the inductive effect when the large E.M.F. was applied to  $E$ , if the quadrants of the electrometer were insulated at the same time as  $E$ , the electrometer was disconnected by the opening of the key  $K$  before the pendulum was released, and was kept to earth. Immediately after the passage of the pendulum the lever  $L'$  was replaced in contact with  $Q'$ , so that the induced charge was counterbalanced by putting  $E$  to earth again; then the quadrants of the electrometer were insulated and connected to  $E'$  by closing the key  $K$ , and the deflexion of the electrometer-needle observed. This deflexion should therefore be proportional to the maximum number of ions  $N$  in the given volume of the gas. This then gave a measure of the quantity  $N$ .

The measurements of the different values of  $n$  were made in exactly the same way, except that the levers were separated at known intervals from one another along the line  $xy$ . By separating these levers at definite distances from each other, the electromotive force could be applied to E at definitely known times after the rays were stopped. By this means different values of  $n$  were obtained corresponding to different known intervals of time  $t$ . Values corresponding to N and  $n$  were thus obtained. The values of  $t$  corresponding to the different values of  $n$  were determined by calibrating the pendulum for the different distances between the two levers.

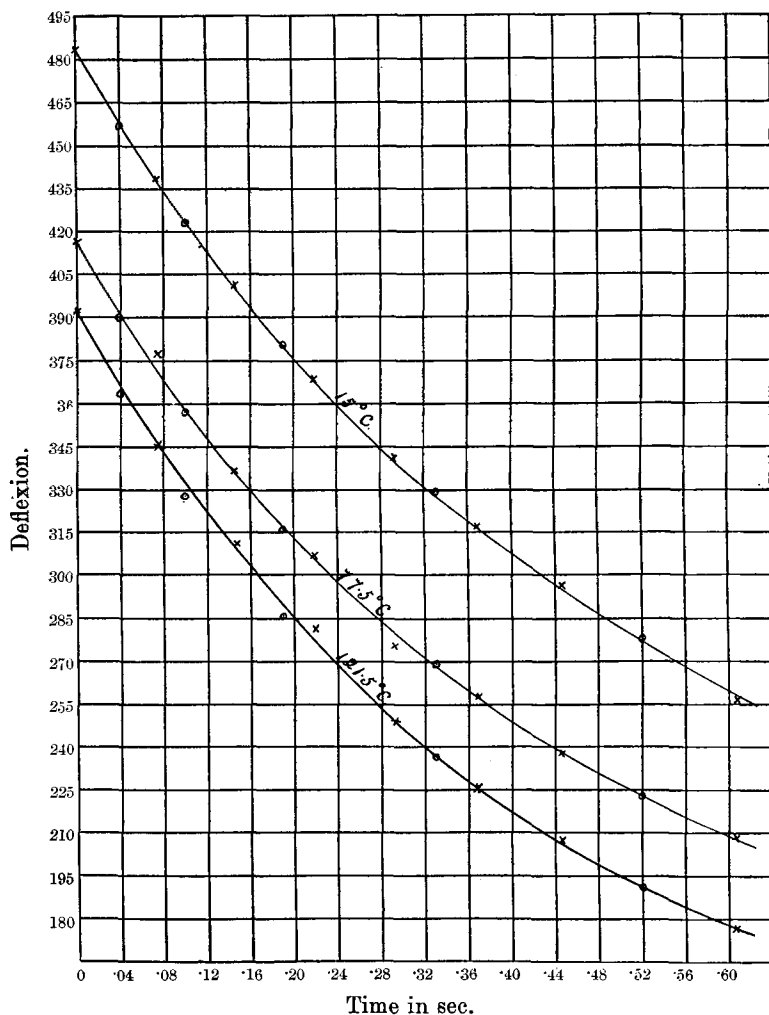
In making these measurements, as is almost always the case in working with Röntgen rays, some difficulty was experienced on account of the tendency of the rays to vary slightly in intensity. Even with an automatic regulating bulb, it is almost impossible to keep the intensity of the rays quite constant during a whole series of observations. In order to obviate this difficulty as much as possible the bulb was run at regular intervals, as far as could be done throughout the series; and in addition, instead of depending upon a single reading for any one quantity, several readings were taken in each case and the mean of these taken. This system of means was followed throughout the whole investigation.

To test the validity of the law of recombination at the various temperatures, experimental curves were obtained showing the relation between the number of ions  $n$  and the time  $t$ . These curves were plotted, and then taking two of the experimental points on the curve with which to calculate  $\alpha$  from the formula, several arbitrary values for  $t$  were chosen, and the corresponding theoretical values for  $n$  were calculated from the equation (2). These theoretical points were then plotted and compared with the experimental curve. Experimental curves were obtained for several different temperatures ranging between  $15^{\circ}\text{C.}$  and  $300^{\circ}\text{C.}$  Some of these curves are shown in figures 3, 4, and 5. In these curves the ordinates represent numbers corresponding to the different values of  $n$ , while the abscissæ represent the corresponding values of  $t$  in seconds. The experimental points in these diagrams are marked with crosses, while the theoretical points are marked with circles. To avoid confusion the experimental curve alone is drawn in each case.

The agreement between the theoretical and the experimental points, as shown by these diagrams, is quite close. Any slight variations which may occur can easily be accounted for by variations in the intensity of the rays, experimental

error, &c. ; for it is difficult to keep all the conditions absolutely steady during a whole series of observations, such as is represented by any one of these curves, especially at the

Fig. 3.

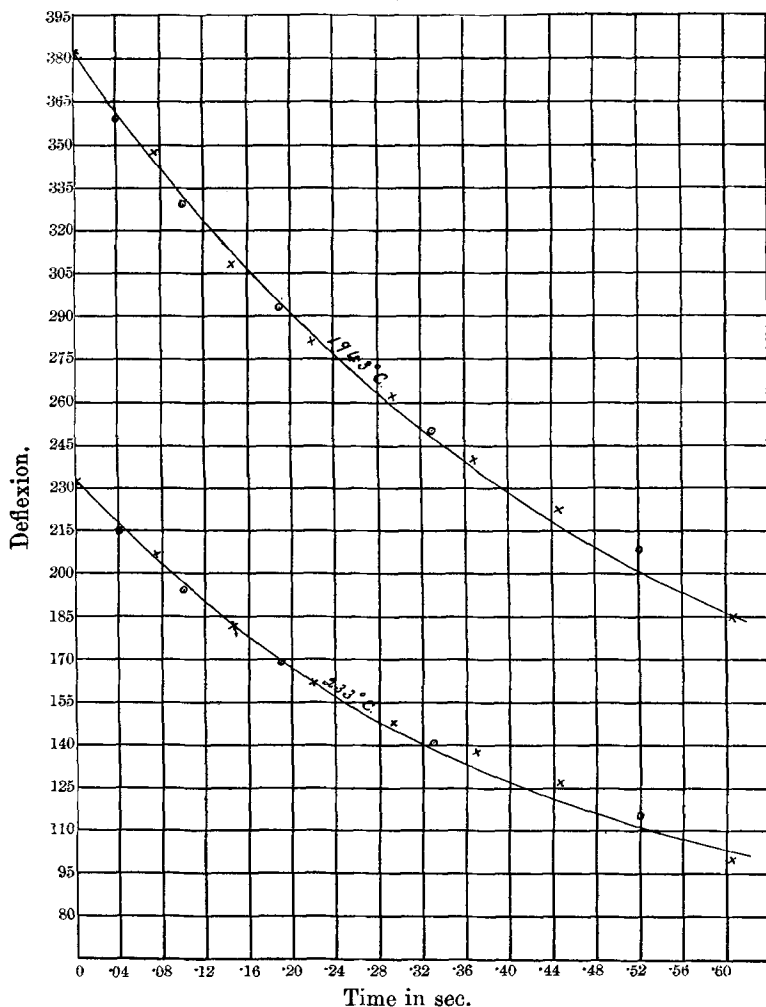


higher temperatures. The agreement is therefore quite close enough to show that equation (2) represents the law of recombination at these higher temperatures quite as well as



at the ordinary temperature of the air. It appears then that the rate of recombination follows the same law at different temperatures, at least over the range of temperatures investigated.

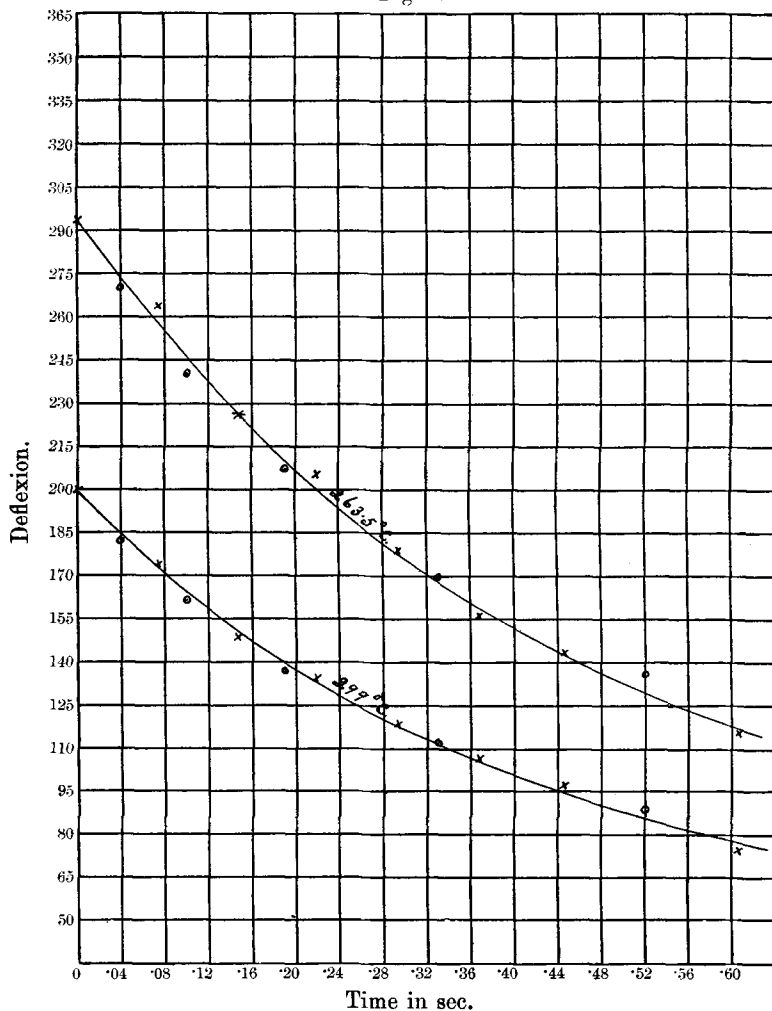
Fig. 4.



It may be just noted here that the density of the air decreased as the temperature increased, inasmuch as the air was free to expand into the outside air. It was, however, shown by the author in the former paper that within the

range of densities of the air occurring in this instance, this same law of recombination holds true. Therefore in this case the validity of the proof of the law at the various

Fig. 5.



temperatures is not affected by the change of density of the air. Taking into consideration the present experiments in connexion with the previous investigation on pressure, this law of recombination of ions in air appears to be a universal one, at least within the range of temperatures and pressures that have been investigated.

*Relation between Temperature and Coefficient of Recombination.*

The other question which we set out to investigate was the effect which a change of temperature of the gas produced upon the value of the coefficient of recombination  $\alpha$ . Although it has been shown that the same law of recombination holds true at the various temperatures, we cannot say from this that the value of the coefficient  $\alpha$  remains the same at the different temperatures. There still remains to be settled the question of the relation between the temperature of the gas and the value of  $\alpha$ .

From the well-known equation  $q = \alpha n^2$  it follows, as has been shown by the author in the paper already referred to, that the absolute value of  $\alpha$  is given by the equation

$$\alpha = K \frac{Q}{N^2},$$

where  $K$  is a constant quantity depending entirely upon the dimensions and position of the particular apparatus used, and  $Q$  is the total number of ions produced per second in a given volume of the gas, while  $N$  is the total number existing in the same volume at the instant the rays are shut off. Now if it is only a question of comparing the value of  $\alpha$  at one temperature of the air with the value at another temperature,

it is only necessary to compare the values of the ratio  $\frac{Q}{N^2}$

at the two temperatures, if the dimensions and position of the apparatus are kept unchanged, for  $K$  will be the same in both cases. In making this comparison, then, the only two quantities to be measured are  $Q$  and  $N$ .

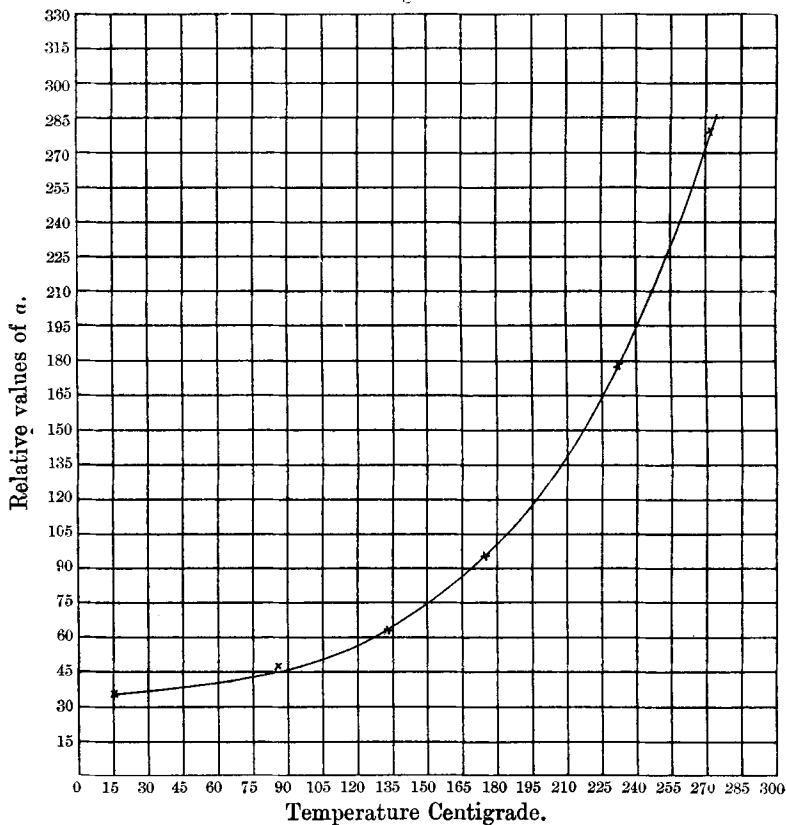
$N$  was measured as has been already described in testing the law of recombination. If the electrode  $E$  be kept at a steady saturation voltage, and the rate of leak per second between the electrodes be measured in the usual way, then the deflexion of the electrometer-needle, which is proportional to the charge received by the electrode  $E'$ , is proportional to the number of ions which are produced in the gas per second. Therefore  $Q$  is proportional to the deflexion of the electrometer-needle per second. If  $d_1$  is the deflexion of the electrometer-needle per second corresponding to  $Q$ , and if  $d_2$  is the deflexion corresponding to  $N$ , then  $\frac{d_1}{d_2^2}$  is proportional to  $\frac{Q}{N^2}$ . Therefore, to compare the values of  $\alpha$  at the different

temperatures it is only necessary to compare the values of the

ratio  $\frac{d_1}{d_2^2}$  at these temperatures, provided all the conditions are kept constant except of course the temperature.

In comparing these values, then, the observations were taken in the following manner:—The deflexions  $d_1$  and  $d_2$  were measured at the temperature of the room. The air in the cylinder was then heated up to a given steady temperature, and when it had become steady the deflexions  $d_1$  and  $d_2$  were again measured. The air was then heated to a still higher temperature, and when it reached a steady point  $d_1$  and  $d_2$  were measured once more. This was repeated in the same manner for several temperatures. The values of the

Fig. 6.



ratio  $\frac{d_1}{d_2^2}$  thus found were then plotted against the corresponding temperatures. A number of these series of observations were made, and one of the curves is given in fig. 6.

In this curve the ordinates represent numbers proportional to the relative values of  $\alpha$ , while the abscissæ represent the temperatures of the air in degrees centigrade.

As will be seen from this curve, it was found that as the temperature of the air increased the value of  $\alpha$  also increased, at first fairly rapidly, and at the higher temperatures much more rapidly. The rise in temperature of the gas appears to cause the value of the coefficient of recombination to increase to a considerable extent.

The density of the air decreases of course with the rise of temperature, but, as in the previous case, this need not be taken into account; for it was shown in the paper on the relation between pressure and  $\alpha$ , that over the range of densities of the air which are involved in this experiment the value of  $\alpha$  was practically a constant, so the change of density of the air need not be taken into account in considering the relation between  $\alpha$  and the temperature.

This relation between  $\alpha$  and the temperature does not appear to be a very simple one, for the curve showing the connexion between them does not seem to be capable of being represented by any simple mathematical formula. Whatever the changes are which take place among the ions, either in the individual ions or in their relation to one another, when the gas is heated they would appear from this to be somewhat complicated. As seen from the curve, however, the relation between the coefficient of recombination and the temperature of the gas seems to be quite a definite one.

### *Summary.*

The results which have been obtained during this investigation may be summed up as follows:—(1) The rate of recombination of ions in air follows the same law, namely,

$$\frac{dn}{dt} = -\alpha n^2, \text{ at different temperatures, at least over the range}$$

of temperatures investigated, that is between 15° C. and 300° C. (2) A rise in the temperature of the air causes a considerable increase in the value of the coefficient of recombination, and the relation between the temperature and this coefficient appears to be of a somewhat complicated nature.

In conclusion I wish to express my appreciation of the kindly interest shown and the advice given by Professor Thomson during this investigation.

Cavendish Laboratory,  
Cambridge, July 29, 1903.