On the Evidence of the Existence of Isotopes of Chlorine.

By

Matakichi Ishino.

(Received July 22, 1920.)

---

§ 1. Introduction.

The positive rays of many substances have been investigated by W. Wien, J. J. Thomson, Retschinsky, Königsberger and Kutschenski, Stark, Bärwald and others. J. J. Thomson[1] used the crossed deflection method, and obtained many important results as to the value of $\frac{m}{e}$ and the nature of the charged particles in a positive ray tube.

The great advantage of this method for the determination of the mass of particles lies in the fact first, that the method does not depend upon the purity of the substances used; secondly, that the method requires only a very minute quantity of the substance; and thirdly, that the method furnishes the knowledge of the existence of some intermediate states of a substance in the discharge-bulb.

The positive rays of chlorine were studied by J. J. Thomson, and he found the existence of the types Cl^{+}, Cl^{-}, Cl^{++}. Stark also observed the same carriers by means of the Doppler effect. When about four years ago the author worked on this gas at Cambridge, the line corresponding to Cl^{+} appeared as if its breadth was somewhat wide. But owing to pressure of work, the author postponed further research in this field. The aim of the present investigation is to attack the above important problem of the positive rays of chlorine atoms.

§ 2. The Experimental Details.

The apparatus, which was used for the analysis of the positive rays of chlorine, was constructed on the principle of Thomson's crossed deflection method. The positive-ray particles resolved by the electrostatic

---

1 "Rays of Positive Electricity and their Application to Chemical Analysis" Longmans, Green and Co, London, 1913.

and magnetic fields were photographed on a plate placed at right angles to the direction of the ray. In order to secure the exact coincidence of the direction of the electrostatic and magnetic fields, two soft-iron blocks with parallel plane faces were used at the same time, as the electrodes and the magnetic poles. The diameter of the cathode-canal used was about 0.1 m.m. The pumping of the apparatus was carried out by a Gaede molecular pump with his ordinary mercury pump as an auxiliary. After many preliminary experiments, the author found that the intensity and sharpness of the lines on the photographic plate depend remarkably upon the pressure of the camera-side of the apparatus. This is obviously due to the absorption and scattering of the positive rays by the residual gas-molecules in the camera-side. Therefore, it is of primary importance in this work to produce extremely high vacua. Every part of the apparatus was washed thoroughly with suitable reagents and boiled in water for several hours, and finally thoroughly dried. This was to remove any volatile substance remaining in adherence to the walls of the apparatus. After properly setting the apparatus, the whole was exhausted with the pumps mentioned above, and then sufficiently heated. The exhaustion was continued for two or three days after the photographic plate was placed in the camera. This was found to be very necessary, because otherwise some gases or vapours would contaminate the surface of the film. The vacuum attained in this way was about 0.00001 m.m. of mercury.

The resolving power of the apparatus may be, of course, increased by raising the intensity of the magnetic field. If this be done, however, the intensity of the lines necessarily falls off. Therefore in order to obtain fine lines with great resolution, a very sensitive photographic plate for the positive rays was necessary. The author has tried the various photographic plates available, among which the Schumann plates from Adam Hilger were found to bc very good. The author has newly prepared Schumann plates with the kind help of Assist. Prof. Miyata. The prescription of the plate was the same as that of Schumann,[1] except for a certain modification to render the film as thin as possible, and to contain as much silver as possible. This plate prepared thus was found very sensitive, so that the time of exposure to to the positive rays was reduced to only a minute or a half minute to get measurable fine lines.

1 Ann. Physik, 5, 349 (1901).

The chlorine gas to be studied was prepared by electrolysis of hydrochloric acid, dried with Cl_2Ca and P_2O_5, and introduced into the discharge-bulb through fine capillary tubes. The gas was also obtained by means of the bombardment of the powder of natrium chloride with cathode rays, the salt being introduced in a side-tube connected with the discharge-bulb.

§ 3. Results.

The photographs of the broadened line of chlorine were repeatedly taken under different conditions. When the magnetic field was sufficiently intense, and the pressure in the camera was as extremely low as 0.00001 m.m. the broadened line under the consideration was separated into two lines. The separation occurred equally for the positive carriers and the negative ones. The photographs are shown in the accompanying plate, the time of exposure of which was about one minute, and the pressure in the discharge-bulb about 0.001 m.m. The measurement of the value of m/e for the above two lines proved to be **34** and **36**, compared with that of the hydrogen atom. The intensities of the two lines appear not to be equal, that of the line 34 being much the fainter.

In addition to these lines a line 37 appeared on the positive side, i.e. the side where the positive carriers impinge.

The line 36 has the second bead midway between the first bead and the vertical line, i.e. the line corresponding to the deflection due to the magnetic field alone, and another line 18 is seen on the plate. But the second bead of the line 34 is so faint that it is only observable on the original plate. The second beads of the lines 34 and 36 are also seen on the negative side of the plate.

In some plates the third bead is often observed at a distance one third of that of the first bead from the vertical line. Considering this third bead we may expect the occurrence of a line $36/3=12$, and in fact, an intense line 12 is seen on the plate. But since this line just coincides in value with the line of the carbon atom, it is not possible to tell whether the line is due to the atom corresponding to the third bead of the line 36, or the carbon-atom.

J. J. Thomson was not able to find any case in which a molecule of either an elementary or compound gas carries multiple charges; and he had never found molecules with a negative charge, though molecules with the positive charge are quite common. Considering these empirical facts, it is highly possible that the lines 34 and 36 are due to elementary atoms.

Now these two lines appeared only when the chlorine gas was introduced into the discharge-bulb, and consequently it may be concluded that these two lines are due to chlorine atoms. But a question arises as to the nature of the line 34, because this line may be due to H_2O_2. To test this point, a new apparatus was constructed using fresh materials. The gas H_2O_2 was prepared by adding concentrate sulphuric acid to barium peroxide, and was then introduced into the discharge-bulb. With this gas, the author could not observe any trace of the line 34 and 36 on the photographic plate.

It is also possible to consider the line 34 as due to H_2S (=34). In a side-tube connected with the discharge-bulb, molten SO_2HNa was introduced. On heating or bombardment with cathode rays this substance evolved H_2S gas. Many photographs were now taken of this gas by using a newly constructed apparatus, but the suspected line did not make any appearance at all.

So far as the experiments are concerned the author is inclined to think that the line 34 and 36 are both due to chlorine atoms.

If this conclusion is correct, then we must accept the existence of the isotopes of the element chlorine. Let the atoms of these isotopes be denoted by the symbols $Cl_I = 34$, and $Cl_{II} = 36$.

Then the ordinary chlorine of the atomic weight 35.45 would be a mixture of $x.\,Cl_I + y.\,Cl_{II}$, where x and y represent the relative coefficients of the amount of isotopes.

The line 37 is clearly due to the hydride of Cl_{II}, i.e. HCl_{II}. Another hydride HCl_I (=35) is not seen on the plate, but the broadening of the line 37 seems to show the existence of such a hydride.

Finally it is to be noticed that in addition to a number of the atoms of chlorine with negative charge, there exists also the atoms with positive charge. This fact is against the expectation of some scientists, who thought that positive ions of chlorine can hardly exist in a discharge-bulb, because chlorine is a very strong electro-negative element.

§ 4. Discussion.

It is rather remarkable that the atomic weights of the lighter elements up to cobalt are approximately whole numbers, with just a few exceptions, Ne, Mg, Si, and Cl. The same facts occur also in the case of very heavy radioactive elements. Such facts are much too conspicuous to be considered merely accidental.

According to Rutherford's atom-model, the mass of an atom mainly resides in the positive nncleus, which is surrounded by electrons rotating in certain orbits. The study of radioactive phenomenon shows that a positive nucleus of an atom has a complex structure, and consists probably of the positive nuclei of helium and of hydrogen, and some cementing electrons. With this conception we can understand to some extent why the whole-number rule is held for the atomic weights.

The atomic weights of the majority of the moderately heavier elements and a few elements among the lighter ones above mentioned deviate remarkably from the whole-number. This deviation is apparently contradictory to such a nuclear structure as given above. It is therefore very important for the problem of atomic structure, to inquire into the cause of this deviation from the whole-number.

The cause of the deviation may be ascribed to the existence of isotopes. Suppose now that there are isotopes to an element, and an ordinary element is a mixture of such isotopes. According to this view the atomic weight of an element is only the average of the atomic weights of the constituent atoms. Hence even if the whole-number rule holds good for each atom, the average atomic weight may be generally different from the whole number.

The deviation of the atomic weight of chlorine is, as is well known, the greatest among the ligher elements. Judging from the results of the present study, the large deviation in the case of chlorine, can be explained by the existence of the isotopes.

It is here dcsirable to notice that this investigation was carried out in Sept. of last year. But owing to the pressure of work in the Institute and the author's illness, the publication was greatly delayed. Meanwhile Mr. Aston's letter was published in *Nature*[1], stating that he had found isotopes of chlorine by using a new method of positive-ray spectrography, the atomic weights obtained being 35 and 37, respectively.

In conclusion, the author wishes to express his indebtedness to Professor T. Mizuno for the interest he has taken in this investigation. The author's thanks are also due to Mr. Arakatsu for his useful help.

1 Aston, Nature, Jan. 1920.

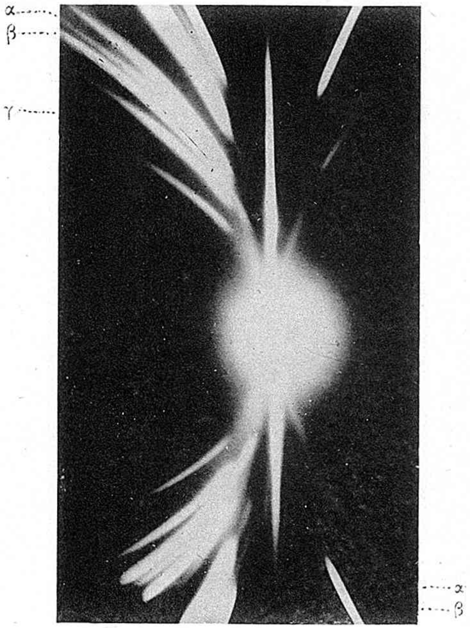

Fig. 1

$\alpha = 34 \ldots Cl_{I}$
$\beta = 36 \ldots Cl_{II}$
$\gamma = 72 \ldots Cl_2$

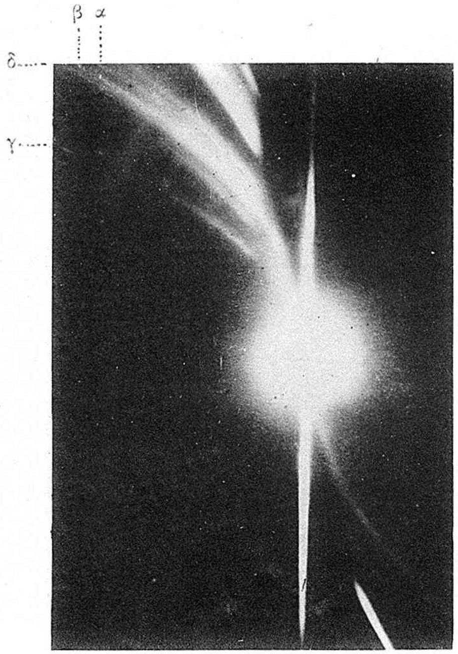

Fig. 2

$\delta = 37 \ldots Cl_{II} H.$

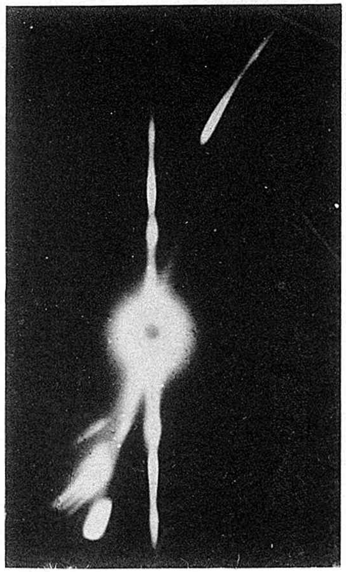

Fig. 3

The second and the third beads
of chlorine-atom