Second Series. *March, 1920.* *Vol. XV., No. 3*

THE

PHYSICAL REVIEW.

THE NATURE OF THE PROCESS OF IONIZATION OF GASES BY ALPHA RAYS.

By R. A. Millikan, V. H. Gottschalk and M. J. Kelly.

Synopsis.

Ionization of gases by α-rays; valency of the ions.—By catching an ionized molecule upon an oil drop at the instant of ionization and then measuring the charge thus added to the drop, it has been directly proved that the ionization of an air molecule by either β-, γ-, or X-rays uniformly consists in the detachment of one electron. In the case of ionization by α-rays, the authors show by an extended discussion of previous work bearing on the subject that while some experiments indicate the possibility of the formation of multi-valent ions, none of them is conclusive. Therefore, the droplet method was used to supply direct evidence. The necessary modifications of apparatus are described and the experimental procedure. Uncovered radium furnished the α-rays. The gases tested were *air, carbon dioxide, carbon tetrachloride, methyl iodide,* and *mercury dimethyl;* so that α-rays were shot through atoms of H, C, O, N, Cl, I and Hg, which vary in atomic weight from 1 to 200. *Experimental results.* Altogether 2,900 ions were each caught on an oil drop at the instant of ionization, and each had its charge determined. Of these captures, only 5 corresponded to a double charge and no ion was caught which carried three or more elementary charges. How many of the 5 double charges obtained were due to doubly-charged ions and how many to simultaneous catches of two singly charged ions, is unknown. In any case the results prove that, at least 99 times out of 100, ionization by an α-ray, in the case of each of the gases and vapors studied, consists in the detachment of a single electron from a molecule. The observations for 170 captures by three droplets in three gases are given in detail. The paper ends with a *discussion* of the circumstances under which multi-valent ions may possibly be produced by α-rays.

I. Introduction.

By directly catching upon an oil drop at essentially the instant of ionization the residue of the ionized atom and then measuring the charge thus communicated to the drop, Millikan and Fletcher[1] obtained the direct proof that the act of ionization of air by β and γ rays of radium, as well as by X-rays, uniformly consists in the detachment from a neutral molecule of one single negative electron. The extension of the same

[1] R. A. Millikan and Harvey Fletcher, Phil. Mag. (6), 21, 753 (1911).

method to the determination of the nature of the act of ionization produced by α rays is more difficult and more interesting. It is more difficult because it is necessary to make the observations at a pressure so low as to render negligibly small the chance that two nearby molecules, separately ionized by a given α particle, may be thrown by the field simultaneously upon a given drop. It is more interesting because the enormously powerfully-ionizing α particle, with its relatively huge mass and strong field, might be expected to knock off in some instances more than one electron from a given atom. The number thus detached might well depend upon the complexity and chemical characteristics of the atom traversed. Indeed J. J. Thomson's results with canal rays discussed below made more than likely the discovery of multi-valent ions resulting from α ray ionization.

II. Preceding Work Bearing upon this Problem.

The only preceding work dealing directly with the ionization by α rays is that by Townsend and his pupils, and that by Franck and Westphal.

In 1908 Townsend[1] devised a method for measuring directly the ratio u/D, where u denotes the mobility of the ion and D its coefficient of diffusion. Utilizing the equation $ne = (u/D)P$, where n is the number of molecules in a cubic centimeter of gas at a pressure of P dynes per square centimeter, he could obtain the value of ne. If the ions measured were *all* univalent, the value of ne should be 1.23×10^{10} electrostatic units, while if a fraction of them had multiple charges, the value would be greater. Haselfoot[2] modified the Townsend method which was used for X-rays, so that he could determine the value of ne for the ions of air when radium was the ionizing agent. For positive ions he obtained values ranging from 1.24×10^{10} to 1.37×10^{10} electrostatic units; for the negative ions when he used dry air he could not obtain values consistent with the Townsend theory of the experiment, but when moisture was admitted, the results indicated that all ions were univalent. Haselfoot[3] repeated these experiments three years later, using the pressure and field strengths found most suitable in his previous work. Of the experiments made, the seven which gave results closest to the mean were made some with positive and some with negative ions. The mean value of ne deduced from these was 1.22×10^{10}, the value given by each experiment not differing from the mean by more than 5 per cent. These experiments then, so far as they go, give no indication of multiple charges produced *in air* by α rays.

[1] J. S. Townsend, Proc. Roy. Soc., A, 81, 464 (1908).
[2] C. E. Haselfoot, Proc. Roy. Soc., A, 82, 18 (1909).
[3] C. E. Haselfoot, Proc. Roy. Soc., A, 87, 350 (1912).

Franck and Westphal[1] determined *ne* for ions produced in air by polonium, which gives only α particle ionization. They determined the coefficients of mobility and of diffusion separately and found from their results no indications that α particles produce other than univalent ions in air. The conclusion is based on diffusion measurements which differ among themselves by 7 per cent.

The conclusion from both of these investigations is that they furnish no evidence that multi-valent ions are produced in air by α particles. It has been pointed out however[2] that such measurements have to do with the charges carried by ions at a considerable time after their formation and, because of the possibility of recombinations, do not necessarily justify a conclusion as to the valency of the ions actually formed in the ionization process.

Wilson's[3] well-known photographs of the paths of α particles throw no real light on this question, since he obtained no photographs in which all the drops in a known length of the cloud trail left by the α particle could be counted. However, by a modification of the Wilson expansion apparatus, Bumstead[4] has obtained photographs of the tracks of α particles in hydrogen, and has found distinct evidence of electronic trails radiating from the paths of the α particles. He attributes these to ionization by swift δ rays liberated from the molecules by the α particles. Thus evidence is furnished that a considerable portion of the ionization by α particles takes place in this indirect way. As we know that swiftly moving corpuscles ionize by liberating only one electron from an atom, we should expect from this evidence that at least a large portion of the ions would be univalent. Indeed, even if the evidence obtained from experiments on mobilities and diffusion coefficients were altogether precise and unambiguous, *the Bumstead experiments would leave quite open the question as to what happens to the atom when the alpha particle itself goes through it.*

Nor is any decisive evidence on this point found in Geiger's[5] measurement of the total ionization produced by α rays per mm. of path, although these experiments deserve consideration in this connection. In air at atmospheric pressure and at 12° C. Geiger found the number of ions produced by α rays of radium *C* in traversing the first millimeter to be 2250, while the number produced per mm. of path at the end of about 65 mm. was 7600. Now the mean free path of air under these condi-

[1] J. Franck and W. Westphal, Verh. d. Deutsch. Phys. Ges., 11, 276 (1909).

[2] R. A. Millikan, loc. cit.

[3] C. T. R. Wilson, Proc. Roy. Soc., A, 87, 277 (1912).

[4] H. A. Bumstead, PHYS. REV. (2), 8, 715 (1916).

[5] Geiger, Proc. Roy. Soc., 82, page 486 (1909). Also see page 164 of Rutherford's "Radioactive Substances and their Transformations" (1913).

tions is .0001 mm. Hence introducing the factor 4 to take account of the fact that the dimensions of the α ray are negligible in comparison with the diameter of the atom, and the factor $\sqrt{2}$ to allow for the fact that the velocity of agitation of the molecules of air is negligible in comparison with the speed of the α ray, it will be seen that the number of molecules penetrated by an α particle in going 1 mm. through air under the aforesaid conditions is

$$\frac{1}{.0001 \times 4\sqrt{2}} = 1{,}750.$$

Hence it is clear from Geiger's results that the α ray produces at all points in its path a number of ions (unit charges) which is larger than the number of molecules through which it passes—1.3 times as large at the beginning, and 4.5 times as large near the end of the path. Whether the whole of this excess is due to the delta rays brought to light by Bumstead's experiments, or whether the alpha rays sometimes form multivalent ions is beyond the power of Geiger's method to determine, or indeed of any method which does not separate sharply the different types of ions, if such exist, from one another.

Sir J. J. Thomson,[1] however, from his investigations of canal rays has brought forward good reasons for concluding that positively charged atoms or molecules may ionize a molecule of gas through which they are moving, by two distinct methods. They may, first, pluck a single corpuscle out of an atom or molecule past, or through, which they are moving. This process would, of course, produce only univalent positive ions. They may, second, collide with the atom as a whole with enough energy so that "if there were several corpuscles connected with about the same firmness to the atom, the result of the atom acquiring a high velocity in a collision might be the liberation of all the corpuscles and the production of a multiply charged atom." Thomson found large numbers of such multivalent atoms for every element investigated, with the notable exception of hydrogen. The number of charges liberated appeared to be independent of any chemical properties of the atom, although an increasing function of the atomic weight: thus, nitrogen showed two; oxygen, two; neon, three; krypton, four or five; mercury, eight.

In this work of Thomson then, we find conclusive evidence for the formation of ions with more than one charge. In the case of mercury Thomson brings forward good evidence to support the view that the process of ionization always consists in the detachment from the neutral atom of mercury either of one corpuscle or else of eight corpuscles. He thinks that the parabolas which he found corresponding to 2, 3, 4, 5, 6

[1] Sir. J. J. Thomson, Phil. Mag. (6), 24, 671 (1912). Also Positive Rays, pages 37, 38, 52 and 74.

and 7 charges on the mercury atom appeared because some of the eight lost-charges had been regained before the ion entered the crossed magnetic and electric fields, the action of which on the moving ion produced these parabolas. Further, by comparing the intensity of the parabola corresponding to one charge with the sum of the intensities of the parabolas corresponding to 2, 3, 4, 5, 6 and 7 charges, we can gain some notion of the relative numbers of atoms which, from this point of view, acquire one charge and eight charges respectively in the act of ionization. Such a study reveals the fact that though the number of multivalent ions formed in Thomson's experiments was perhaps a small fraction of the number with one charge, it was not at all negligibly small. The sum of the intensities of the doubly and trebly valent argon parabolas is apparently quite comparable with the intensity of the univalent argon parabola (see Plate XV., Fig. 2, Phil. Mag., 24, 1912). Similarly in the case of mercury, parabolas 2, 3, 4, 5, 6 and 7 (Fig. 28, Rays of Positive Electricity) sum up to an intensity not of a wholly different order from parabola 1. Thomson says:[1] "The ratio of the number of atoms which have only one charge to that of those which have two or more charges is very variable and depends on conditions which are not yet fully understood. For example in the case of the carbon atom this ratio seems to depend to a very great extent on the type of gaseous carbon compound in the discharge tube. With some hydrocarbons the doubly charged carbon atoms are relatively much brighter than with others. Again, in the case of oxygen I have found that the purer the oxygen the fainter was the line due to the doubly charged oxygen atom in comparison with that due to the atom with only one charge. It would thus seem that atoms torn from chemical compounds were more likely to have a double charge than those obtained from a molecule of the element. Chemical combination can not, however, be the only means by which the atoms acquire multiple charges, for the atoms of the inert monatomic gases, neon, argon and crypton, are remarkable for the ease with which they acquire multiple charges." When it is recalled that in Thomson's experiments not only positive rays, but in addition β and X-rays are acting as powerful ionizing agents, and that these latter practically always produce singly charged positives, it will be seen that the inference is justified that a considerable part of the ionization produced by the positive rays corresponds to the production of multivalent ions.

These experiments of Thomson's then quite justified the expectation that since alpha rays are only a particular kind of positive rays, they would in many instances produce multivalent ions.

Further, the method of attack herein taken, consisting as it does of

[1] Thomson, Rays of Positive Electricity, page 53.

catching the residue of the individual atoms at practically the instant at which the act of ionization takes place, should enable decisions to be reached upon certain moot questions upon which the positive ray method of Thomson was incapable of giving an unambiguous answer. In particular,

1. Can the act of ionization of the mercury atom by a central impact from a positive ray be definitely proved to consist of the detachment of eight corpuscles as Thomson inferred? If so, our method should reveal positive residues carrying eight charges. Thomson observed no parabola corresponding to more than seven charges. He *inferred* that eight had been produced, but that 1, 2, 3, etc., had been regained in forming the ion which produced the parabolas corresponding to 7, 6, 5, etc., charges.

2. Does a positive ray which, instead of making a central impact, passes through the outer regions of an atom, ever detach two or more electrons in so doing? Such a result is to be expected, and, although the positive ray experiments present no evidence in its favor, they also do not present conclusive evidence to the contrary. How does this effect, if it exists, depend upon the atomic weight of the atom?

III. EXPERIMENTAL WORK.

The type of apparatus previously described[1] was used in the present work, with, however, certain important changes. A narrow beam of α particles passing immediately underneath the oil drop was obtained by placing about 0.1 milligram of radium bromide in a small tin box, 6 mm. wide by 2 mm. high by 12 mm. deep, which fitted tightly into a cylindrical lead plug held at the proper height and placed just at the edge of the condenser. (See Fig.) A slit, made in the ebonite sheet encircling the condenser, corresponded to the opening of the tin box. A small door of lead in a brass frame, operated by a crank from without the partially exhausted chamber, allowed the beam of α particles to enter the condenser when desired. To lessen difficulties due to drift, it was found expedient, especially with vapors, to close also the small slit in the ebonite by a spring attachment to the lead door of the radium container.

It was of course recognized from the first that it is difficult to distinguish between the practically simultaneous advent upon a drop of two or more separate ions and the advent of a multiply-charged ion having the same total charge. To eliminate this uncertainty, a sufficiently small quantity of radium was placed at such a distance from the oil drop that the probability of two α particles crossing the space beneath the drop at the same instant was very small. This probability was further diminished

[1] R. A. Millikan, PHYS. REV., 32, 349 (1909).

by using very small drops. For the drop of average size, if the α particles from 0.1 milligram of radium bromide were emitted at regularly spaced intervals of time and equally in all directions, one α particle a minute would have passed under the drop. Finally the chance that a single α particle would pass through two different molecules of the gas both of which were immediately beneath the drop was made as small as possible by working at low pressures and using small drops. These precautions could be sufficiently well taken to insure that the probability of simultaneous catches from these causes was vanishingly small. But the "induced radioctivity," discussed later, introduced another source of simultaneous catches, and this unwelcome interference was only under partial control.

The vessel was exhausted to pressures ranging from 4 to 10 centimeters of mercury, a number of oil drops were produced (by means of a "capillary tube atomizer" designed by us for use at these pressures), and a very small one of these drops, holding a positive charge, was suspended in the upper part of the field between A and B, Fig. 1, by adjusting the field

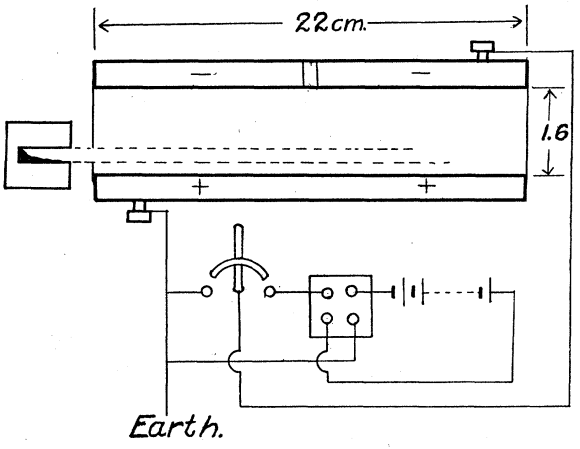

Fig. 1.

strength until the drop was nearly balanced. The lead door of the radium container was then opened so as to allow a stream of α particle to shoot underneath the drop. A molecule beneath the drop, when ionized, is thrown immediately upwards by the field, impinges on the drop and increases its positive charge. The question of the valency of the ion may at once be settled by computation from the observed change in the speed of the drop.

That only those ions which are formed beneath the drop, contribute to the changes in speed was very effectively brought into evidence several

times when improper alignment of the beam from the radium made it impossible to make captures other than those due to the "induced radioactivity," even with the radium door open. Proper alignment at once corrected this defect, so that the conclusion is fully warranted that the great majority of the catches recorded were due to the beam of α rays passing immediately beneath the drop. This part of the experiment also shows the complete untenableness of the position taken by Frank and Westphal[1] relative to Millikan and Fletcher's work on X-ray ionization, namely that a possible reason for their failure to observe doubles was the slow rate of diffusion of doubles. Neither in those experiments nor in these can diffusion play any rôle whatever, for the catches are all made in fields so powerful that an ion is thrown to the appropriate plate within something like a ten-thousandths of a second of the instant at which it is formed, and one having a double charge would move with still greater speed.

For convenience in the measurements of speed, a scale containing 80 divisions was placed in the focal plane of the observing microscope. The procedure followed was, to select a drop with the proper speed under gravity, and then to get a unit positive charge upon it by opening the radium door and throwing the field on and off until the proper charge was obtained, and finally to adjust the field for an approximately balanced condition. The radium door was then opened until a sudden start in the drop showed that an ion had been caught. The radium door was then immediately closed and the time required for the passage of the drop over ten divisions of the scale, observed. The door was again opened until another sudden increase in the speed indicated a second capture; the door again closed and the speed taken as before. When the drop came too close to the upper plate, the field was reversed (with the radium door closed) and the drop pulled down to the desired distance above the lower plate, when the field was again reversed and observations continued. Occasionally, the drop would make a catch as it was being drawn down from the upper plate. This was due either to "induced radioactivity" or to stray accidental ionization. It was decided at the beginning that when such a catch did occur, it would be considered a break in the series of observations and would not be counted; for, first, such a catch cannot come from the source under investigation; and, second, the observer needs the brief interval for rest. After the advent of the second or third charge, the speed had usually increased so much that further changes were more difficult to observe and at this point the field was always decreased to such a value that the next two or three catches produced

[1] J. Franck and W. Westphal, Phil. Mag. (6), 22, 547 (1911).

easily observed changes in speed. In some of the observations, two such changes were made. After the number of positive charges on the drop had reached five, this excess was removed by throwing off the field for a fraction of a second and opening the radium door for an instant. Proceeding in this way, in a very few trials a unit positive charge could be obtained upon the drop. It is then an easy matter to bring the drop back to unit charge, or to any other desired number of charges and then to repeat the series of operations detailed above.

The same drop was usually kept under observation for a long interval of time, in one instance for three hours, long series of catches upon it observed (160 on drop No. 10 in air), and the "valency" of the charged molecule in the case of each capture determined

As indicated in preceding papers the determination of the valency is very simple, since for a given drop, at a particular pressure and in a constant field, there is a definite speed for the drop when it carries 1, 2, 3 or n charges. Indeed the recurrence of these definite speeds scores and, in some instances, hundreds of times furnishes a most striking confirmation of the atomic structure of electricity and demonstrates the non-existence in all these experiments of subelectrons. In this work no attempt was made to obtain a precise determination of the speeds, since great accuracy was not necessary for the purposes of the investigation. A stop-watch was used throughout and timings taken only over the small distance represented by the ten divisions of the microscope scale. Neither was great precaution taken to obtain dust-free air, which has been shown in preceding work to be essential in obtaining the value of e wth accuracy. We are concerned only with the *relative* values of the charges carried by a given drop after successive captures of ions from the gas under investigation. These relative values can be determined from the equation:

$$ne = \frac{mg}{Fv_1}(v_1 + v_2),$$

where v_1 is the velocity of the droplet downward under gravity,

v_2 is its velocity upward under the field,

m is its mass,

e is the elementary charge,

F is the field intensity,

n is the number of charges on the drop.

Substituting for v_1 and v_2 respectively d/t_1 and d/t_2 where d is the distance between ten divisions of the reading microscope, and t_1 and t_2 are the seconds required for the droplet to traverse the distance d under gravity and under the field respectively, and substituting also the

expression pN for F where N is the number of trays of storage batteries employed (the storage batteries were built in trays of about 160 volts and a whole number of trays was always used) and p is the volts per tray divided by the distance between the condenser plates, we readily obtain:

$$n = \frac{mg}{pe}\left(1 + \frac{t_1}{t_2}\right)\frac{1}{N}.$$

In all of the records we have tabulated the quantity $\left(1 + \frac{t_1}{t_2}\right)\frac{1}{N}$ which is proportional to the number of charges on the droplet. If we divide this quantity by the greatest common divisor of the series of its values for any drop, we obtain the number of charges. This greatest common divisor was in every case also an observed quantity, since the unit charge on each droplet was identified before beginning the series of observations. The results of observations on the various gases and vapors are given below.

IV. AIR.

After the radium had been enclosed in the apparatus for a few days it was found that the frequency of catching was increasing to such a degree that there could be no certain differentiation between succeeding catches which were almost simultaneous and possible multi-valent ions. Also, with the door of the radium container closed, a series of observations exactly similar to those with the door open could be taken. Even when the radium was removed, the rate of capture was found to be about the same as that anticipated from the radium. Series of captures with different drops were observed in this way over a period of three weeks in which time 620 captures were recorded with seventeen drops. *Of these 620, there was only one capture which was either a doubly charged ion or two singly charged ions captured simultaneously.*

The rate of capture was undiminished at the end of one month and it was concluded that the interior of the apparatus had become coated with the active deposit of slow transformation, radium $D + E + F$, which was first studied by Rutherford[1] who found the curve of activity practically straight for the first few months. There was probably present also some "recoil radiation of radium," as the activity seemed too great to ascribe to the active deposit of slow transformation alone.

While the greater portion of the foregoing captures were undoubtedly due to α particles, the rate of capture was entirely uncontrollable and it was thought best therefore to return to the original plan of producing the ionization by a single beam of α rays. Polonium was unfortunately

[1] E. Rutherford, Phil. Trans., A, 204, 169 (1905).

TABLE I.

Drop No. 2 in Air.

Pressure, 9.75 cms. Time of run, 2:00 hours. Blank, 3 negative and 1 positive in 1 hour. Total captures, 67 (58 positive, 9 negative).

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.	t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.
16.8	12 *B*	47.0	0.112	1	1 P.	16.5	12 *B*	54.0	0.108	1	..
		9.6	.227	2	1 P.			10.2	.216	2	1 P.
		5.2	.349	3	..			5.4	.334	3	1 P.
	6 *B*	15.8	.342	3	1 P.		6 *B*	16.7	.328	3	..
		9.6	.455	4	..			10.0	.437	4	1 P.
								7.0	.543	5	1 P.
		15.6	.344	3	..						
		45.0	.228	2	1 N.		12 *B*	54.0	.108	1	..
		16.0	.340	3	1 P.			10.0	.219	2	1 P.
16.4		10.0	.444	4	1 P.			5.2	.344	3	1 P.
		6.9	.567	5	1 P.		6 *B*	17.0	.325	3	..
								10.0	.437	4	1 P.
	12 *B*	47.2	.112	1	..			7.2	.543	5	1 P.
		9.6	.226	2	1 P.						
		5.6	.330	3	1 P.	16.0	12 *B*	57.0	.107	1	..
	6 *B*	16.0	.338	3	..			10.0	.217	2	1 P.
		9.8	.446	4	1 P.						
16.4		6.9	.563	5	1 P.			58.0	.107	1	..
								16.0[1]	.000	0	1 N.
	12 *B*	48.0	.111	1	..			58.0	.107	1	1 P.
		9.9	.221	2	1 P.			10.0	.216	2	1 P.
		5.2	.344	3	1 P.			6.0	.306	3	1 P.
	6 *B*	16.0	.337	3	..		6 *B*	17.2	.322	3	..
		10.0	.438	4	1 P.			10.0	.434	4	1 P.
		7.0	.553	5	1 P.			7.2	.534	5	1 P.
16.2	12 *B*	50.0	.111	1	..		12 *B*	58.0	.106	1	..
		9.85	.223	2	1 P.			10.0	.216	2	1 P.
		5.5	.331	3	1 P.			5.8	.314	3	1 P.
	6 *B*	16.5	.332	3	..		6 *B*	17.2	.322	3	..
		10.0	.439	4	1 P.			57.5	.216	2	1 N.
		7.1	.550	5	1 P.			17.1	.322	3	1 P.
								10.0	.434	4	1 P.
	12 *B*	50.5	.110	1	1 P.			7.3	.533	5	1 P.
		10.0	.220	2	..						
		5.4	.336	3	1 P.	16.1	12 *B*	59.0	.106	1	..
	6 *B*	16.5	.332	3	..			10.2	.213	2	1 P.
		50.0	.221	2	1 N.			5.6	.326	3	1 P.
		16.5	.332	3	1 P.		6 *B*	17.3	.319	3	..
		10.0	.439	4	1 P.			10.2	.426	4	1 P.
		7.0	.555	5	1 P.			7.0	.543	5	1 P.

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.	t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.
15.6	12 B	58.0	0.106	1	..	16.0	6 B	18.8	0.306	3	..
		10.2	.212	2	1 P.			61.0	.209	2	1 N.
		5.5	.323	3	1 P.			18.0	.313	3	1 P.
	6 B	18.4	.309	3	..			61.0	.209	2	1 N.
		10.7	.413	4	1 P.		12 B	60.0	.105	1	1 N.
		17.8	.314	3	1 N.			10.8	.205	2	1 P.
		10.6	.415	4	1 P.			5.6	.318	3	1 P.
		7.2	.531	5	1 P.		6 B	18.6	.306	3	..
								10.6	.415	4	1 P.
16.0	12 B	60.0	.105	1	..			18.8	.306	3	1 N.
		10.8	.205	2	1 P.			10.5	.417	4	1 P.
		5.8	.310	3	1 P.						

[1] Going downward (neutral).

not available at the time. However, by repeatedly washing the apparatus and etching with acid, it was found possible to reduce the rate of capture due to this induced radioactivity to one or two captures an hour. Then in all subsequent work the radium container was placed in the apparatus at the beginning of observations each day and withdrawn immediately after the close of the day's run, and in the interval between succeeding periods of observation the apparatus was washed and etched with acid if necessary. In order that the exact magnitude of this effect could be known for each series of observations, a "blank" determination of from thirty minutes' to an hour's duration was made each day at the beginning and end. In these "blank" determinations, the procedure was the same as in a regular run except that the radium door was not opened and thus the rate of capture due to induced radioactivity alone was determined. Blanks made in this way ranged from one to six captures an hour, being practically always greater at the end of the day.

Table I. gives a typical series of observations on a drop by this method. Column 1 gives the times under gravity: column 2, the times under the field (the notations 12B and 6B refer to the number of trays of batteries). It is to be noted that there is a gradual downward drift of the successive values of $[1 + (t_1/t_2)]1/N$ for the same charge on the drop. This is due to the slight change in the value of the weight of the drop and to the fact that mg/pe has been taken as constant. p is not absolutely constant as the voltage of each tray of 160 volts falls here at a rate of about 1.5 volts per hour. Hence the value of p is less at the end of the run than at the beginning, and if this correction were made, it would increase the various values. This is not at all necessary, however, as there can be no possible ambiguity in any instance in the choice of the number of charges on the drop.

It will be seen from Table I. that *out of 67 catches of ions there is not even one multiple charge. Such observations were taken in air with ten drops and a total of 624 captures with not a single multiple charge.* Table II. gives a summary of the data for air.

TABLE II.

Air.

Drop Number.	Positive Singles.	Negative Singles.	Multiple Captures.
1	11	3	0
2	58	9	0
3	39	8	0
4	49	29	0
5	79	39	0
6	37	15	0
7	13	13	0
8	21	11	0
9	17	13	0
10	101	59	0

V. CARBON DIOXIDE (CO_2).

This gas was made in a Kipp's generator using 50 per cent. nitric acid and marble (previously boiled out in nitric acid) washed by passing through a solution of sodium bicarbonate to eliminate acid spray, and passed through a drying system and dust filter before entering the apparatus. The carbon dioxide was passed into the oil drop chamber near the bottom under the condenser, and was always allowed to flow twice as long as was required to extinguish instantly a lighted match held an inch above the top of the vessel. Then the lid was put on air-tight and the vessel evacuated to a pressure of from 1 to 2 mm.; the final pressure of carbon dioxide was established by allowing the vessel to come into communication with a 20-liter bottle of the same air-free, dry carbon dioxide. This was considered to give an atmosphere sufficiently free from air to leave no doubt as to the effect of ionization of carbon dioxide.

With carbon dioxide, one double catch, or one set of two simultaneous single catches was observed; Table III. shows the observations on the droplet which caught this apparent double, while Table IV. gives the summary of the seven drops with which observations were conducted in carbon dioxide, *a total of 356 captures, all singles with the one exception noted above.*

VI. CARBON TETRACHLORIDE ($C.Cl_4$).

To obtain substances of higher molecular weight which could be used in the chamber of the oil-drop apparatus, it seemed best to choose liquids

TABLE III.

Drop No. 1 in Carbon Dioxide.

Pressure, 9.30 cm. Time of run, 48 minutes. Blank, 1 positive and 1 negative in 30 minutes. Total captures, 37 (28 positive, 8 negative, 1 apparent double positive).

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.
15.0	12 *B*	800	0.085	1	1 N.
		15.0[1]	.000	0	..
		800	.085	1	1 P.
		15.0[1]	.000	0	1 N.
		800	.085	1	1 P.
		7.4	.251	3	2 P.
	6 *B*	25.6	.263	3	..
		13.9	.346	4	1 P.
		10.0	.417	5	1 P.
		7.2	.513	6	1 P.
	12 *B*	Balanced	.085	1	..
		14.0	.171	2	1 P.
		7.4	.250	3	1 P.
	6 *B*	26.0	.261	3	..
		13.8	.345	4	1 P.
		10.0	.416	5	1 P.
14.6	12 *B*	Balanced	.083	1	..
		14.0	.170	2	1 P.
		6.8	.262	3	1 P.
	6 *B*	29.0	.251	3	..
		14.6	.333	4	1 P.
		28.7	.251	3	1 N.
		15.2	.326	4	1 P.
		10.0	.410	5	1 P.
14.6	12 *B*	Balanced	.083	1	..
		14.5	.168	2	1 P.
		7.6	.244	3	1 P.
	6 *B*	29.4	.249	3	..
		Balanced	.166	2	1 N.
		29.4	.249	3	1 P.
		15.0	.329	4	1 P.
		9.6	.420	5	1 P.
	12 *B*	Balanced	.083	1	..
		15.0[1]	.000	0	1 N.
		Balanced	.083	1	1 P.
		15.0[1]	.000	0	1 N.
		Balanced	.083	1	1 P.
		14.5	.167	2	1 P.
		7.4	.248	3	1 P.

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.
14.6	6 *B*	29.4	.250	3	..
		14.5	.334	4	1 P.
		10.0	.410	5	1 P.
	12 *B*	Balanced	.083	1	..
		15.0[1]	.000	0	1 N.
		Balanced	.083	1	..
		14.6[1]	.000	0	1 N.
		Balanced	.083	1	1 P.
		15.2	.163	2	1 P.
		7.4	.248	3	1 P.

[1] Going downward (neutral).

TABLE IV.

Carbon Dioxide.

Drop Number.	Positive Singles.	Negative Singles.	Multiple Captures.
1	28	8	1 double
2	53	20	0
3	77	23	0
4	13	2	0
5	37	13	0
6	4	0	0
7	64	13	0

of sufficiently high vapor tension to make it possible to work at the pressures which had been found to give the most suitable rate of capture. Of these liquids carbon tetrachloride appeared very promising on account of its indifference chemically, its stability, and its vapor pressure which at ordinary temperatures is about 10 cm. Three methods of filling the vessel with the vapor were employed, of which one was used with the first drop only and consisted in placing about five times as much of the liquid as would be required to fill the vessel as vapor at the working pressure and pumping until the saturation stage was just passed. As the time for attaining equilibrium was found to be excessive and as the vapors do not permit of proper operations of the pump, this method was abandoned for the more expeditious one of placing in a thin-walled glass bulb an amount of the liquid just sufficient to produce the proper pressure, suspending this in the ionizing chamber, and, after evacuating the latter, releasing the bulb by a device from without and thus breaking it and vaporizing the liquid. This method worked well, except that there were frequent failures of the glass bulb to break, but it was found that

TABLE V.

Drop No. 13 in Carbon Tetrachloride Vapor.

Pressure, 4.6 cms. Time of run, 1:40 hours. Blank, 4 catches in 40 minutes. Total captures 63 (49 positives, 14 negatives).

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.	t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charg s.	Captures.
14.2	10 *B*	42.4	0.133	1	..	10.9	6 *B*	13.1	0.305	3	1 P.
		8.6	.263	2	1 P.		4 *B*	50.4	.304	3	..
	5 *B*	56.0	.276	2	..			16.6	.413	4	1 P.
		16.0	.366	3	1 P.			10.2	.515	5	1 P.
	4 *B*	30.0	.358	3	..						
		14.6	.466	4	1 P.			50.4	.304	3	..
		9.3	.575	5	1 P.			16.6	.411	4	1 P.
								10.2	.515	5	1 P.
11.8	10 *B*	86.8	.114	1	..						
		9.0	.230	2	1 P.	10.6	10 *B*	Balanced	.105	1	..
	6 *B*	40.0	.215	2	..			10.2	.204	2	1 P.
		11.8	.324	3	1 P.		6 *B*	49.0	.203	2	..
		40.0	.215	2	1 N.			12.4	.309	3	1 P.
		12.2	.320	3	1 P.		4 *B*	54.0	.299	3	..
	4 *B*	40.0	.320	3	..			16.0	.416	4	1 P.
		16.4	.418	4	1 P.			10.8	.496	5	1 P.
		40.0	.320	3	1 N.						
		16.4	.416	4	1 P.	10.4	10 *B*	Balanced	.104	1	..
		10.0	.523	5	1 P.			10.4	.207	2	1 P.
									.201		
10.8	10 *B*	160	.107	1	..			Balanced	.104	1	..
		9.8	.210	2	1 P.			9.8	.207	2	1 P.
	6 *B*	40.4	.211	2	..		6 *B*	50.0	.201	2	..
		11.8	.319	3	1 P.			12.2	.309	3	1 P.
		42.0	.210	2	1 N.		4 *B*	65.0	.290	3	..
		12.6	.309	3	1 P.			18.4	.392	4	1 P.
		42.0	.210	2	1 N.			10.8	.491	5	1 P.
	10 *B*	220	.105	1	1 N.						
		9.6	.213	2	1 P.	10.2	10 *B*	[1]	.100	1	..
	6 *B*	48.8	.204	2	..			10.2	.202	2	1 P.
		12.4	.312	3	1 P.		6 *B*	51.0	.201	2	..
	4 *B*	47.1	.314	3	..			12.8	.302	3	1 P.
		17.8	.402	4	1 P.			50.0	.201	2	1 N.
		9.6	.532	5	1 P.		10 *B*	[1]	.100	1	1 N.
		17.2	.407	4	1 N.			10.4	.200	2	1 P.
		9.6	.532	5	1 P.			[1]	.100	1	1 N.
								10.2	.202	2	1 P.
10.9	10 *B*	250	.105	1	..		6 *B*	50.2	.201	2	..
		9.2	.217	2	1 P.			13.0	.296	3	1 P.
		250	.105	1	1 N.			51.0	.201	2	1 N.
		9.6	.213	2	1 P.			13.0	.296	3	1 P.
	6 *B*	44.6	.207	2	..			51.0	.201	2	1 N.

t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.	t_1.	N.	t_2.	$\left(1+\frac{t_1}{t_2}\right)\frac{1}{N}$.	No. of Charges.	Captures.
10.2	6 B	13.0	0.296	3	1 P.	10.3	4 B	18.4	0.390	4	..
	4 B	18.8	.388	4	1 P.			10.6	.493	5	1 P.
		10.8	.491	5	1 P.						
						10.1	10 B	[1]	.100	1	..
10.3	10 B	[1]	.100	1	..			10.1[2]	.000	0	1 N.
		10.2	.200	2	1 P.			[1]	.100	1	1 P.
	6 B	50.0	.201	2	..			10.2	.200	2	1 P.
		12.0	.310	3	1 P.			[1]	.100	1	1 N.
		7.4	.399	4	1 P.			10.2	.200	2	1 P.

[1] Going downward very slowly.

[2] Going downward (uncharged).

the introduction of the same amount of liquid through the capillary of our atomizing arrangement worked satisfactorily and indeed yielded a steady state even more rapidly than did the plan just mentioned.

All droplets in carbon tetrachloride vapor exhibit a remarkable decrease in the time of fall under gravity. This is illustrated by drop No. 13 for which the data is reproduced in Table V. (see column headed t_1). This decrease is sufficiently explained by the solubility of the vapor in the watch oil used for the drops. That this is the correct explanation is shown by the fact that, after each atomization, there was an actual decrease of pressure due to the absorption of carbon tetrachloride vapor by the excess of oil in the large vessel.

Table VI. gives the summary of the fourteen drops with which observations were conducted in carbon tetrachloride vapor, totalling 457

TABLE VI.

Carbon Tetrachloride.

Drop Number.	Positive Singles.	Negative Singles.	Multiple Captures.
1	16	5	1 double
2	27	10	0
3	28	7	0
4	27	17	0
5	19	6	0
6	5	2	0
7	11	3	0
8	12	3	0
9	21	4	0
10	30	8	0
11	23	19	0
12	42	19	0
13	49	14	0
14	26	12	0

captures. *These are all singles with one exception which is again apparently a double.*

VII. METHYL IODIDE (CH_3I).

The methyl iodide was the ordinary commercial liquid not purified from the iodine which is always liberated when this substance is allowed to stand. The iodine, however, caused no disturbance because of any action on the metallic parts of the apparatus. In fact, this vapor acted much better than did the carbon tetrachloride in that there was less change in pressure and hence greater constancy in the speeds, although even here there is an unmistakable indication of the solubility of the vapor in the watch oil. The methyl iodide was introduced into the

TABLE VII.

Methyl Iodide.

Drop Number.	Positive Singles.	Negative Singles.	Multiple Captures.
1	15	3	0
2	43	9	0
3	38	22	0
4	22	7	0
5	19	7	0
6	92	32	0
7	48	13	0
8	42	23	1
9	27	16	0

ionizing chamber through the capillary tube of the atomizer after pumping down to 2 mm. Table VII. gives the summary of the nine drops used with the methyl iodide vapor, *showing a total of 478 single captures and one apparent double.*

VIII. MERCURY DIMETHYL $Hg(CH_3)_2$.

As Thomson's most striking results were obtained with mercury, this element was included in our list, the compound mercury dimethyl fortunately being sufficiently volatile to adapt itself to the procedure employed with the other liquids. The mercury dimethyl was prepared by the method of Frankland and Duppa,[1] and had the characteristic odor and gave nacreous crystals on treatment with alcoholic solution of iodine. It was introduced into the apparatus exactly as described under carbon tetrachloride and methyl iodide, *i.e.*, through the capillary tube of the atomizer. However, the vapor pressure did not rise above 2.5 cm., so that air was allowed to enter to bring the pressure up to 4.35 cm.: this means that the 24 liter vessel contained ten grams of mercury di-

[1] E. Frankland and B. F. Duppa, Jour. Chem. Soc., 16, 415 (1863).

methyl and one gram of air. On account of the extremely poisonous nature of the vapor, we made but one filling of the vessel, continuing the observations the second day until the blank reached a prohibitive value.

The 347 captures made with eleven drops are listed in Table VIII. *There are 346 "singles" and one apparent, double.*

TABLE VIII.

Mercury Dimethyl.

Drop Number.	Positive Singles.	Negative Singles.	Multiple Captures.
1	1	2	0
2	6	2	0
3	15	8	0
4	6	1	0
5	11	8	0
6	27	8	0
7	7	1	0
8	29	14	0
9	89	36	1 double
10	17	5	0
11	41	12	0

IX. DISCUSSION.

Over 2,900 captures of ions from atoms of atomic weight ranging from 1 to 200 have been observed. Of this number, there are only 5 captures which give any evidence of multiply charged atoms. These were all double positives. They could be attributed either to actual doubly-charged atoms, or to the simultaneous advent upon the drop of two singly-charged ions. That the latter is the correct conclusion seems to be fully warranted by the evidence. It has been shown that there were in reality two sources of ionization acting,—the α particle beam and the active deposit. While the latter was kept as low as possible, yet when both were acting, there would be a certain probability that captures from the two would occur simultaneously. In further support of this, some observations were taken when the background of ionization due to the active deposit was exceedingly high and then captures were observed following one another in such rapid succession that distinguishing them as separate events required the greatest vigilance on the part of the observer. Of the 5 captures which appeared to be doubles, 3 occurred just at the end of the day's run when the background had a value of 5 or 6 an hour and when the observer was not as alert as usual because of the long period of observation. It is not to be overlooked, too, that even at the low pressures used two separated molecules of the gas might be so situated as to be ionized by the same α particle and yet be thrown together upon the drop.

All of the heavier atoms used in this work were in chemical combination. This, according to Thomson[1] should rather favor the formation of multiply-charged atoms, yet we obtained no real indication of multiples.

Although all of the foregoing results are surprising, they are not at all irreconcilable with those obtained by Thomson. The time-integral of the force acting between any unit charge, moving through an atom, and any charge within the atom, varies inversely as the speed. The most rapid of the α particles used in these experiments were moving with a speed of 2×10^9 cm. per sec. If Thomson used potentials as high as 100,000 volts to produce his positive rays—and it is probable that this estimate is several times too high—the speed acquired by the hydrogen atom would have been but 5×10^8 cm. per sec. or one fourth that of the α rays. Since the time-integral of the ionizing force is directly proportional to the charge of the moving atom and inversely proportional to its speed, the 100,000-volt hydrogen atom would have twice as large a chance of producing ions as would the α ray. An oxygen atom which had acquired its speed in the same field as that acting upon the hydrogen atom would be moving but about one fourth as fast as the hydrogen, and hence would possess four times the ionizing power.

It is altogether conceivable, therefore, that slow positive rays might make multivalent ions when fast α rays would not. It is hoped to test this point by catching the positive residues of atoms formed by rays *at the very end of their range*, where they should be moving as slowly as the positive rays in Sir Joseph's experiments. No such attempts were made in the present work, in which the distance of the oil drops from the source of the rays amounted to but about one tenth of the range of the particles.

Again, it is to be remembered that the positive residues formed in these experiments practically never arise from nuclear or central impacts. For if the nucleus of the atom has a radius of the order 10^{-13} cm. while the atom itself has a radius of the order 10^{-8} cm., there would be ten billion atoms traversed by α rays to one nuclear impact, and the chance of catching on an oil drop a positive ion which arose from a nuclear impact would accordingly be altogether negligible.

There are, however, recent scintillation experiments of Rutherford's[2] which deal only with nuclear impacts, and *these seem to show that even such impacts upon atoms of nitrogen and oxygen produce primarily singly, not doubly or trebly charged atoms.*

[1] Sir J. J. Thomson, p. 54, Rays of Positive Electricity and their Application to Chemical Analysis, Longmans, Green, & Co.

[2] Phil. Mag., XXXVII., 578 (1919).

Since in Rutherford's experiments, the energy of impact of the α rays upon the nucleus is much greater than the energy of impact of positive rays can ever be, his failure to obtain multivalent nitrogen and oxygen atoms is certainly surprising, and this, taken in connection with the present experiments, shows clearly that the conditions under which multiply charged atoms may be formed are quite limited. Such atoms are surely not formed in the positive ray work primarily, if at all, by nuclear impacts; for the numbers in which they appear seem to be much greater than the possible number of such impacts. And further, according to Rutherford, such impacts produce in general singles, not multiples, in these gases. Again, the present experiments show that multivalent ions are not formed by the non-nuclear impacts of high speed α rays. It is probable that they are formed only in a narrow range of speeds just above that which makes interpenetration of the atoms possible.

Only in the cases of carbon and helium does Rutherford infer multiply charged atoms as a result of his nuclear impacts and the inference is here drawn from negative evidence rather than positive, viz., from the failure to obtain scintillations at the ranges at which such scintillations should appear, if singly charged carbon and helium atoms were formed. Our own experiments, while they gave in carbon dioxide only singly charged positive residues, might conceivably give doubly charged ones with helium. It is hoped in the near future to subject this gas to tests of the sort herein reported.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
July 30, 1919.