MULTIPLE VALENCY IN THE IONIZATION BY ALPHA RAYS.

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SYNOPSIS.

Valency of Ions Produced by α-rays.—The well-known Millikan oil-drop method, in which the valency of individual ions caught on the droplet immediately after they are produced is determined by the change of speed of the droplet due to each, was used with slight modifications which simplified the procedure. *In air*, out of 350 positive ions produced by x-rays at the end of their range, only 3 per cent. could have been doubly charged and most if not all of these were probably not doubles but two successive singles. *In helium*, an extensive series of 2,150 positive catches were observed with gradually increasing pressure to determine not only whether doubles were produced but also the *variation of the number of doubles with the range.* It was found that an appreciable proportion of real doubles is produced when the ranges of the rays are equivalent to between 4 and 30 mm. of helium at atmospheric pressure, the maximum proportion being about 10 per cent., for the range of maximum ionizing power. That this result was real was proved by the fact that when *hydrogen* was substituted, even for the range of maximum ionization, the proportion of apparent doubles was only 5 out of 200 positive ions. The previously reported negative result for *mercury dimethyl* was confirmed.

Relative stopping power for α-rays, of air and helium, came out close to 3.8, in agreement with the Bragg-Kleeman law.

INTRODUCTION.

THE nature of the process of the ionization of gases by alpha rays was investigated by Millikan, Gottschalk, and Kelly [1] by catching an ionized molecule upon an oil-drop at the instant of ionization and then measuring the charge thus added to the drop. The results prove that at least 99 times out of 100, ionization by an alpha ray, in the case of the following gases and vapors (air, carbon dioxide, carbon tetrachloride, methyl iodide, and mercury dimethyl), consists in the detachment of a single electron from a molecule.

These results, along with much other work, summarized by Millikan, Gottschalk and Kelly, point to the formation of univalent ions. Indeed the only evidence for the formation of multivalent ions was the positive ray work of Sir J. J. Thomson.[2] Millikan pointed out, however, that these results were not at all irreconcilable, as a consideration of the velocities and the forces involved, made it conceivable that slow positive rays might make multivalent ions when fast alpha rays would not. It

[1] R. A. Millikan, V. H. Gottschalk, M. J. Kelly, PHYS. REV., 15, 157, 1920.

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

became desirable, therefore, to test this point and, accordingly, such work has been undertaken.

Reference was also made to the scintillation experiments of Sir Ernest Rutherford on the "swift atoms" resulting from ionizing gases by the nuclear impact of alpha rays, in which the inference was drawn from negative, rather than positive evidence, that doubly charged ions of helium were formed. The importance of extending the oil-drop experiments to include a study of the alpha-ray ionization of helium was obvious, both because of the fundamental rôle played by the helium atom in the present-day theories of atomic structure and the fact that in alpha rays themselves we really have doubly charged helium ions. Recently it has become possible to secure helium in sufficient quantities for use in the oil-drop apparatus, the chamber of which has a volume of about twenty litres, and the results of a study of the alpha-ray ionization of helium are here given.

The results in helium, as will appear, made it seem desirable to extend the work to hydrogen, and this has also been done.

Apparatus.

The apparatus used was identical with that already described [1] except that polonium was used instead of radium bromide as a source of alpha rays. Unfortunately polonium was not available at the time of the earlier work. While not altering the procedure in any way, this substitution brought two advantages: first, it removed the annoyances encountered in the earlier work which were caused by the formation of an "active deposit" on the walls of the chamber, and the consequent increased and uncontrollable ionization due to this cause; secondly, it provided a "simple" source of ionizing rays for which a random distribution of ejection could be assumed in a study of the frequency of catches.

The polonium was prepared by Mr. E. T. Johnson and Mr. B. A. Rogers, who also conducted some observations on the ionization of air, to which reference will be made later. To obtain the polonium some old radium preparation was used and the usual method followed.[2] The product was tested in an electroscope for the presence of beta rays by covering it with sufficient aluminum foil to absorb the alpha rays but not the beta rays, and it was found free of beta radiation.

The coarse adjustment to obtain ionization at the end of the range was made by interposing absorbing foil of the necessary thickness and the finer adjustment made by varying the gas pressure in the chamber. In this way a very delicate adjustment could be obtained.

[1] R. A. Millikan, V. H. Gottschalk, M. J. Kelly, loc. cit.

[2] Practical Measurements in Radioactivity, W. Makower and H. Geiger, Longmans, Green & Co., p. 123.

A concentrated filament lamp replaced the arc used in the earlier work and gave a very steady illumination and did away with the necessity of frequent adjustments of the arc.

A potentiometer switch was arranged so that the plate voltage could be varied through wide ranges in steps of 15 volts.

PROCEDURE.

The general procedure followed was that already described.[1] For the greatest possible simplicity of observation it was always arranged to have but one charge on the drop when the polonium door was open.

The field between the condenser plates was adjusted to balance the drop when it had this one charge on it and measurements were made at this one voltage. Thus the duties of the experimenter were very much lightened. As soon as a catch was made and measured, the drop was made ready for another catching by getting rid of all but one charge. This was done in the usual way.

The experimental testing of the number of charges on the drop is very simple under this procedure for there is then clearly an exact multiple relation between the characteristic speeds corresponding to various numbers of charges. And, further, no time is wasted in first determining the characteristic speeds or in redetermining them as the voltage of the cells drops, for if the voltage drop, the potentiometer switch is moved a peg till the original balance is secured. This was of help in the work on mercury dimethyl vapor, where the temperature was raised considerably to raise the vapor pressure while a run was in progress. No confusion resulted, for although the numerical values of the speeds changed, each one altered so that a multiple relation again held. For example, the speed corresponding to a catch of one charge changed from 16 to 18 seconds as the temperature and vapor pressure rose. That corresponding to a catch of a double rose, proportionately, from 8 to 9 seconds, and similarly, the triple speed changed from 5.3 to 6 seconds.

To express these relations in mathematical form, we have the two following equations:

(1) $V_g = kmg$ where V_g = the vel. of fall under gravity.
k = a constant of proportionality.

(2) $V = k(neE - mg)$ V = vel. of rise when the drop has a positive charge.
n = number of charges on drop.
e = the elementary charge.
E = the P.D. between condenser plates.

[1] Millikan, Kelly and Gottschalk, loc. cit.

Now, if $Ee = mg$, *i.e.*, if the potential applied is just sufficient to balance a drop with unit charge, (2) becomes,

$$V = k(n - 1)mg. \tag{3}$$

and so if

$$n = 1, \quad V = 0.$$
$$n = 2, \quad V = kmg.$$
$$n = 3, \quad V = 2kmg.$$
etc.

thus, when a charge is caught, the drop will start upward with a speed equal to kmg—if two charges are caught, with twice that speed; and if three charges are caught, with three times that speed, and we immediately have the number of charges caught because of this multiple relationship in speeds.

As evidence of the careful balancing of the drop and the control of the ionization, it may be mentioned that the drop was often left suspended for intervals of a quarter to half an hour and in one case a drop was left for an hour and a quarter and was in practically the same spot when the observers returned from dinner.

An attempt was made to take as long runs as possible on the same drop and in no case have fewer than 21 catches been reported on the work in air and in the work in helium not fewer than 50 catches of positives. As many as 150 catches are reported on some drops corresponding to from six to eight hours' observation on the same drop. Most of the drops remained bright right up to the end of the run, but in the work on mercury dimethyl vapor, where an attempt was made to raise the vapor pressure by raising the temperature some 15 or 20 deg. C., the drops soon lost their lustre and only short runs were possible.

Data—Air.

Table I.

Drop Number.	Pressure (Cm. of Hg).	t_g (Secs.).	Total No. of Catches (Pos. Negatives).	Double Positives.
1	8	103	95	2
2	8.1	95	21	0
3	8.1	150	68	1
4	8.05	102	35	0
5	8.1	105	108	0
6	8.15	114	66	3
7	8.3	103	21	0
8	8.15	138	48	2
9	8.2	110	52	2
			514	10

Table I. shows that out of 514 catches, 350 of which were positives, 10 were apparently doubles. It will be noted that the work here summarized was all done at approximately the same pressure. About as many more data were first taken under various conditions of pressure to determine the most suitable value at which to work. If the pressure is a little too low, too many alpha particles get through and the catches come too frequently. If the pressure is too high, the interval between catches becomes too long. It was thus found desirable with rays already slowed down by aluminum foil to the extent these were, to work with air at pressures between 8 and 8.5 cms. This corresponded very nearly to the end of the range of the alpha rays.

The column t_g represents the time taken for the drop to fall 50 scale divisions, approximately 5 mm., under gravity and thus indicates, roughly, the smallness of the drops.

In another set of observations of this same kind in air taken by other observers, namely Messrs. Johnson and Rogers, 519 catches of positive ions were made on 18 drops under approximately the same conditions as those just summarized. They found 15 catches which they counted as doubles and 5 which, though measuring up as doubles, they classed as "doubtfuls." By a doubtful double they meant that two jerks were observed in the drop's motion—a second jerk taking place before the shutter could be closed to prevent further ionization. While the second jerk might have been a Brownian movement jerk, as it often proved to be when measurement showed only a "single," yet it was felt that the second jerk might have been caused by the catching of a second ion and such catches were therefore classed as doubtful doubles.

It will be seen that these two sets of measurements are in very good agreement; Johnson and Rogers data showing about one double in 34 positive catches and the data here given showing one in 35.

To decide whether these were real doubles or whether a large fraction of these, too, were actually doubtful doubles, it was only necessary to find what was the average interval during which the polonium shutter was open before a catch was made and to calculate what the chance would be of two single ions being caught in an indistinguishably small interval. The observations showed that if the pressure was 8.1 cms. (in the case of air), the average exposure for a catch was 43 secs. but when the pressure rose, less than half a cm., to 8.5 cms. of mercury, the interval increased to 167 secs. and when a pressure of 9 cm. was reached, no catches were made after several intervals of ten or fifteen minutes, waiting. Hence, for alpha rays which had already been slowed down by the foil to the extent which these had, a pressure of between 8.1 and 8.5 cms.

of air enables us to make measurements at practically the end of the range. The discussion of the probability of two single ions being caught in an indistinguishably small interval is given below.

The Probability Function.

It has been shown repeatedly that a random distribution of ejection can be assumed for the alpha rays emitted in radioactive changes. But it is a familiar result, taken from the theory of probability, that if a series of events happens with a random distribution of intervals, the probability of there being an interval as long as t seconds between two successive events is

$$P = e^{-ut}, \tag{1}$$

where $1/u$ is the average interval.

It was estimated that 1 second was a fair value to take for the time interval within which it was impossible to distinguish with certainty two successive catches as actually separate events for it required about this time for closing the shutter after a catch had been seen to have occurred and during the act of closing another catch might occur without being noticeable. In the various measurements made, the average interval varied from 13 to 170 secs. The probability function may be calculated for each interval but it will be legitimate for the purpose in hand, to consider only the general average, namely, 43 secs.

From (1), the probability of an interval as long as 1 sec. between two successive catches $= e^{-u}$. The probability that there will be an interval between 0 seconds and 1 second $= 1 - e^{-u}$. Now

$$e^{-u} = 1 - u + \frac{u^2}{2!} - \frac{u_3}{3!} + \text{etc.}$$

$$1 - e^{-u} = u - \left(\frac{u^2}{2!} - \frac{u_3}{3!} + \text{etc.}\right)$$

With $u = 1/43$, all terms of the last expression, save the first, are negligible, *i.e.*, the chance of two successive catches following within an interval of 1 sec. is simply u.

It appears then that since the average interval, as given below, is about 43 secs., that one catch in 43 under such conditions should appear as a double. This number is so near the total number of doubles obtained that we are justified in the assertion that no evidence is herewith presented for the formation of doubles in air. We may at least conclude with certainty that the act of ionization of air by alpha rays produces no more than two or three per cent. of doubly charged ions and practically never produces ions of larger valency than 2.

Helium.

It was decided to undertake quite an extensive investigation of helium as no work of this type had been done in that gas. Accordingly some 2,150 positive ions were caught; an attempt being made to approach *gradually* to the end of the range of the alpha particles. This was done by gradually increasing the helium pressure in the oil-drop chamber as successive oil drops were blown in with helium. As the "stopping power" of helium is much less than that of air, it was found that to slow down the alpha particles to the end of their range, a much larger helium pressure was required than was necessary in air. The gas pressure was steadily increased and measurements taken at various stages.

Data—Helium.

It will be noticed from Table II. that the interval between catches decreased at first as the pressure was increased since more atoms of helium were present to be ionized. The interval became a minimum

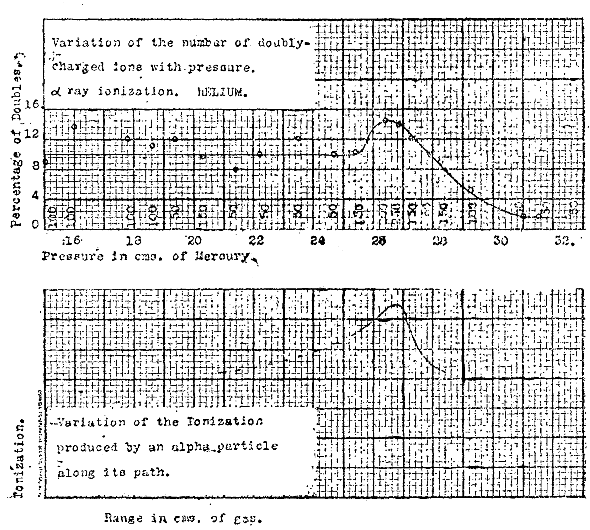

Fig. 1.

at a pressure of about 26.6 cms. and then gradually increased indefinitely. Thus the ionizing power of the alpha ray is a maximum a short distance from the end of its range, which is in agreement with other work. (See Fig. 1.) As the pressure was further increased, the number of alpha rays getting through was cut down and so the interval was lengthened.

TABLE II.

Press.	No. of Positives Caught.	t_g of Drop.	Average Interval.	Per Cent. Doubles.	Average Per Cent. Doubles.	Range Beyond Point of Lip.*
8.9	50	74 secs.	44 secs.	2	2	4.0 cm.
13	50	73	23	4	4	3.3
15	100	112	19	9	9	
16	100	78	18	14	14	2.8
17.8	100	98	17	12	12	2.5
18.6	50	99	18	10 }	11	2.4
18.7	50	109	13.6	12 }		
19.4	50	113	20	12	12	2.3
20.1	50	127	21	16 }		
20.3	50	108	27	6 }	9.3	2.1
20.3	50	129	23	6 }		
21.4	50	141	20	8	8	1.9
22.2	50	127	31	10	10	1.8
23.5	50	124	28	12	12	1.6
24.7	50	130	27	10	10	1.4
25.4	100	140	26	9 }	10.5	1.3
25.5	50	143	26	12 }		
26.3	50	142	23	14 }		
26.4	50	161	29	18 }	14.7	1.1
26.6	100	155	17	12 }		
26.8	150	163	26	9 }		
26.85	50	192	30	20 }	14	1.0
26.9	100	139	23	13 }		
27.1	50	163	20	18 }		
27.3	50	157	39	2 }	12	1.0
27.5	50	174	31	16 }		
27.9	50	135	40	10	10	0.8
28.1	50	157	30	6 }	9	
28.4	100	171	28	12 }		
29	50	153	66	4 }	5	0.7
29.5	50	154	56	6 }		
30.95	50	138	67	2	2	0.3
31.5	50	155	88	2	2	
32.5	50	148	154	2	2	0.08
	2150					

The data show distinct evidence for the formation of doubly charged helium ions and show, moreover, that the formation of doubles does indeed depend on the speed of the ionizing particle. The number of doubles rises to a maximum when the ionizing power of the particles is a maximum and amounted, in this work, to as many as 15 per cent. of

* Reduced to atmospheric pressure. This reduction was suggested and outlined by Dr. G. S. Fulcher. It indicates that doubles are produced when the ranges of the rays are equivalent to between 4 and 30 mm. of helium at atmospheric pressure.

the number of ions formed. The probability of two singles being caught in an indistinguishably short interval would not account for more than three or four per cent. of the total catches being doubles, for the average interval at the peak of the production of doubles was about twenty-five seconds and thus, on the basis of the reasoning given above, one ion in twenty-five might be expected to be a spurious double. This still leaves a large margin for considering this a real effect, and this is made even more apparent in the light of some remarks under the head of hydrogen, below.

Grouping the data corresponding to pressures between 15 and 24 cms., it will be seen that the number of doubles is about 10 per cent. of the total number of positive ions produced, but from this region to the end of the range, a marked rise and subsequent decline is noticeable. Large fluctuations appear from this 10 per cent. but this is to be expected from any such probability measurement as this if only a small number of observations is taken. There seemed no special object in multiplying the observations in this region, but there was reason to expect that the region toward the end of the range might prove of special interest, for Geiger had shown, as is checked by the data above, that toward the end of the range the ionization rises very markedly.[1] Accordingly, a much larger number of observations was made in this region, and Fig. 1 shows that the curve is fixed quite definitely for this region of interest.

An interesting comparison may be made between the data on air and those on helium. It was found, as already noted, that with air, an interval of 167 secs. ensued between catches if the pressure were raised to 8.5 cms. Table II. shows that in helium an interval of 154 seconds accompanied a pressure of 32.5 cms. So the alpha particles were ionizing about as infrequently in one case as in the other. In other words, 8.5 cms. of air have about as great stopping power for alpha particles as 32.5 cms. of helium. This is in very nice agreement with Bragg and Kleeman's results that the stopping power of an element for alpha particles is proportional to the square root of the atomic weight and for complex molecules is an additive property.[2] Adams has already done work on the testing of this law for helium and other gases.[3] Using Adams's calculations for

$$\frac{\Sigma\ \sqrt{\text{At. Weight air}}}{\Sigma\ \sqrt{\text{At. Weight helium}}} = 3.8$$

and remembering that the stopping power is inversely proportional to

[1] Rutherford, Radioactive Substances and their Transformations, p. 153.

[2] Bragg and Kleeman, Phil. Mag., 6, 1905, p. 338.

[3] Adams, PHYS. REV., 24, 1907, p. 108.

the pressure, we calculate that the pressure of helium necessary to stop the alpha particles to the same extent as would be done by 8.5 cms. of air would be 8.5×3.8, or 32.3 cms. of helium. This is to be compared with the 32.5 cms. for approximately equal stopping power mentioned above.

Hydrogen.

The law given by Bragg and Kleeman for the stopping power of gases for alpha particles has been shown, above, to be beautifully checked in the work on helium. It follows from the law, that hydrogen should have the same stopping power as helium, for though of different atomic weight, helium is monatomic and hydrogen, diatomic. If the doubles in helium were spurious in any way, the same effects should occur in hydrogen. A series of runs was therefore taken at that pressure at which the maximum effect was found in helium. Theoretically, there would be no expectation of doubles in hydrogen for the hydrogen atom is pictured as having but one electron and even though hydrogen is diatomic, the chance of catching a double, formed by the electrons being pulled off from each atom, would be negligible, for the positive nuclei remaining, would, presumably, at once repel each other and not be caught together. Commercial hydrogen was used.

Table III.

No. of Pos. Catches.	Press.	t_g.	Av. Interval.	Doubles.	Per Cent.
50.........	26.2	114	64 secs.	1	2
100.........	26.5	95	61	4	4
50.........	27	110	74	0	0
200				5	2.5

Thus hydrogen showed 5 doubles in 200 but since the probability calculation, as given above, would class 4 of these as spurious, it seems fair to conclude that not only were no real doubles secured in hydrogen but, because of the identity of stopping power and the conditions of temperature and pressure, the evidence is confirmed that those secured in helium were real and in no way due to faulty shielding, to the catching of two separately ionized molecules or to any such effects.

Mercury Dimethyl.

The work of Millikan, Gottschalk and Kelly was repeated in this case also but no evidence for real doubles was secured. The delicate adjustment for the end of the range could not be made, in the case of this poisonous vapor, as with the other gases, so the vapor pressure was raised by raising the room temperature. The multiple relationship between the different valence speeds shown in the first part of the paper proved of great value here as the characteristic speeds constantly changed with the vapor pressure changes.

In conclusion, the writer wishes to thank Professor R. A. Millikan for outlining the problem and for his valuable suggestions during the course of the work. The present paper is but a continuation of Professor Millikan's earlier papers as has been indicated in the references above.

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