THE PROCESS OF IONIZATION OF ARGON

BY ALPHA-PARTICLES.

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by

A Lloyd Greenlees.

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I. Introduction.

To ionize an atom of any element requires the expenditure of a certain amount of work, dependent upon the particular element concerned. This energy may be acquired through impact with a rapidly moving electron, positive ion, or neutral atom, or through absorption of radiation. We shall be concerned with ionization by the impact of positive ions and α-particles. Suppose the colliding particle has more than sufficient energy to affect the removal of one electron, what is the net result of the collision? May it happen under certain favourable conditions that a second electron is removed, or does the ionization process invariably consist in the removal of a single electron? It was the object of this research to supply further experimental proof for the theory that more than one electron may be dislodged by single impact.

Up until 1911 we had no unambiguous information as to what really happens when a high speed particle collides with a normal atom. It was not known with certainty whether one two or more electrons are dislodged by the impact. True, Townsend and his students had deduced evidence, from measurements of the ratio of the mobility to the diffusion coefficients, that the ions formed in air by Roentgen rays and the rays from radium bore only a single charge. On the other hand, Sir J.J.Thomson, from his work on positive rays, had shown that in a relatively large number of instances the ions formed by this method were multivalent. In the case of oxygen and nitrogen he obtained parabolae corresponding to ions bearing one and two charges, while in mercury the multiplicity went as high as seven. In both types of experiment the ions were received by the recording apparatus at a relatively long interval of time after their formation. It was therefore possible that they may have had time to recombine, or in Thomson's experiments, to have suffered a second or third impact and consequent loss of additional electrons.

The first really direct evidence bearing on the question of valence in ionization was supplied by the experiments of Millikan and Fletcher (Phil.Mag. vol.21, 1911, p753). By catching the positive ions on oil drops almost at the instant of their formation they were able to show conclusively that ions formed in air by Roentgen, β- and γ-rays were invariably univalent. The work was continued by Millikan Gottschalk and Kelly (Phys.Rev. vol.15, 1920, p157), who extended the measurements to carbon dioxide, carbon tetrachloride, methyl iodide, and mercury dimethyl. They also checked the previous work on air. The ionizing agents were the rays from radium. The vanishingly small number of apparent doubles was explicable on the assumption of a simultaneous capture of two singly charged ions.

Direct proof for the formation of multiply charged ions by single impact came in 1922 from the work of RA Millikan and T.R.Wilkins (Phys. Rev, vols. 18 p456 and 19, p210). In Thomson's experiments the ionization was affected by positive rays. Alpha-particles are only a special type of positive ray so that it would be natural to look for these multiply charged ions when α-particles were the ionizing agent.

Also it is known that an α-particle is much more effective as an ionizing agent near the end of its range, and so if doubles or triples are produced it is to be expected that they would occur in greater number near to the end of the α-particle's path. It was the object of the Millikan and Wilkins' experiment to test this hypothesis. Their experimental conditions were identical with those of their predecessors save that they used polonium, which gives rise to α-particles only. They selected helium as the gas with which to experiment. The range of the α-particles was varied by altering the pressure of the helium. In this way it was possible to test the charge carried by the ions formed by α-particles of very different energies. Results indicated that a small percentage of the ions were doubly charged; but of those formed near the end of the range as many as 15% were doubles. Going beyond this point the proportion fell off quite rapidly. The curve showing the fraction of doubles to singles plotted against the distance from the source was similar in general form to the curve representing the ionizing power of the particles against distance from the source. Millikan and Wilkins also tested hydrogen and mercury dimethyl for doubly charged ions. As was to be expected the hydrogen showed no trace of them. Their results on the mercury compound were likewise negative, confirming the earlier work of Millikan Gottschalk and Kelly.

Thus the process of ionization in the commoner gases has been shown to consist in the removal of a single electron. Only in the case of the inert gas helium is the process different, in that out of one hundred ions formed, as many as fifteen of them may have lost both electrons. It is to be noted that in this method of studying the ionization process, the ions, moving under the influence of a powerful potential gradient, are caught by the oil drop almost at the instant of their formation, and hence there is a vanishingly small chance of their recombining or of being struck by a second α-particle. Thus the uncertainties inherent in the experiments of Townsend and Thomson are obviated.

Inasmuch as helium appeared to be unique in showing this interesting property of multiple valence, it seemed worth while to extend the method to other members of the same chemical family. Though helium, neon, argon, etc. are identical chemically, there seemed to be no a priori reason for believing that they would be similar in this particular respect. Because an α-particle is able to remove both electrons from a normal helium atom, one would not necessarily expect that it would do likewise to a neon atom with its complete L-shell of eight electrons, or to an argon atom with its M-shell also complete.

II. Apparatus.

Since argon was readily obtainable, it was decided to apply Millikan's oil drop method to it, to find whether or not it behaved like helium in the formation of doubly charged ions. Inasmuch as the apparatus and method of experimentation are now quite familiar, only a brief description will be given.

Tiny drops of watch oil are sprayed into the space between two parallel and horizontal metal plates, 21.7cm in diameter and 1.53cm apart, through a few small holes in the upper plate. The condenser is contained in a large iron cylinder 12 inches in diameter and 11 inches deep, immersed in another vessel containing about ten gallons of ordinary lubricating oil. The oil served the double purpose of supplying a tight oil seal and also keeping the temperature nearly constant. A large proportion of the drops entering the condenser bear frictional charges, so it is generally easy to pick out one of about the right size and balance it against gravity by means of an electrostatic field applied across the condenser plates. Under these conditions

$$ne \frac{dV}{dx} = mg$$

It is to be noted that in the case of argon with its relatively low ionizing potential, it is not feasable to have a large value of the potential gradient, for in this case a discharge occurs between the plates, thereby introducing an extraneous and wholly uncontrollable source of ionization. In the experiment to be described, the gradient never exceeded 400 volts per centimeter.

The source of α-particles was a bismuth disc bearing a small amount of polonium, separated in the usual way from the active residue in old radium emanation tubes. The radioactive source was so placed at the edge of the gas chamber that the α-particles were projected into the condenser just above the surface of the lower plate. The α-rays could be cut off at will by a lead shield operated from without. In this work no absorbing screens were used to cut down the range of the α-particles, so that argon pressures up to 22cm of mercury were found necessary.

The light source was a 500c.p. pointolite lamp with a suitable condensing lens system to render the beam parallel. This form of illumination proved very satisfactory indeed. A water cell was interposed in the light path to absorb the infra-red rays, which would produce local heating and thence convection currents. The observing was done with the aid of a special telescope of large aperture, kindly lent to us by Dr C.F.Eyring of Brigham Young University. The incident beam and the direction of observation made an angle of about 160 degrees.

For the production of the oil drops, an ordinary medical atomizer was incorporated into the system. Condenser potentials were obtained from a battery of small storage cells arranged in banks of 160 volts. These were in series with a potentiometer arrangement so that a continuous variation of potential up to 1200 volts could be had. Because of the avidity with which argon is absorbed by charcoal immersed in liquid air, it was found a very easy matter to change gas pressure without loss of argon or tedious working of a Toepler pump.

III. Procedure.

Having selected a suitable drop, that is one having an appropriate speed of fall under gravity, a single positive charge is put upon it and the drop balanced near the upper plate. Then the shield over the polonium is raised, causing the projection of α-particles into the condenser just underneath the oil drop. Of the ions formed the positive are drawn to the upper plate and the negative to the lower. When it happens that a positive ion strikes and adheres to the oil drop, the balance is disturbed and the drop moves upward at a uniform rate. As soon as an ion is caught the shield is dropped over the polonium so that there will be no more captures. If the drop catches a singly charged ion the resultant force on the drop is edV/dx and its upward velocity is given by the modified Stokes' Law. If on the other hand the ion is doubly charged the force is $2edV/dx$ and the velocity just twice as great. Thus there is absolutely no ambiguity about the interpretation of the observations, for if in general the drop requires 20 sec. for a transit over a given number of scale divisions, and then after a particular capture traverses the same path in 10 sec. it is obvious that the captured ion carried twice the charge of its predecessors. These large-scale differences require no very accurate timing device, an ordinary stop-watch was used for the purpose.

It is to be noted that due to Brownian movements the times of transit after the capture of single charges vary slightly among themselves, but these differences are small compared to the sort that we are looking for. The time of transit having been measured, an electron is captured, thus restoring the balance, and the drop brought back to its original position and the process repeated. Electrons or positive ions may be caught almost at will by opening up the polonium and shorting the condenser plates momentarily. In this way it is possible to put any desired charge upon the droplet. By means of a second stop-watch the time required to make a capture is measured, that is, the time from uncovering the polonium to the instant of capture. The average value of this interval will be denoted by T in the following. Provided that the number of ions caught is so large that we may apply probability considerations then it is evident that this interval T is a measure of the α-particle's efficiency in producing ions at any given point in its path. Inasmuch as the number of ions caught at any one pressure is not large (250 in most cases) it is perhaps not justifiable to stress this correspondence too heavily.

IV. Experimental Results.

The results of the capture of about 2500 argon ions are contained in the following table.

Table I.

1 Press.	2 T	3 No. catches	4 Doubles	5 % doubles
95 mm	63 sec.	560	16	2.9
106	42	190	3	1.5
138	30	250	14	5.6
157	32	480	23	4.8
177	18	250	25	10.0
187	17	250	28	11.2
196	22	260	28	10.7
212	23	200	13	6.5
220	31	73	4	5.5

The first column gives the gas pressure, the second the average time necessary to make a capture, the third the total number of ions caught, and the fourth is the number of this total which were apparent doubles. The fifth column is identical with the fourth save that the number of doubles is expressed in the form of a percentage.

To obtain the data for any one row, the number of drops worked with varied from eleven in the case of the first to three in that of the last. Of course the balancing potential was different for every drop, but any systematic differences due to this cause were quite imperceptible. Table II. contains in detail the figures which are combined to form the fourth row of Table I.

Table II.

Press.	P.D.	T	No. catches	Doubles	% doubles
154.5mm	347 volts	30 sec.	100	3	3.0
154.5	409	29	50	5	10.0
157.0	355	23	41	1	2.4
157.0	554	31	42	2	4.8
157.5	584	30	75	4	5.3
158.0	395	33	50	3	6.0
158.0	479	40	122	5	4.1

From a consideration of column 5 Table I. it appears that there is an appreciable number of doubly charged argon ions formed by the impact of a single α-particle. The variation in the number of these doubles with the pressure of the gas resemble closely the variations found by Millikan and Wilkins in the case of helium, with this difference that the maximum number of doubles in argon is 11% while in helium it is nearly 15%.

V. Discussion of Results.

In analysing the above results it is necessary to take account of an important ambiguity which this type of experiment is unable to overcome. It is quite impossible to distinguish between the capture of a double and the almost simultaneous capture of two singles. The capture of two singly charged ions within a very short interval of time may occur in one of two ways. It may conceivably happen that an α-particle produces more than one ion directly underneath the comparatively large oil drop, and these if they are drawn on to the drop, will be captured simultaneously. It is absolutely impossible to distinguish this type of capture from that of a true double. It may also happen that two α-particles pass beneath the drop at about the same time and the drop catches an ion formed by each. The observer will also record this pair of close singles as a double. To this latter type we may apply the theory of probability for we know something of the frequency with which α-particles are projected under the drop. If independent events are occurring with a perfectly random distribution and are separated by an average interval of T seconds, then the chance that two of these events will be separated by an interval not greater than t seconds is

$$P = 1 - e^{-t/T} = t/T - \frac{1}{2!}(t/T)^2 + \frac{1}{3!}(t/T)^3 \text{ ------}$$

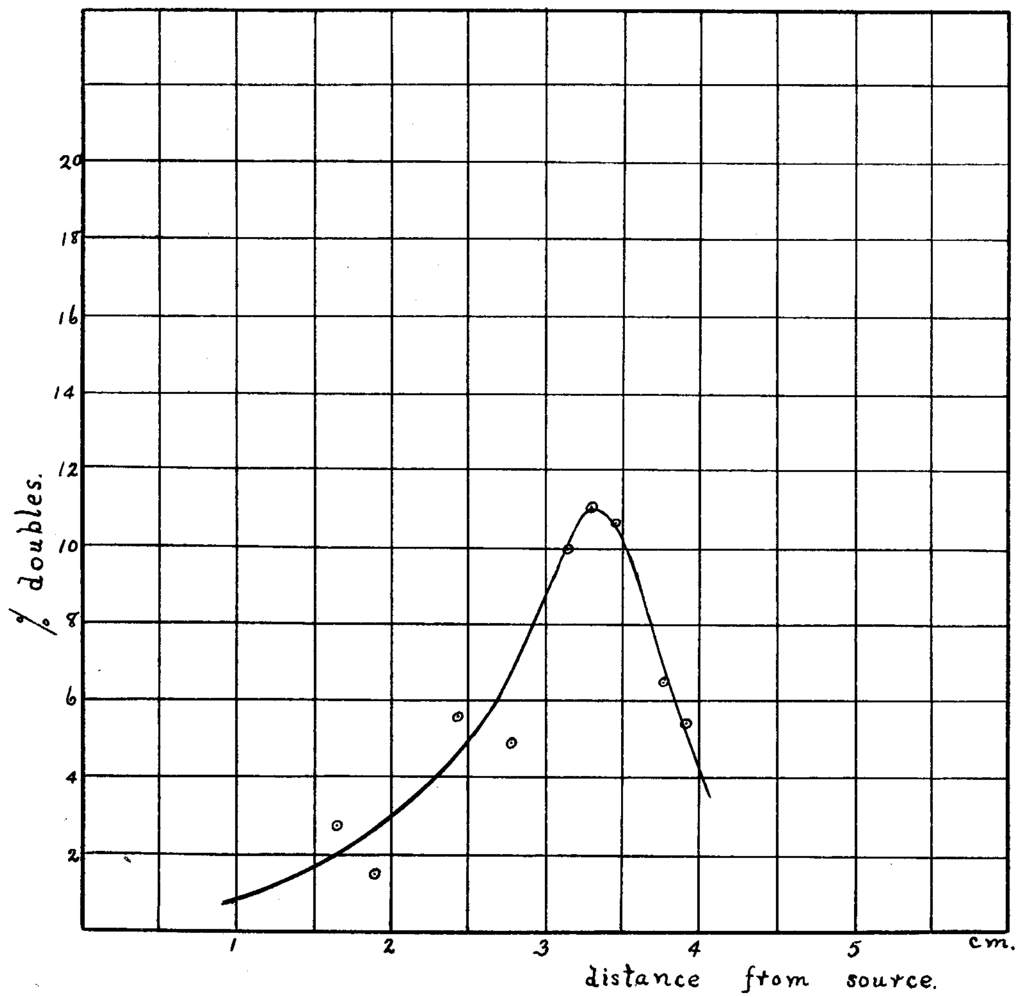
Due to Brownian movements it is improbable that an observer will be able to distinguish the capture of a true double from that of two close singles if the singles are caught within one second. Thus since t = 1 and T varying as it does between 17 and 63 sec.

we may neglect all terms of higher order than the first. Then the chance of catching two ions produced by two different α-particles so close together as to be indistinguishable is 1/T, and the number of close singles per hundred catches is 100/T. In the most unfavourable case recorded, i.e. T = 17, there should be six close singles out of every hundred captures. It is to be noted however that the above reasoning is only valid provided the number of captures is very large for only then are we justified in applying probability considerations.

The objection might be raised that while T is the average interval required to catch a positive ion upon a drop which already bears one positive charge, we are really interested in the time required to catch a positive ion on a drop which carries two positive charges. It seems probable that the difference between these two intervals must be insignificant.

There is an experimental point bearing on this same subject which is of importance. In no single instance did the writer observe a capture which he felt justified in recording as a pair of close singles. It seems strange that out of some five thousand captures it was not possible to observe one which could definitely be set down as belonging to this class. Also it is to be noted that if one gas can be found which gives no evidence of apparent double charges at all then the previous considerations are valueless. Millikan Gottschalk and Kelly found in air no doubles out of six hundred and twenty-four ions observed. However they did not make any adjustment for the end of the range so that the particles were not travelling at their most efficient ionizing speed.

In view of these uncertainties the experimental results have been recorded without applying any of the corrections which the theory of probability would seem to demand. For these reasons the actual figures for the relative number of doubles to singles are not to be taken as exact but as a qualitative indication of the way in which the ratio varies with the ionizing power of the α-particles. It seems safe to say that α-particles do certainly produce doubly charged ions in argon, and the figures given in Table I. are upper limits to their number. The following graph shows the relation between percent doubles and the distance from the polonium source reduced to atmospheric pressure of argon.



In the light of Henderson's experiments (Proc.Roy.Soc. vol.102, 1923, p496) it is not a surprising fact that α-particles should be able to produce doubly charged ions. His work shows that the process of ionization consists in the binding of one or two electrons by the particle, and then at a subsequent collision these recently acquired electrons are lost. But this can only be a part of the truth, for he finds no trace of neutral or singly charged helium atoms unless the velocity of the particles emerging from the absorbing material is less than a certain definite value. It is of course possible that the binding of the captured electrons is relatively loose, so that the high speed nucleus is unable to hold them for any appreciable time. As is to be expected the binding of the first electron by the α-particle is quite firm and the band due to H^+ first appears when the range is 55.3mm of air. The band produced by the neutral helium atom does not appear however until the range is reduced to 4.5mm. But the energy varies as the 2/3 power of the range so that the energies are in the ratio of 5.3 : 1. However the ionizing potential of helium is 25.3 volts and the ionizing potential of H^+ is 54 volts. Thus the relative firmness of binding in the two cases should be in the ratio of 2.1 : 1. The agreement is at least qualitative.

As Millikan pointed out (Phys.Rev. vol.18, 1921, p456) the determining factor in the production of doubles is one of chance rather than energy. An α-particle, provided its energy lies within certain fairly broad limits, may or may not produce a doubly charged ion depending upon the direction of incidence relative to the orientation of the struck atom. The duration of impact is also of importance for if this be not too short there is a greater chance of a second electron coming within the sphere of influence of the particle and becoming bound to it.

It is currently supposed that the normal helium atom consists of a nucleus with two electrons rotating about it in opposite directions but in the same plane, thus the nucleus and electrons form a plane configuration. Argon with its eighteen electrons arranged in three shells is almost certainly spherical in form. Hence one would naturally expect that an α-particle's chance of capturing two electrons from the argon atom should be much greater than from a helium atom. However Millikan and Wilkins' results show a maximum of 15% doubles in helium while the present results show a maximum of only 11% in argon.

But any theory which will explain the process of ionization must also show why doubly charged ions may be formed in helium and argon and are not in nitrogen, oxygen, chlorine, etc. It is not easy to see why this should be so. Of course it must be borne in mind that the experimental proof for the non-existence of doubles in the latter gases is not wholly satisfactory. The inert gases are unique in that they are monatomic. But our knowledge of molecular, as opposed to atomic, structure is so limited, that it is not possible to say whether or not this is the reason for the difference. Mercury, of course, has been tested by this method, but only in the form of the compound, mercury dimethyl, and this may behave quite differently from the monatomic mercury vapour.

It is of interest to note that Adams (Phys.Rev. vol.24, 1907, p108) in his confirming experiments of the Bragg-Kleeman law, viz, that the stopping power of a gas for α-particles is proportional to the sum of the square roots of the atomic weights of all the atoms comprising the molecule, found that no scintillations were detectable from a polonium source immersed in argon, when the product of the pressure of argon in centimeters of mercury and the distance from the source to the flourescent screen measured in centimeters was greater than 301. In this present work the distance from source to oil drop was 13.4 cm. and captures became difficult at pressures greater than 22 cm. of mercury. Thus the product pd = 294.8, in satisfactory agreement with Adams' figure.

In conclusion, the writer wishes to express his appreciation to Professor Millikan for suggesting the problem and for his generous encouragement throughout the progress of the work. Also he is deeply indebted to Mr B.Beverly for assistance in making observations.

Norman Bridge Laboratory of Physics,
California Institute of Technology
Pasadena, California.
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