SINGLE AND DOUBLE IONIZATION OF ARGON BY ELECTRON IMPACTS

By Henry A. Barton

Abstract

The magnetic deflection method, described in the preceding paper by H. D. Smyth, has been applied to a study of the ionization of argon, and the minimum potentials for the production of singly and doubly charged ions have been separately observed. Assuming that for A^+ to be 15.2 volts, the correction for the apparatus was determined and the corrected minimum potential for the production of A^{++} ions was found to be 45.3 ± 1.5 volts. No A^{3+} nor A_2^+ ions were observed. Spectroscopic evidence has shown that the blue spectrum is excited by impacts of 34 volts, and it has been assumed that doubly charged ions are produced at this potential. Four ways of reconciling the direct evidence of this paper with the spectroscopic evidence are suggested and discussed. (1) A cumulative process may produce A^{++} ions with only 34 volts in discharge tubes with high current density, though not in the author's tube in which conditions were unfavorable. (2) The 34 volt lines may represent only a partial excitation of the spark spectrum, double ionization not being required. (3) This potential (34 volts) may correspond to the limit of spectral terms of negative values, involving the simultaneous excitation of two electrons. (4) A more closely bound electron with an ionizing potential of 34 volts may undergo transitions without disturbing the electron whose transitions produce the arc spectrum.

Introduction

A VERY large number of determinations have been made of the critical potentials associated with the argon atom. Experimental tubes of widely varying designs, and having two or more electrodes of different shapes and arrangement, have been used. The significance of the critical potentials has been determined by a study of the breaks in the curves representing the current between the several electrodes, and by spectroscopic observation of the radiation emitted by the gas. Results so obtained have been brought, within the last several years, into good agreement. Thus, Horton and Davies,[1] Dejardin,[2] and Hertz[3] give for the first critical potential 11.5, 11.5, and 11.55 volts respectively. They report this to be a radiating potential, except for Dejardin, who gives it as an ionizing potential only appearing when the pressure is relatively high. For the first ionizing potential under ordinary conditions, these observers

[1] Horton and Davies, Proc. Roy. Soc. A **97**, 1 (1920)

[2] Dejardin, C. R. **172**, 1347 and 1482 (1921); **178**, 1069 (1924). Ann. de Physique **10**, 241 (1924)

[3] Hertz, Proc. Amsterdam Akad., **25**, 179 (1922); Zeit. f. Phys. **18**, 307 (1923)

give 15.1, 15.2 and 15.3 volts respectively. This close agreement is convincing and an average of 15.2 volts may be taken as the potential necessary to remove one electron from an argon atom by a single impact.

Dejardin,[2] Horton and Davies,[4] and Shaver[5] have made use of spectroscopic observation to extend the study of critical potentials to the range above the ionizing potential. They found that the red spectrum of argon was already completely excited at this point, and therefore concluded that it was identical with the ordinary arc spectrum. As the potential was increased no additional lines were observed, at low pressures, until a critical potential in the neighborhood of 34 volts was reached. At higher voltages the agreement between different observers is no longer exact. However, Dejardin and Horton and Davies conclude that a large number of lines of the blue spectrum are associated with this value and that some additional lines appear or are strengthened at 38 volts. Recently, the order of succession of these stages of excitation has been confirmed with the aid of an electrodeless discharge.[6] Horton and Davies also found a discontinuity in the current-voltage curve at 34 volts indicating an increase of ionization at this point. At higher pressures and with greater current densities, the lines characteristic of 34 volts appeared at 19 volts, the difference between 34 volts and the ionizing potential.

A general consideration of these results led the above observers to assume that the 34 volt lines composed the spark spectrum of argon, although the presence of the 38 volt lines introduced some uncertainty. Therefore, in order to effect the removal of two electrons, which is necessary to excite the whole spark spectrum, neutral atoms must be given 34 volts and single ions, 19 volts energy. This view is supported in a general way by the work of Stark and Kirschbaum[7] and, later, Friedersdorff[8] with canal rays of argon, in which it was shown that the lines of the blue spectrum were emitted by faster moving particles than those of the red spectrum. These particles, presumably, had gained greater speed in falling through the field of the discharge tube because they were more highly charged. This being the case, they would be expected to emit spark lines.

The value 34 volts, on the other hand, appears, by comparison with other elements, to stand in a smaller ratio to the first ionizing potential than would be expected. In view of this consideration, the present work

[4] Horton and Davies, Proc. Roy. Soc. A **102,** 131 (1922)
[5] Shaver, Trans. Roy. Soc. Canada **16, III,** 135 (1922)
[6] L. and E. Bloch and Dejardin, C. R. **178,** 766 (1924)
[7] Stark and Kirschbaum, Ann. der Phys. **42,** 255 (1913)
[8] Friedersdorff, Ann. der Phys. **47,** 737, (1915)

was undertaken with the principal purpose of determining directly the second ionizing potential of argon.

METHOD

The apparatus employed and the method of using it to detect, and distinguish between, positive ions of different types have been described fully in the preceding paper by H. D. Smyth.* In order to change the substance under consideration from hydrogen to argon, it was only necessary to rearrange the gas supply system, and to use a stronger magnetic field in the positive ray analysis. The latter change was preferred over the alternative of using a weaker electric field V_2+V_3 to accelerate the ions because it is desirable to have V_2+V_3 large compared with V_2. The actual magnetic field strengths necessary were from 2000 to 3000 gauss.

The effect of the finite size of V_2 as compared with V_3 has been discussed in the preceding paper. As was explained there, most of the ions will be produced in that portion of the region R_2 nearest the gauze E_1. However, ions produced near E_2 have a better chance of getting through S_1. Thus, the probability of an ion being formed and also getting through the slit system is the product of two probabilities, both functions of V_2, one of which has a maximum near E_1, the other, near E_2. If V_2 is relatively small, it would be expected that the maximum number of ions detected would come from somewhere between these two. If, however, V_2 is large, these maxima could separate, and it is possible to observe, in curves showing electrometer current as a function of V_2+V_3, two maxima corresponding to ions of a single type, one being due to ions from the neighborhood of E_1 and the other, to ions from near E_2. In such cases, if V_2 is reduced without changing other conditions, these maxima are brought together and merge. The total width of the peak is also reduced thereby, which is important because it improves the resolving power of the apparatus. At first V_2 was derived from the same source as V_1, being, however, somewhat smaller by a constant ratio. When the importance of a smaller V_2 was realized, it was kept constant for all values of V_1 by a separate battery either at 4.5 or 12 volts. The experimental curves then obtained were considerably sharper and smoother than with V_2 variable.

The same filament, a platinum strip coated with barium and strontium oxides, was used throughout the experimental work. The potential drop due to the heating current was less than .7 volt.

* The hydrogen apparatus was used without any change in its design. The reader is referred to the preceding paper for its description and also for an explanation of the nomenclature used in both papers.

Two independent supplies of argon were used, the first, for the bulk of the work, and the second, for a check of the results obtained from the first. Both supplies were obtained originally from the General Electric Company. The first supply was given its final purification in this laboratory by passing through it a 110 volt arc between calcium electrodes. The arc was run until no nitrogen bands were visible. In the spectrum of a spark passed between the same electrodes, a faint band system persisted. After some of this supply of argon had been withdrawn from the purifying system and used in the earlier experiments, it was found that the impurity present was hydrogen. It is not thought that this impurity affected the results, especially as these were checked with the second supply. The latter, already very pure, was contained in a small glass tube obtained directly from the General Electric Company. This tube was equipped with calcium electrodes making it possible to further purify the argon after it had been sealed in place and, thus, to eliminate any transfer of the gas between purification and use.

In many of the runs taken it was found that water vapor was present. The source of this was never satisfactorily determined. Presumably, it entered the tube with the argon, since no water vapor ions were observed when the gas supply was shut off. Also it was possible to reduce it by passing the gas through a trap immersed in a mixture of carbon dioxide snow and alcohol, or in liquid air. Owing, probably, to the rapidity of flow through the trap, even this did not entirely eliminate water vapor. An attempt to remove it by passing the gas through charcoal immersed in carbon dioxide snow was made later, but without complete success.

Experiments and Results

Identification of ions. The curves of Figs. 1 and 2 are typical of a number taken to determine what positive ions were being formed. The method of obtaining such curves has been described in the preceding paper. The value of the fields and pressures are given below each figure. In both cases the thermionic current was 200 micro-amperes. The very large peak is assumed to indicate the detection of singly charged ions A^+ and the m/e scale thus tentatively determined. Ordinarily this could be checked by the value of m/e calculated from the fields and apparatus dimensions. The magnetic field would have to be determined from a calibration curve of the electro-magnet as a function of the exciting current. Such a calibration was made before assembling the apparatus, but later more shielding had to be introduced. This acted as a shunt for the flux, altering the calibration in an uncertain way, and making the

check impossible except as to order of magnitude. In order to make sure of the identification, the range of the curves was extended, in several cases, to values of m/e well over twice that of the large peak and, in the other

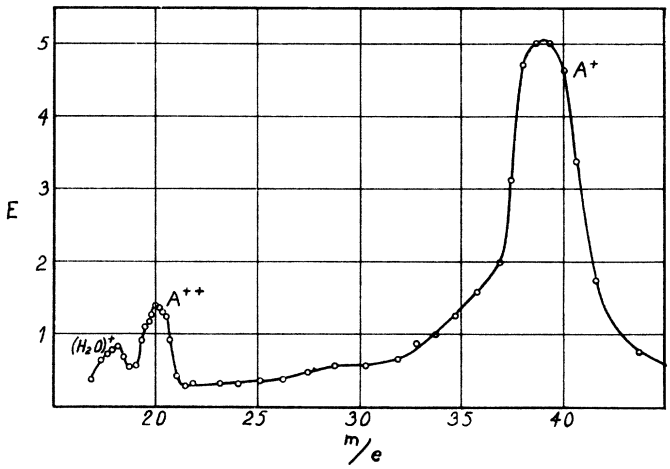

Fig. 1. Peaks indicating ions formed at $V_1 = 55$ volts.
($V_2 = 4.5$ volts. Pressure = 03 mm.)

direction, to values less than half that of the peak given in Fig. 1 at 20. Except for indications of slight impurities the peaks shown were the only ones observed.

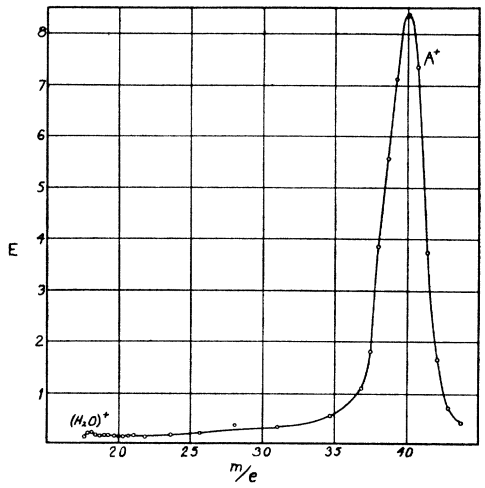

Fig. 2. Peaks indicating ions formed at $V_1 = 43$ volts.
($V_2 = 4.5$ volts. Pressure = .008 mm.)

On account of the width of the A^+ peak, no conclusions can be drawn from these or other curves taken as to the presence or absence of the

isotope reported by Aston[9] at 36. This isotope would be expected, from the chemically determined atomic weight, to compose about 3 per cent of the total number of argon atoms. Such a small peak is difficult to resolve. It remains to be seen whether or not a larger peak could have been separated out by the present apparatus.

The scale roughly determined by assuming the large peak to be A^+ at $m/e=40$ places the small peak, visible on both curves, at $m/e=18$. The effect of passing the incoming gas through cold traps, as discussed before, is observed in the behaviour of this peak. Its height, relative to that of the other peaks, could be very much reduced by this procedure. Thus, it was assumed to be due to water vapor partly for this reason, and partly because no other likely impurity has this molecular weight. The ion present was apparently $(H_2O)^+$ and not $(OH)^+$, confirming an earlier conclusion of Smyth.[10]

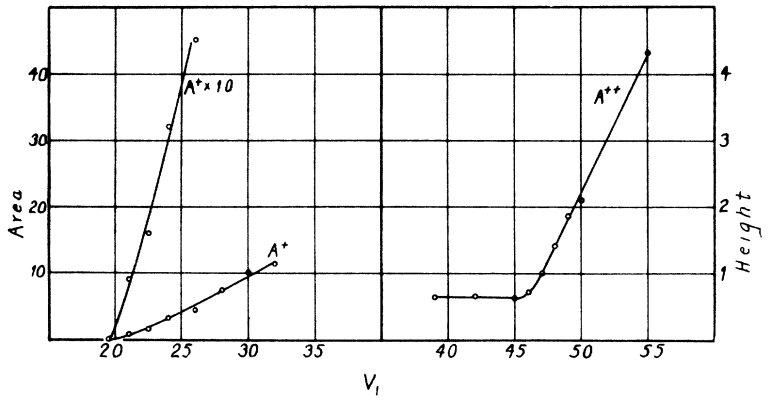

Fig. 3. Number of ions as a function of V_1

The peak at $m/e=20$ on the curve of Fig. 1 was assumed to represent doubly charged atomic ions. That this peak was not, like the peak at 18 due to an impurity was shown by the fact that at high values of V_1 it could be made very large compared with the latter and of the same order of magnitude as the A^+ peak. Therefore the small size in Fig. 1 of the A^{++} peak at 20 must be due to the fact that electrons of 55 volts energy are not highly efficient in producing doubly charged ions, and, accordingly it is concluded that this potential is not far above the minimum required. It will be noticed that there is no sign of this peak on the curve of Fig. 2 with $V_1=43$ volts.

[9] Aston, Isotopes, p. 66.

[10] Smyth, Proc. Roy. Soc. A **104**, 121 (1923)

The more accurate m/e scale shown on the figures was determined by a consideration of the positions of all the peaks.

Determination of critical potentials. When the identity of the peaks had been satisfactorily established, a series of runs at different values of V_1 was taken to observe the critical potential at which each peak first appeared. The heights of the peaks (or the areas if the peaks were irregular in shape) were then plotted as a function of V_1, and curves such as those given in Fig. 3 were obtained. These curves are typical of a number taken at various pressures and with a thermionic current of 200 micro-amperes. The results for A^+ and A^{++} are summarized in Tables I and II. These tables give the pressure for each series, the critical potential observed, and an estimated weight for each determination.

TABLE I

Determinations of minimum potential for A^+.

Series No.	Pressure (mm)	Observed minimum potential	Weight
1	.0070	18.8	1
2	.0070	17.2	7
3	.0061	18.3	1
4	.0064	17.0	10
5	.0125–.0028	19.0	1
	Weighted mean	17.3	

TABLE II

Determinations of minimum potential for A^{++}.

Series No.	Pressure (mm)	Observed minimum potential	Weight
11	.0070	50	1
12	.0070	49.2	5
13	.0064	46.4	4
14	.072–.032	46.7	10
	Weighted mean	47.4	

It is estimated that the error may be as large as 1 volt in the case of A^+, and 1.5 volts in the case of A^{++}. Accepting 15.2 volts as the correct value for the first ionizing potential, the correction it is necessary to apply to determinations made with the present apparatus on account of initial velocities, contact potential difference, etc., is evidently -2.1 volts. This gives for the minimum potential at which A^{++} ions appeared, the value 45.3 ± 1.5 volts.

Having thus failed to observe the critical potential of 34 volts for A^{++} ions predicted by the results of others,[2,4,5] an attempt was made to

observe a discontinuity at this point in the A^+ curve which might account for their results. Unfortunately this was not successful. On some of the curves there appeared to be a slight irregularity in slope between 30 and 40 volts, but this might have been accidental. In general the curves were not smooth enough in this region to prove either the presence or absence of a break.

Several of the curves of A^+ as a function of V_1 were extended to values beyond 50 volts and, in one case, curves were taken simultaneously for A^+ and A^{++} up to $V_1 = 95$ volts. They are interesting in that they show significant features above the respective ionizing potentials. The A^+ curves, for example, all come to a maximum between 40 and 55 volts. In the single high run there are breaks upward at about 55 and 85 volts. The highest A^{++} curve shows a pronounced increase of slope at about 90 volts. The significance of these irregularities is uncertain. However, it is probable that the falling off of the A^+ curves at 45 volts is due to the fact that electrons were here first able to produce A^{++} ions, and the energy of many which would otherwise be available for the production of one or more A^+ ions was used up in this way. After a temporary set back, the A^+ curves rise again as would be expected if the probability of ionization still increased with velocity. The break upward in the A^{++} curves at about 90 volts suggests that electrons may have twice collided effectively after this point. If this is so, it is a check of the 45 volt critical potential.

Ions of other types. An attempt was made to produce A^{+++} ions by raising V_1 to somewhat higher potentials, the highest being 210 volts. However, none were detected. Also, in the course of the experiments, the range including $m/e = 80$ was several times explored. No evidence for the existence of singly charged molecular ions A_2^+ was found. If any A_2^{++} ions were formed their va ue of m/e would be 40 and they could not be distinguished from the A^+ ions. However, a combination of this sort appears highly improbable.

Discussion of Results

The outstanding feature of these experiments is the disagreement between the 45.3 volt minimum potential for double ionization and the apparently corresponding value of 34 volts observed by Dejardin[2] and Horton and Davies.[4] The work of these observers was most carefully and accurately done: That of Dejardin was further confirmed by his discovery of exactly similar effects in krypton and xenon, in which, as he points out, the ratio of the higher critical potential to that of single ionization is numerically the same as in argon.

On the other hand, under the conditions available, the writer was not able to observe any A^{++} ions at all below 45.3 volts. The objection may be made that the positive ray method of detecting ions is not sufficiently sensitive to observe the A^{++} ions until a large number are being produced. A general answer may be given to the effect that, in all cases of critical potentials observed by this method which could be reliably checked by the results of other methods, the agreement has been good. In the case under consideration, moreover, Dejardin and Horton and Davies report that the blue spectrum lines had already gained nearly their maximum intensity below 45 volts. Certainly therefore, the writer should have found a critical potential at least below this value, providing the experiments are comparable at all. The fact that they found no indication of the writer's 45 volt discontinuity further confirms the existence of the discrepancy. Both results must be explained, and any theory which does this may have a wide bearing on the study of atomic structure. For this reason, it is profitable to discuss, at some length, several possibilities.

Cumulative ionization. If the appearance of blue spectrum lines truly indicates the production of doubly charged ions, it is only possible to explain the apparent contradiction of the present results by the difference in experimental conditions. Of these, it is difficult to say which are significant. Aside from differences in the electrode arrangement, there are slight differences in pressure and, possibly, larger differences in thermionic current. The first of these is probably not significant because the pressures used by the writer were, first, about .007 mm and later .05 mm, which bracket those used by Dejardin. Horton and Davies apparently worked with somewhat greater pressure than either but came to the same conclusions as Dejardin.

It is not possible to compare the electron currents. However that used by the writer was quite small, usually 200 micro-amperes. There exists the possibility, therefore, that the above observers, contrary to their opinion, had to do with ionization by cumulative action, and that the writer, by using small currents, avoided this. If such is the case, a scheme somewhat as indicated in Fig. 4 suggests itself. This figure shows, in the form of an energy diagram, the several known critical potentials of the argon atom. It is extended upward to include those of the ion. The base line corresponding to the normal neutral atom is taken as the beginning of the energy scale. The dotted line X at 11.5 volts indicates the level of excitation corresponding to the lowest critical potential. The level A^{+} at 15.2 volts represents the energy state of the normal simple ion. A^{++} at 45.3 volts is the same for the double ion.

At very low pressures and current densities, the arrow (a) indicates the transition by a single impact from A to A^{++}. At medium pressures and currents, a possible scheme consists of a combination involving a 33.8 volt impact (b') with a neutral excited atom in the X state, to which it has previously come as the result of either an electron impact (b) or the absorption of resonance radiation (b_1). It is suggested that the critical potential of 34 volts, found by Dejardin and Horton and Davies, may be explained in this way. The numerical agreement of their result with the value of transition (b') is at least remarkable.

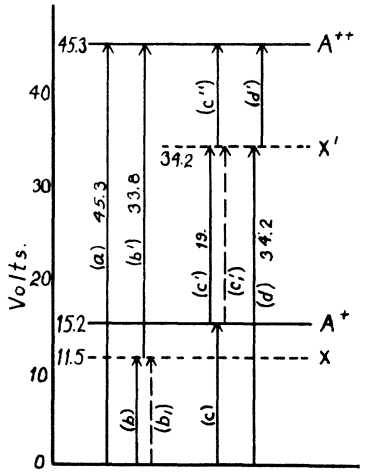

Fig. 4. Cumulative processes leading to double ionization.

Of course it has to be assumed that the concentration of atoms in the excited state X is large, even compared with the number of A^+ ions. Otherwise the observed critical potential would be 30.1 volts, the difference between the energies of states A^{++} and A^+. In the work of Dejardin, Horton and Davies, and Shaver, some lines, presumably the strong ones, were actually observed somewhat below 34 volts, as would be expected in this case. The fact that, in argon, an arc may be maintained with comparative ease below the ionizing potential[11] is evidence in favor of a large concentration of atoms in states of the X sort.

If, now, pressures of .1 mm or more are considered, provision must be made for the 19 volt threshold for the lines previously appearing at 34 volts. To do this, an excited state X' of the A^+ ion (Fig. 4) is assumed 19 volts above the ionizing potential for A^+. The production of A^{++} ions is then accomplished by three actions: (1) a 19 volt impact (c') or ab-

[11] Compton and Eckart, Phys. Rev. **25**, 139 (1925)

sorption of spark spectrum resonance radiation (c_1') by an atom previously ionized by (2) an impact (c) of 15.2 volts and, finally, (3) an impact (c'') of 11.3 volts. Perhaps it should be assumed that X, and not A^+, should be taken as the starting point for the 19 volt transition. This, however, would presumably destroy the possibility of reaching X' by resonance. Compton and Turner[12] have recently shown, working with mercury, that positive ions may be powerful absorbers of resonance radiation of the spark spectrum. It is to be noted that the energy of the state X', so defined, is 34.2 volts. This suggests the obvious transitions (d) and (d') as a possible other explanation of the 34 volt critical potential. It is uncertain whether such transitions as (d) are possible either by impact or absorption of radiation. Some evidence regarding the production of an excited ion by a single increment of energy will be discussed later.

Examining the consequences of the scheme of Fig. 4 critically, several points remain to be cleared up. For example, if the X state is probable, A^+ ions would be expected to appear by cumulative action at 11.5 volts. This is, indeed, probably the explanation of Dejardin's observation of an increase in ion current at this point, for the possibility of this being an ionizing potential is denied by Hertz and Horton and Davies, and it is not observed by the writer.

Dejardin and Horton and Davies give current-voltage curves showing increases in ionization at 30 volts. They attribute this to the ability of an electron of this energy to produce two A^+ ions, one after the other. In addition to this, there now appears the possibility of changing A^+ to A^{++} by an impact of 30.1 volts, which would increase the positive current even though not the number of ions. The failure of the above authors to observe a discontinuous increase in intensity at 45 volts would appear to discredit this value. However, it is known that when cumulative effects come into play, this point may easily be completely masked, at least so far as spectroscopic observations can discern.

If the scheme of Fig. 4 is correct, a similar explanation must be applicable to krypton and xenon. If it is assumed that the ratio of the double to the single ionizing potential is the same in each gas, then the difference between the double ionizing potential and the first critical potential of the neutral atom, as given by Dejardin, agrees numerically in each case with his experimental value corresponding to the production of the higher spectrum.

[12] Not yet published.

The final test of the scheme must probably come from a study of the ultra-violet spark spectrum. All that can be said now is that the preliminary work of Lyman is not in contradiction.[13]

Partial excitation of spark spectrum. So far, it has been assumed, in agreement with Dejardin and Horton and Davies, that the lines of the blue spectrum appearing at 34 volts do compose the spark spectrum of argon, and, with Dejardin, that the additional lines appearing at 38 volts are, in reality, part of this same group. This is not altogether satisfactory, and suggests that the process observed may be one of partial excitation. Thus, it is supposed that 34 volt impacts ionize and raise the ion to one level of excitation, and those of 38 volts, to another. In the subsequent transitions to lower levels, some, but not all, of the spark lines would be emitted. That the parts of a spectrum can be successively excited in this way, has been shown by Hertz[14] for the arc spectra of several gases. It has not been shown for spark spectra.

However, this hypothesis meets two obstacles. In the first place, it is difficult to account for the large number of lines which appear at the two potentials mentioned, even if it is assumed that the terms of the A^+ spectrum are very highly multiple as is the case with the neon spectrum.[15] In the second place, the lines of the blue spectrum appearing at 34 volts are of such wave-length as to require another multiple level about 3 volts lower than this. If this existed, transitions between it and the normal state of the A^+ ion would lie in a region of the ultraviolet in which Lyman found no lines.

Transitions of two electrons. Although both of the possibilities discussed above have shortcomings, they have been placed first as being more in accord with previous notions of intra-atomic alteration. However, a new and very interesting possibility which has much to recommend it, is suggested by the recent discovery by Saunders and Russell[16] and by Wentzel[17] of terms in the spectrum of calcium which have negative wave numbers. They ascribe these terms, which have energy values higher than that ordinarily sufficient to eject one electron completely, to simultaneous states of excitation of two electrons.

That changes involving the transition of two electrons at the same time are consistent with the correspondence principle has since been

[13] Lyman, Astrophys. J. **43,** 89 (1916); and Spectroscopy of the Extreme Ultraviolet, p. 86.

[14] Hertz, Zeit. f. Phys. **22,** 18 (1924)

[15] Paschen and Götze, Seriengesetze der Linienspektren, p. 30.

[16] Saunders and Russel, Phys. Rev. **22,** 201 (1923)

[17] Wentzel, Phys. Zeits. **24,** 104 (1923); **25,** 182 (1924)

shown by Epstein.[18] In his discussion of these, he points out that the possibility of a transition of two electrons is associated with the breakdown of the Bohr-Rubinowicz selection principle to permit changes of the azimuthal quantum number of 2 and 0 as well as of 1. This breakdown appears first in the spectra of the alkali earths. The suggestion is that, in elements having positive valences of more than one, there is a coupling between the valence electrons and some or all of them may undergo a transition simultaneously. This is indicated by the further breakdown of the selection principle in the later columns of the periodic table. In argon, where the positive valence may be taken as eight, transitions of this type should assume very great importance. However, even in cases where the valence is greater than two, Epstein states that lines involving more than two electrons should have a much lower intensity.

In view of these considerations, it seems profitable to apply the idea of two simultaneous transitions to argon with the purpose of explaining the formation of ions and the excitation of the blue spectrum at 34 and 38 volts. Suppose one electron is in an excited state. Then the atom has at least 11.5 volts energy. Now if a second electron is displaced from its normal orbit, the new orbits it can occupy will be different from those which it could occupy if the first electron were not already displaced. There would be a series of orbits possible for this second electron leading up to infinity when it is totally removed. After its removal, the residue is an ion which has one electron (the first) in an excited orbit. Thus the energy required to produce such an ion is greater than the simple ionizing potential. Its amount can be estimated from the following consideration.

If an electron is removed from an atom which was, until then, normal, the energy required corresponds to the first ionizing potential, here 15.2 volts. If an electron is removed from a normal single ion, the energy required corresponds to the ionizing potential of the ion, here 30.1 volts. If, now, as in the present case, an electron in its normal orbit is removed from an excited atom, a form which is intermediate between the normal atom and the ion, the energy required must lie between these limits. Suppose, for the present purpose, the actual value is 22.5 volts. Then, if the whole process of exciting the first electron and removing the second takes place at a single impact, this energy must be added to the 11.5 volts needed for the preliminary excitation, and the 34 volt ionizing potential is explained. The 38 volt limit is, then, explainable by the assumption of a preliminary excitation to a different orbit from that corresponding to 11.5 volts.

[18] Epstein, Proc. Nat. Acad. Sci. **10**, 337 (1924)

Thus, a possible conclusion is that the ionization found at 34 volts by Horton and Davies was due to singly charged ions of this sort, and that another similar ionizing potential exists at 38 volts. The lines of the blue spectrum on this hypothesis, correspond to transitions involving spectral terms whose limits are these ionizing potentials. That is, they are emitted by transitions of an electron falling into the excited atom; or, after it has fallen part way in, transitions to other orbits of the electron first excited; or, finally, simultaneous transitions of both. At high pressures, the 19 volt critical potential, on this hypothesis, corresponds to excitation of an ordinary ion to the same state as was reached before by a single impact with a normal atom. The subsequent emission of the blue spectrum is, then, the same as the above.

It will be noted that the production of an excited ion from a normal atom in the above described manner is effectively the same as transition (*d*) of Fig. 4 although the explanation of the blue spectrum is different.

Transitions of a more closely bound electron. Another possibility which should be mentioned is that, in ionizing an argon atom, an electron may be removed from a sub-level of the M shell nearer the nucleus than that of the electron which is most easily removed. That such an ionization may sometimes occur is shown by the work of Foote, Mohler et al.[19] with the alkali metals. In the case of these elements it was possible to extract an inner electron without removing the outer one. In argon where the electrons concerned are all in the outer shell, the choice as to which is to be ejected at an impact should be more even.

Suppose that removing this second type of electron requires 34 volts energy. It would be expected to have excited states up to this limit and the blue spectrum involving these would thus be a second arc spectrum, and not associated with doubly charged ions at all. An examination of a Moseley diagram[20] giving the x-ray levels of the elements in which the M shell is in process of completion, yields no definite evidence concerning this view, because the data relative to the early stages of the M levels are incomplete and indefinite. However, the existence of a sub-group of the M shell which would give a considerably higher ionizing potential than the ordinary one at 15.2 volts is strongly indicated. The difference between 15.2 volts and 34 volts appears to be quite reasonable.

[19] Mohler and Foote, Bur. Standards, Sci. Paper No. 425 (1922)
Foote, Meggers and Mohler, Astrophys. J. **55,** 145 (1922)
Mohler, Foote, Ruark and Kiess, J. Opt. Soc. Amer. **7,** 62 (1923)
Mohler, Science **58,** 468 (1923)

[20] Compton and Mohler, Bull. Nat. Res. Council; Critical Potentials, p. 109.

Summary of possibilities. The above detailed consideration of atomic transitions of several types may be made clearer, from a physical point of view, by the following general summary. At first it is assumed that the production of the 34-38 volt lines of the blue spectrum requires the displacement from their orbits of two electrons of the same group in the M shell. It may be necessary to remove them from the atom. If such a removal is not accomplished by a single impact it may be accomplished by cumulative action, in which case the numerical agreement with experimental observations which can be obtained is quite convincing. However, the reasons for assuming less cumulative action in the writer's experiments than in those of Dejardin et al. are not conclusive. As an alternative, therefore, the identity of the 34 volt lines with the spark spectrum is abandoned as an hypothesis, and the possibility of a partial excitation of this spectrum considered. This appears to fail since it does not account for the number of lines observed.

The hypothesis is then made that an ionizing potential exists at 34 (and possibly 38) volts but that the resulting iqns are singly charged. To reconcile this with the known 15.2 volt value for singly charged ions it is assumed that the resulting ion is excited and that such excitation consists in the displacement of a second electron to an abnormal orbit. Transitions involving this and another electron falling into the atom then emit the blue spectrum lines. Similar to this is the explanation which assumes that an electron of the type which we have until now always considered, remains in its normal orbit while an electron of a new type, one more closely bound to the nucleus, is removed and then is replaced through successive levels with the consequent emission of radiation.

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