SOME EXPERIMENTS IN POSITIVE ION KINETICS

By Gaylord P. Harnwell[1]

Abstract

Mean free path and mean energy loss per collision of positive ions of potassium and caesium in helium, neon, argon, hydrogen and nitrogen.—The motion of certain positive ions through gases was investigated in an experimental tube of simple design. The ions were obtained from the potassium and caesium catalyst sources developed at the Fixed Nitrogen Laboratory, and their behavior was studied in helium, neon, argon, hydrogen, and nitrogen. It was found that the results were best explained on the basis of a free path approximately equal to the kinetic theory value, and on an average fraction of energy lost per collision considerably less than would be expected on ordinary considerations. It is suggested that the explanation of this is to be found in a more accurate consideration of the fields of force involved at these encounters.

CERTAIN anomalous effects have been observed by all experimenters who have worked with positive ions in an analysing apparatus. One class of these effects appears to be due to an abnormality in the length of the free path of a positive ion or to the behavior of these ions at a collision with a gas molecule. A. J. Dempster[2,3] has found that protons with a velocity corresponding to a potential drop of 900 volts pass through a large number of helium atoms without neutralization, with very little change in direction, and with a loss of energy of less than half a volt per collision. The singly charged hydrogen molecule was also found to pass through a number of helium atoms without dissociating and with very little loss of energy. Singly charged helium atoms were found on the average to be neutralized after two or three collisions. The writer in working with a similar apparatus under slightly different conditions found evidence of the same type of phenomenon in neon, argon, and nitrogen. The average energy lost at a collision was found to be less than one hundredth the energy possessed by the ion before the impact. In a positive ion analyser when the magnetic field is held constant and the accelerating voltage for the ions varied, the peak corresponding to a certain ion is registered at a particular voltage, say V_1. Let this value, V_1, be obtained when the pressure is so low that very few collisions are made by the ion before reaching the collector. If the pressure is increased, after a certain point the area under the peak begins to decrease showing that certain of the ions are being deflected and are not being recorded. Also the accelerating voltage corresponding to the particular peak has shifted to a slightly different value, V_2. The difference between V_1 and V_2 is the average energy loss of an ion in passing over the necessary path through the gas at that pressure. It is easy to explain these effects qualitatively, but some

[1] National Research Fellow.
[2] A. J. Dempster, Phys. Rev. **27**, 108, 514 (1926).
[3] A. J. Dempster, Phil. Mag. **3**, 115 (1927).

very surprising results are obtained when the deduced free paths are compared with the calculations from kinetic theory. For the free path for a deflection is found to be from ten to a hundred times the length of the kinetic theory mean free path at that pressure, or if the free path is considered normal there is practically no deflection at a collision and the energy lost is only a small fraction of what would be predicted from ordinary mechanics. It is well known that investigators working with electrons have found abnormally long free paths when the velocity is approximately that of the positive ions we have been considering. It is not difficult to conceive that any explanation of this phenomenon will be applicable also to the case of the proton which is a simple positive charge, but it seems very much more difficult of explanation when the same anomalous free path phenomenon is observed for more complicated ions which are positive charges with a definite electronic structure around them. It was with the idea of investigating these effects under different conditions than had heretofore been used that the present experiments were undertaken.

The apparatus was essentially the same in form as that used for the investigation of inelastic impacts of electrons. A source of positive ions was surrounded by two coaxial cylindrical grids, closed at one end, and beyond the second grid was a cylindrical plate. The tube containing this system could be evacuated and then disconnected from the pumps by a mercury cut-off. Different gases could then be admitted in known quantities and the resulting pressure measured by a McLeod gauge connected with the apparatus. There were liquid air traps separating the tube from the McLeod gauge and mercury cut-off. The positive ion sources were those which have been described by C. H. Kunsman.[4] Both the potassium and the caesium sources were used during the course of the experiments. The potassium source was known to emit only singly charged potassium ions, but probably there were slight traces of rubidium in the caesium source.[5] No doubly charged ions were present. After some experiments a slightly different form of filament was evolved which was found to be more stable and less likely to burn out than those which have been used previously for these sources. It consisted of a thin walled hollow semi-cylinder of very pure graphite, supported at each end by the filament leads. A platinum wire to carry the heating current ran down the center of the trough and the powdered source was packed in on top of it. It was found more convenient to mount it in a horizontal position, but after the necessary reduction process the powdered source forms a hard cake and it could be mounted vertically if desired. The apparatus and connections are represented diagrammatically in Fig. 1. D_1 and D_2 were about 1.5 cm each and D_3 was between 0.2 and 0.3 cm. A variable field could be applied across D_1. This potential was obtained from a two thousand volt generator and potentiometer, the current flowing in this circuit was measured by the multimeter, M. The filament was capable of supplying a milliampere but during these experiments currents of less than twenty-five microamperes

[4] C. H. Kunsman, Jour. of Phys. Chem. **30,** 525–534 (1926).

[5] Barton, Harnwell, and Kunsman. Phys. Rev. **27,** 739–746 (1926).

were used as the thermionic emission was found to be more stable below that value. A small constant field of about three volts per centimeter was applied between G_1 and G_2. The potential between F and P was constant during any run but several values of this potential were used in the course of the experiments. The current in this circuit was measured by the galvanometer, G. This system of connections allowed great flexibility and all the necessary experimental conditions could be obtained with it. The filament leads entered the tube through a ground glass joint so that it could be easily removed, but it was found most convenient to perform the necessary reduction of the positive ion source with the filament in place. For this purpose a hydrogen generator was connected with the apparatus. The hydrogen was purified by passing it over heated platinized asbestos and then through P_2O_5 and a liquid air trap. The same generator was used for supplying hydrogen later

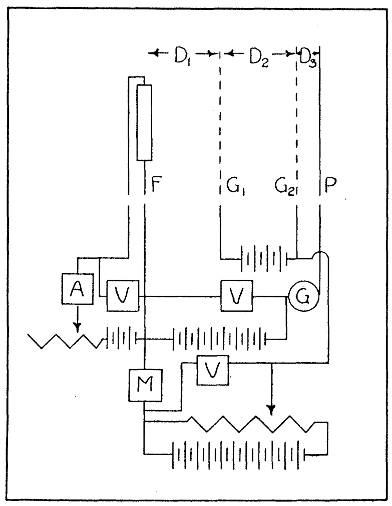

Fig. 1. Diagram of apparatus and connections.

during the experiment. The other gases used were only purified to about the same extent. The nitrogen was left for several weeks in contact with phosphorous. This had been found previously to give a fairly pure sample. Nitrogen and the rare gases used were dried by passing through P_2O_5 and the liquid air traps.

It can be seen from Fig. 1 that the ions pass through no field free region and the field around the filament is in general quite intense so that the possibility of the positive ions being neutralized by electrons emitted from the elements of the tube can be neglected. Also the ionization potentials of potassium and caesium atoms are so low that there will probably be no collision of the second kind with the atoms or molecules of the gas contained in the tube. However, there is the difficulty that photo-electrons will be produced by the grids and the plate under the influence of light from the filament, and an arc will form after the potential across D_1, which will be referred to subsequently as V, reaches a certain value. This value will vary with the nature of the gas in the tube, and with the pressure. A large resistance was put in the circuit to protect the instruments, but because of the entire change in conditions readings were always stopped as soon as the arc struck.

Before proceeding to the main experiments in view it was necessary to determine exactly what ionization was to be expected from these positive ions under the experimental conditions in the tube. It is very doubtful if the ions produce any ionization in the gas through which they pass, but it has been demonstrated by a number of observers that metals emit electrons under the influence of positive ion bombardment. Hence the potentials in the tube were so arranged that the positive ions were drawn from the filament to the first gauze, then slightly retarded in D_2, and retarded in D_3 to such an extent that they could not reach the plate. Under these circumstances any liberated electrons would reach the plate and be recorded by the galvanometer. Also any negative ions produced in D_2 or D_3 would also be registered by the galvanometer. If the potential in D_2 were reversed negative ions produced in D_2 would not emerge in the direction of the plate (neglecting any possible interchange of momentum between the positive ions and the atom or molecule they might ionize). In this way the effect of emission of electrons from the second gauze could be differentiated from the effect of electrons from the first gauze or ionization in the gas, for the region D_3 was so short that collisions in it could be neglected. With these arrangements a small current was observed in the galvanometer and it varied almost linearly with the voltage V until an arc struck. The difference in the galvanometer current when the potential in D_2 was reversed was of such an order of magnitude that the additional current was probably due to electrons emitted from G_1 under the influence of light from the filament or under the positive ion bombardment. Voltages as high as fifteen hundred were used under such pressure conditions that the arc did not strike but no evidence of any negative ionization of the gas by the positive ions was obtained. The gases which were used were: hydrogen, nitrogen, helium, neon, and argon. No polar molecules were worked with in the apparatus.

During the main body of experiments the ptential between the plate and filament was such that positive ions starting from the filament were able to reach the plate. Under these conditions the ions were accelerated to G_1, then moved under a very small accelerating field to G_2, from which place they were retarded till they had a very small velocity by the time they reached the plate. All the ions leaving the filament which were not interfered with by the grids reached the plate, and were recorded by the galvanometer, when there was no gas in the apparatus. Curves obtained by plotting the plate current against the accelerating voltage, V, were very much like the ordinary thermionic saturation curves. Some difficulty was experienced under these conditions, however, by an apparent instability of the tube just as the current reached its maximum value. If readings were taken rapidly over this region a slightly higher curve was obtained than if five minutes were allowed between readings. This effect was attributed to oscillations similar to those in an ordinary three electrode tube. They might theoretically occur and slightly alter the plate current. However, the energy in the oscil-

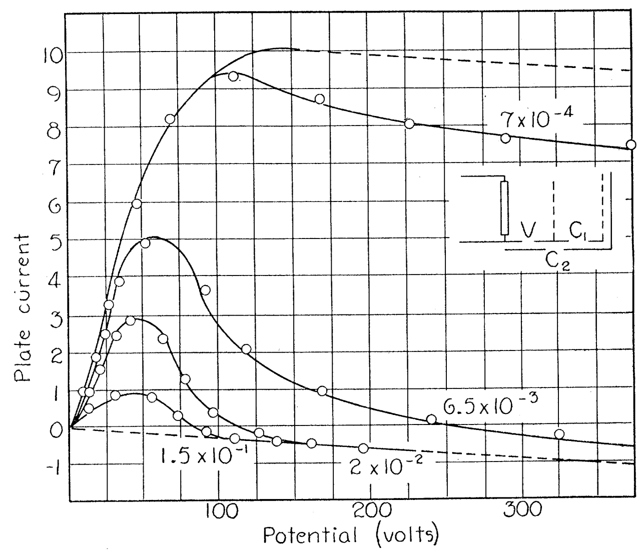

Fig. 2.

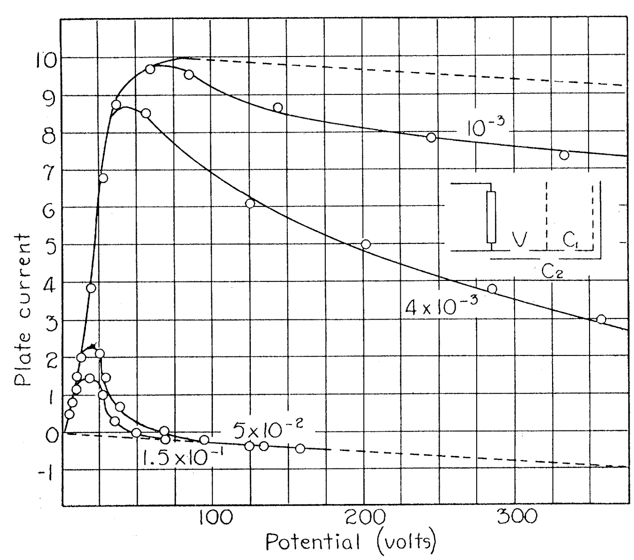

Fig. 3.

lations was so small that they could not be detected by ordinary methods. No similar unstable condition was observed when there was any gas present in the apparatus. As the gas pressure increased, however, the curves altered considerably in shape. The positive ions in moving through D_1 and D_2 collided with the gas molecules in those regions and as a consequence lost some of their energy at these impacts. Hence some of the ions which would have continued on through D_3 to the plate against the reverse field were unable to do so. At still higher values of the pressure this effect increased until as can be seen from Figs. 2 and 3 none of the positive ions were able to reach the plate. At these pressures after a certain voltage is reached the curves lie approximately along the dotted line extending from the origin. This dotted line is the curve obtained by the arrangement of the potentials described in the preceding paragraph. The upper dotted line represents the curve which is obtained when there is no gas in the apparatus.

The experimental results may be conveniently interpreted in the following way. If e is the charge on an ion, V is the potential across D_1, and l_1 is the average free path parallel to V then the energy possessed just before the first collision is: eVl_1/D_1. If an average fraction f of the energy of an ion is lost at a collision, and if this fraction is independent of the total energy of the ion, the energy it will possess after the first collision will be: $(eVl_1/D_1)(1-f)$. The energy it will have at the end of two free paths will be: $(eVl_1/D_1)\{(1-f)+1\}[1-f]$, and if $(1-f)$ is replaced by x the energy after n free paths will be: $(eVl_1/D_1)x\{x^{n-1}+x^{n-2}+\cdots,\}$ which can be written: $(eVl_1/D_1)x(1-x^n)/(1-x)=E_1$. The region D_2 can be considered in a similar way, the potential in that case being c_1 and the free path l_2. The energy at the end of m free paths will be:

$$E_1x^m+(ec_1l_2/D_2)x(1-x^m)/(1-x)=E_2$$

Neglecting collisions in D_3 the current will just cease flowing to the plate when: $E_2=e[V-c_2]$ where c_2 is the difference in potential between the filament and the plate. Since in the experimental tube D_1 was approximately equal to D_2 they can both be put equal to d. Likewise l_1 and l_2 may both be put equal to l. This is not strictly true, for l_1 is the average distance of advance per collision in the field V, while l_2 is the average distance of advance when the ion has an initial velocity but is moving only under a very small field. However, it is not probable that any great error will be introduced by assuming them approximately equal, for what amounts to an average value of the two will be obtained. It also follows that n will be equal to m. On this assumption the following value of V is obtained for which the positive ion current just ceases to flow: $x^{d/l}V+c_1=(V-c_2)d(1-x)/[lx(1-x^{d/l})]$. To a first approximation changes in the direction of the momentum of the ions need not be considered for, neglecting collisions in D_3 with sufficient energy. The value of l obtained from the above equation will not be exactly the mean free path of kinetic theory. For l is the length of the path parallel to the field hence it will be the actual free path times the cosine of the angle between its direction and the radius of the cylindrical electrode through the point. This will give too small a value for the free path, but the ion is also subject to a constant acceleration in the direction of the field which tends to counteract the first effect. The value of l obtained is the result of these two tendencies acting on the ordinary mean free path. They will have greater or less effect depending on the pressure and the strength of the field, but under the experimental conditions used it is unlikely that the order of magnitude of the quantity will be changed.

In the equation given in the last paragraph V, c_1 and c_2 are experimentally determined quantities, hence it can be seen that the equation determines a rather complicated relation between x and l. Taking the expression given by J. J. Thomson[6] for the exchange of energy at an encounter between two bodies of mass m_1 and m_2: $[4m_1m_2/(m_1+m_2)^2]T\ \sin^2\theta$, where θ is half the angle through which their relative velocity is turned and $2T$ is the momentum of the system multiplied by the relative velocity and the angle between these vectors, the loss of energy of the ions at a collision can be calculated. For the simplest case where the ions and molecules are considered as elastic spheres one of which is at rest the average fraction of energy which should be lost at a collision is: $2m_1m_2/(m_1+m_2)^2$. Using this value for f and the experimental values of V, c_1 and c_2 values of l can be calculated. The approximate results of this calculation are given in the table below where the figure at the intersection of a column and row represents the factor by which the kinetic theory mean free path must be multiplied to obtain the calculated value of l.

	H_2	N_2	He	Ne	A
K^+	15	150	5	75	150
Cs^+	5	100	10	100	25

These values are calculated from curves obtained at the highest pressures used. They are most surprising and tend to lead one to look for another explanation.

It was mentioned in the preceding paragraph that the equation used determined a relationship between x and l for a constant value of V. If the reasonable supposition is made in addition that l is an inverse function of the pressure two experimental values of V at different pressures will serve to determine x and l separately. The second alternative of varying c_2 has also been used but this changes the value of the plate current many fold and makes the determination of V more difficult. The values of l given in the preceding paragraph do not satisfy the equation except for the value of the pressure at which they were obtained. When this assumption of the dependence of l on the pressure is made the values of l all come out to be only slightly different from the kinetic theory value of the free path. The method does not serve to determine l accurately but in no case does it differ by a factor of more than three or four from the kinetic theory value. However, the average fraction of energy lost at a collision comes out very much smaller than would be expected from the ordinary kinetic theory concepts. The values obtained are given in the table below.

	H_2	N_2	He	Ne	A
K^+	0.008	0.003	0.025	0.005	0.002
Cs^+	0.005	0.002	0.005	0.003	0.002

[6] J. J. Thomson, Phil. Mag. **47**, 337 (1924).

These values of f are consistent within limits of error with all the data that has been obtained. The value of l coming out very nearly that of the kinetic theory mean free path has additional support from the fact that A. J. Dempster[3] found that positively charged helium atoms were neutralized after going a distance approximately equal to the kinetic theory free path. But the average fraction of energy lost differs very greatly from that calculated on the basis of collisions between smooth, non-attracting, elastic spheres. Of course, this conception is probably very far from the facts but it might be expected to give results of the correct order of magnitude. On referring to the more general expression for the loss of energy at an encounter it is seen to depend on a number of factors. Neglecting T, which is a function of the masses and velocities alone, θ can be considered as a function of these quantities, of the apsidal distance and of the nature of the interacting fields. The calculations for the case of a point charge passing near a molecule in which an electric doublet is induced are given by J. J. Thomson.[7] For more complicated distributions of potential about the interacting bodies the calcalculations are very involved. However, it can be seen qualitatively that if the force of attraction between the two bodies is of the form: $1/r^n$ the factor $\sin^2\theta$ and hence the fraction of energy lost at an encounter will decrease as n increases. The fields of the ions and molecules used in these experiments are doubtless of a rather complicated nature and the fraction of energy lost would be expected to be smaller than for the cases of colliding spheres or inverse square fields. The results obtained then depart from the simple theory in the correct direction, but in the absence of an accurate knowledge of the molecular fields it is not possible to state whether the energy lost is quantitatively what would be expected. Similarly it can be seen from the foregoing table that the values of f in the cases of the rare gases vary in accordance with these considerations. The value of f for K^+ in helium seems out of proportion to the rest of the table. It may be that the conditions are such in this case that the potassium ion may supply energy of excitation at a certain fraction of the collisions which would, of course, entirely change the nature of the phenomenon. No further information was obtained on this point. These explanations are merely qualitative, but are the only ones which can be offered for the low values of f observed. But it should be mentioned that this very small loss of energy at an encounter is exactly what would be predicted from the phenomena observed in a positive ion analyser mentioned at the beginning of this paper.

Figs. 2 and 3 are the experimental curves for the cases of Cs^+ in argon and K^+ in helium respectively. The curves are seen to rise more abruptly in the latter case than in the former which is due largely to the different characteristics of the sources of the positive ions. The curves in the latter case are also seen to descend more abruptly. As was mentioned previously this is the effect that would be expected if f were greater for potassium ions in helium than for caesium ions in argon. This, however, is not as conclusive as the table which has been given, for these slopes will depend considerably on the total plate current and it was not always possible to reproduce this exactly. These figures also illustrate the difficulty of accurately measuring the intersection of the curves with the lower dotted line which represents the negative current to the plate. The values of V obtained from these intersections are the ones substituted in the equation which was developed for the determination of x and l, and the uncertainty in the measurement of V is probably the largest experimental error.

In conclusion it is a pleasure for the writer to express his indebtedness to the National Research Council for its support and to California Institute of Technology for the facilities placed at his disposal.

CALIFORNIA INSTITUTE OF TECHNOLOGY,
November 15, 1927.