

*The Mobility of Ions in Pure Gases.*

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*Introduction.*

Although determinations of the mobility of ions in gases have been made almost continuously during the last 30 years, the nature of the ions still remains obscure. The values obtained by different experimenters, using a variety of methods, differ by amounts far in excess of those to be attributed to observational errors and some methods yield results which are complicated and difficult to explain on any simple theory of the nature of the ion. The main facts which have emerged from the mass of experimental data are summarised in "Conduction of Electricity through Gases."\*

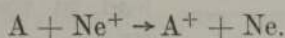
It seems probable that in none of the experiments made hitherto has the gas under examination been spectroscopically pure. In many cases materials such as ebonite and sulphur have been in contact with the gas. In others the apparatus has been made gas-tight by means of waxed flanges or greased joints. In such conditions the purity of the gas leaves much to be desired. It is continually being contaminated by impurities such as water vapour and carbon dioxide coming from the walls of the vessel and from the metal parts of the apparatus as well as by the vapours from the wax, ebonite, etc. Such impurities may have large affinities for electrons and may unite with the positive ions to form groups. In such conditions, in a given gas, the ions may well consist of clusters of which the size and mass vary from one experiment to another. The reason why many observers have found the negative ions to be of molecular magnitude and not electrons in nitrogen, hydrogen, etc., becomes obvious, and it is not surprising that the actual mobilities found are smaller than those calculated theoretically from the standpoint of the classical dynamical theory of gases, assuming the ions to be monomolecular. The present writers, for example, found that in an experiment on nitrogen at a pressure of 600 mm., freshly introduced into an apparatus contained under a bell jar, the negative carriers consisted of a mixture of ions and electrons. The effect of the contamination coming from the walls was clearly shown by the fact that the number of "normal" ions increased, and of electrons decreased, on leaving the gas in the apparatus overnight.

\* Thomson, Cambridge University Press, 3rd ed., 1928.

The effects of impurities are clearly of importance in the case of negative ions. In the case of the positive ions there are grounds for supposing that they may be even more critical. An electron, moving in an electric field through a gas attains a terminal energy which even at moderate fields (100 volts per centimetre) and high pressures (100 mm.), may be of the order of volts. If this energy is greater than the electron affinity of the molecules of the gas itself and any impurities in it, the electron, once it has attained its terminal speed will remain free even in the presence of large quantities of impurity. The positive ions on the other hand have a very small terminal energy and the monomolecular or atomic ions which are the primary products of the action of the ionising agent may be replaced, in the presence of extremely small concentrations of foreign molecules, by others of an entirely different nature. Either or all of the following processes may be involved.

(1) A cluster round the positive ion may form as the result of its impact with a foreign molecule possessing a marked dipole. At high gas pressures three-body collisions must be relatively common so that the probability of collisions leading to the union of the original ion with the impurity molecule may be high.

(2) Various recent results, obtained in experiments on the nature of the positive ions produced by electron impacts and examined by magnetic analysis, are satisfactorily explained on the view that a positive ion can capture an electron from any molecule or atom of lower ionisation potential with which it "collides." In particular in mixtures of argon and neon, Harnwell\* concluded that transfers took place in accordance with the scheme



In a later paper† he obtained evidence in other mixtures for similar transfers; for example, from helium to hydrogen, neon to hydrogen, helium to nitrogen, and neon to nitrogen. Smyth and Stueckelberg quote‡ further cases. In more recent experiments, using a similar method but with a somewhat different procedure Kallmann and Rosen§ have obtained yet further evidence of the same phenomenon.

The results of all these workers are in accordance with the view now generally accepted, that the probability of an energy transfer is greater, the smaller

\* 'Phys. Rev.,' vol. 29, p. 683 (1927).

† 'Phys. Rev.,' vol. 29, p. 830.

‡ 'Phys. Rev.,' vol. 32, p. 779 (1928).

§ 'Z. Physik,' vol. 61, p. 61 (1930).



the energy to be transferred. The electron captured by the ion may enter either the ground state of the new atom, in which case the energy transfer is equal to the difference in the ionisation potentials of the old and new atoms, or it may enter a level of higher energy. In some cases the latter may be the more probable. We may regard the energy transfer as positive when the energy of the captured electron in the new atom is less than its original energy in the old atom, so that energy has to appear as a result of the interaction. Thus if a helium ion captures an electron into the ground state from a normal mercury atom, the energy transfer is equal to + 15 volts, since the ionisation

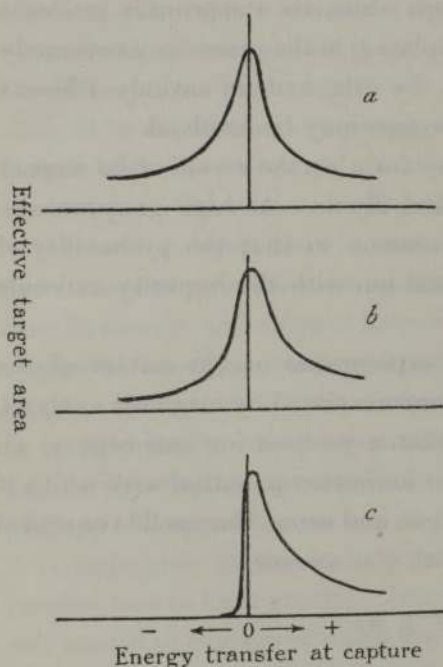


FIG. 1.

potential of mercury is 10 volts, and of helium 25 volts. In general, cases of both positive and negative energy transfer must be considered.

The actual probability of electron capture will depend upon the distance of closest approach of the reacting bodies, and upon the energy to be transferred at capture. Kallmann and Rosen discuss the problem qualitatively from the theoretical standpoint. They express their conclusions by drawing a curve showing the effective target area, presented by an atom to a high-speed positive ion, for those collisions which lead to the capture of an electron. Their curve is of the form shown in fig. 1, *a*. It will be seen that there is a maximum when the energy to be trans-

ferred from one atom to another at collision approaches zero, and that the curve is symmetrical about the ordinate through this maximum. That is, the probability of capture depends only on the magnitude of the energy transfer, and is independent of whether this energy has to be supplied from the kinetic energy of the ion, or is liberated and appears as an increase in the kinetic energy of the system after impact.

In the case of the impact of the high-speed positive ions with molecules as distinct from atoms, any energy liberated as the result of the interaction may appear either as kinetic energy or as vibrational energy in the new molecular ion. On the other hand, for collisions involving an absorption of energy the

required energy can only come from the kinetic energy of the high-speed ion because the vibrational energy of the molecule at ordinary temperatures is small. We may, therefore, expect that a transfer involving a given energy change will be more probable when energy has to be liberated than when it has to be absorbed. This introduces dissymmetry into the curve which may now take the form of fig. 1, *b*.

In the case of the capture of electrons by positive ions of very slow speed such as we find in gases at high pressures, the corresponding curve, whether for collisions with atoms or molecules, will be modified still further. There will still be a maximum for collisions involving zero energy change. But the curve must fall to zero at a point very close to this maximum as in fig. 1, *c*, since with these ions there is no kinetic energy available to satisfy the energy relations if capture involves an absorption of energy.

The following conclusion may be drawn from this curve. Consider, for example, positive helium ions moving through helium at a pressure of 300 mm. Assuming that the mean free path of the ions does not differ widely from the ordinary gas kinetic value, for which there is some evidence, they make, say,  $\times 10^9$  molecular collisions per second. For an ion moving through molecules of its own gas the probability of transfer is a maximum. We may, therefore, expect the charge to remain associated with the same helium atom for only a few collisions. If the helium contains some impurity present to an extent of, say, one molecule in  $10^5$  it is probable that a considerable proportion of the charge originally carried by helium ions will arrive at the collecting electrode attached to molecules of the impurity. For once an impurity molecule has lost an electron, fig. 1, *c*, shows that it is very unlikely to be neutralised by recapture from a helium atom.

Evidently in the presence of minute quantities of even non-polar impurity, the values of mobility obtained may not be the true values for the gas under investigation.

(3) There is yet a third process which may lead to spurious results. In the process of ionisation metastable atoms are produced as well as ions, and under some conditions of excitation, their concentration may be high. Thus for neon in the positive column of glow discharges their number may be comparable with that of the positive ions. Now Franck and Jordan show that metastable helium atoms can react with atoms of impurity to give ions of the impurity by collisions of the second kind. This well-established phenomenon has been used by Penning\* to explain the results of his experiments on

\* 'Z. Physik,' vol. 46, p. 335 (1928).



the changes in sparking potential produced in neon by the addition of minute traces of mercury vapour or of argon.

It is, therefore, quite conceivable that in the presence of small quantities of impurity we may have two groups of ions starting off from the region of initial ionisation, one group consisting of the ions of the gas, and the other of ions of the impurity. The relative amounts of these will depend upon the relative numbers of ions and metastable atoms produced by the ionising agent and upon the concentration of impurity.

In the authors' opinion these processes are of paramount importance in determining the nature and hence the mobility of ions in gases. Their consideration emphasises the necessity for a high degree of purity of the gas especially in the investigation of positive ions in which the possible effect of small amounts of impurity has been largely ignored. In fact, one is led to the conclusion that no significance can be attached to the values of the mobility of the positive ion so far obtained in any gas.

To obtain definite results it is essential to adopt a design of apparatus in which the following conditions are satisfied: firstly, the method should enable one to separate with high resolving power mixtures of ions of different mobilities into their respective groups. None of the earlier methods in closed vessels permit of this, and methods involving a stream of gas do not allow of the use of pure gas. Secondly, the apparatus should be constructed entirely of glass and metal so that it can be subjected to a rigorous heat treatment in accordance with the requirements of modern vacuum technique. Only after this treatment should the purified gas be introduced.

A method described by the writers and Starr\* and used in the experiments on nitrogen referred to above satisfied the first condition. The following paper contains a description of its modification to comply with the second condition and gives an account of the results obtained with two gases. It will be seen that the experiments on positive ions in helium in particular give striking illustration of the part played by minute traces of impurity.

#### *Principle of the Method.*

Briefly, the principle of the method employed is as follows:—

In fig. 2, *a*, A, B and C, D are 4 gauzes and E an electrode connected to an electrometer. Ions are brought up to the electrode A by a suitable directed

\* 'Proc. Roy. Soc.,' vol. 121, p. 172 (1928).

field. The potential between A and B alternates with a certain frequency so that a flash of ions enters the main field BC once in every cycle. After crossing the space BC, in a time depending on the field and on their mobility, the ions reach the gauze C. The potential between C and D alternates in phase with

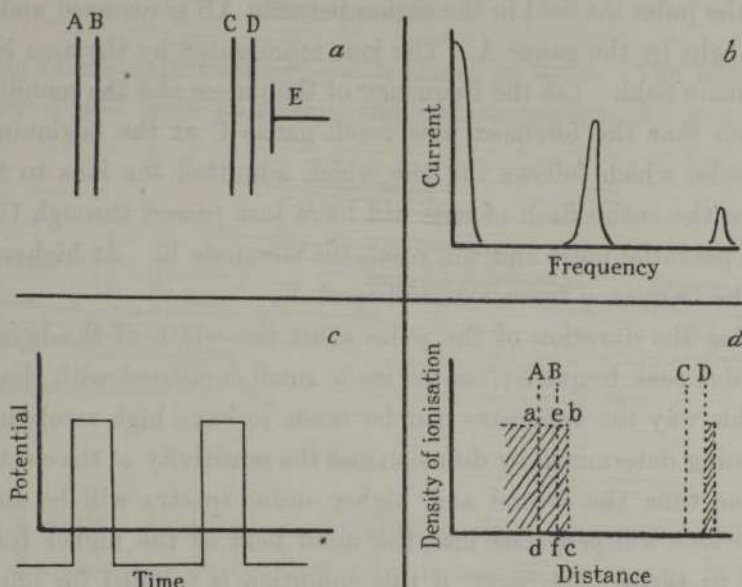


FIG. 2.

that between A and B so that for certain values of the frequency, ions of a given mobility arrive at C at the beginning of the advancing phase of the potential. Those of them which are not caught by the gauzes pass through to the collecting electrode E. If the current passing to the electrode E is plotted against the frequency of the alternating potential, and if ions of one mobility only are present, a curve similar to that shown in fig. 2, b, should be obtained.

Peak values of the current occur for those frequencies  $\nu_1, \nu_2, \dots, \nu_n$ , such that the time  $T$ , taken by the ions to pass from gauze B to gauze D is equal to  $1/\nu_1, 1/\nu_2, \dots, 1/\nu_n$  where  $n$  is an integer.

When ions of different mobility are present, each class gives rise to its own characteristic series of peaks. The apparatus produces, in fact, an ionic spectrum, showing several orders.

In order to avoid confusion through overlapping, it is important to eliminate all but the first order spectrum. In addition it is essential to secure high resolving power for ions of different mobility. That both these conditions



can be fulfilled is seen from the following argument. Suppose for simplicity that the alternating pulse is of the form shown in fig. 2, *c*, and that no ions are absorbed by the gauzes. At the beginning of the voltage pulse, ions enter the space AB, and move across it. At the end of the pulse there will be a distribution of ionisation represented by the shaded area *abcd* in fig. 2, *d*. At the end of the pulse the field in the region between AB is reversed and the ions in it are caught by the gauze A. The ions represented by the area *ebcf* move across the main field. Let the frequency of the pulses and the mobility of the ions be such that the foremost ions reach gauze C at the beginning of the potential pulse which follows the one which admitted the ions to the main field. Then the entire flash of ions will have just passed through CD at the end of this potential pulse and will reach the electrode E. At higher or lower values of the frequency fewer ions will reach E.

By making the duration of the pulse short the width of the layer *ebcf* at the first order peak frequency can be made small compared with the distance AB. In this way the apparatus can be made to have high resolving power, the limit being determined by diffusion and the sensitivity of the electrometer. At the same time the second and higher order spectra will be suppressed because no ions will penetrate into the main field at the higher frequencies pertaining to them. Moreover, if this condition is fulfilled for one type of ion it holds generally for ions of any other mobility.

Similar conclusions can be drawn when the alternating pulse is of simple harmonic form, as in the present experiments. The necessary diminution of the width of the ionised layer can be secured by applying retarding voltages to the gauzes B and D so that ions enter A only during that portion of the cycle in which the voltage is in the neighbourhood of its maximum value.

There remains a possibility of overlap between the first order spectrum and a spectrum of zero order when one is dealing with ions of very different mobility. In practice this is found to occur only with a mixture of ions and electrons. Two examples are shown in the curves discussed later (figs. 5 and 6) in which a peak for the negative ions is superposed on the zero order curve of the electrons. If so desired this zero order spectrum can be cut out by using the alternating potentials out of phase by  $180^\circ$ .

In all the results which are discussed in this paper the values of the steady fields and the peak values of the alternating fields have always been maintained in the same ratio. Apart from diffusion effects, which have been found to be negligible, it will be seen that the current-frequency curve, due to the presence of a single group of ions, should be of a definite form whatever the pressure

and the absolute value of the fields. Any broadening in a peak must, therefore, indicate the existence of a distribution of mobilities in the group, or the presence of two groups of nearly equal mobility.

### The Apparatus.

A diagram of the experimental tube is shown in fig. 3. The ionisation is produced by  $\alpha$ -rays from polonium, the box containing the source being

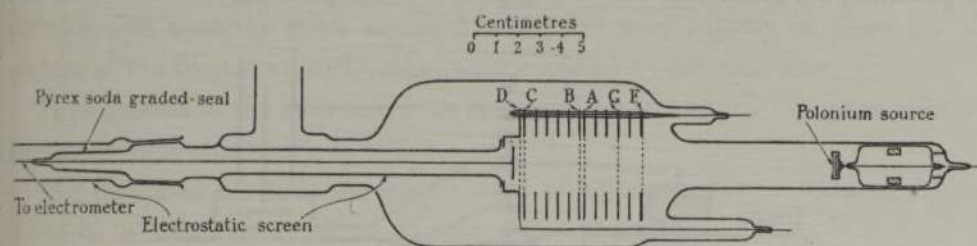


FIG. 3.

attached to a sliding glass tube surrounding an iron disc which enables the position of the polonium to be altered by means of a magnet. When the apparatus is being baked out (at  $420^{\circ}$  C.) the polonium is withdrawn into a glass tube projecting outside the furnace. After the main bake-out has been completed, the polonium is moved up and the projecting tube is in turn heated. To prevent the contamination of the apparatus by co-aggregate recoil of the polonium the source is covered with mica, the residual range of the particles being 5 mm. in air at N.T.P.

The gauzes were made by spot-welding thin nickel wires across circular holes in circular "staybright" steel plates. "Staybright" steel was chosen because it does not absorb mercury vapour. Besides the gauzes A, B, C, and D referred to above, two others G and F are included. In making an experiment the position of the polonium is adjusted so that no ions are produced beyond G. Ions produced between the source and F do not enter the measuring part of the apparatus, but those of one sign from the region FG are driven to A by a suitable field. The average age of the ions entering the main field can thus be controlled within certain limits.

The various fields are provided with guard rings to ensure uniformity and the method of insulation is the same as that used in the previous apparatus.\*

\* *Loc. cit.*



The leads to the various gauzes are taken out through three lead glass "pinches"; only one lead is shown in the figure. The main tube is of soda glass and the connection to the electrometer is taken out through a tungsten wire sealed into "pyrex," the soda glass and the "pyrex" being joined by means of a graded glass seal. Provided the gas is dry, "pyrex" is satisfactory as an insulator for this purpose, when serious surface leakage is prevented by means of earthed guard rings.

The earthed shielding tube for the electrometer lead is provided by a film of platinum on glass, this film being produced by painting the inner surface

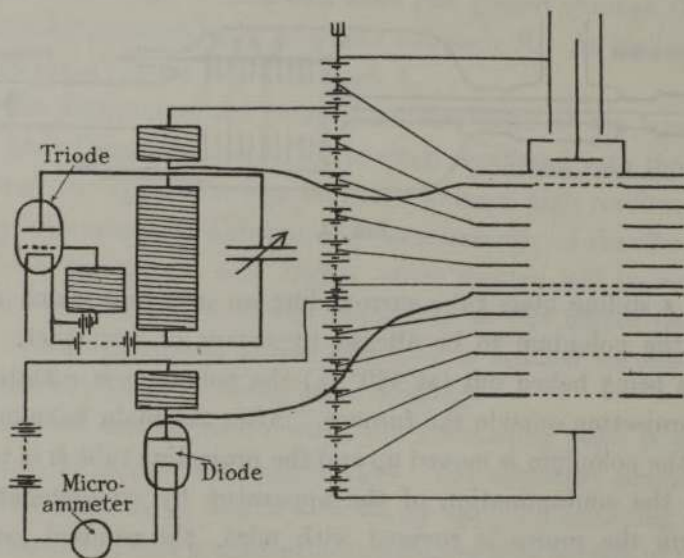


FIG. 4.

of a glass tube with "oil of platinum" and then heating the glass to the annealing temperature. The complete electrical connections are shown in fig. 4. The two alternating potentials required were obtained from a valve oscillator of which the frequency could be changed by altering the capacity of the condenser in the main oscillatory circuit. Two coils were mutually coupled with the main inductance of the oscillator. The peak values of the potentials induced in these two coils, measured by means of a diode voltmeter, could be adjusted by altering the coupling with the main inductance.

No iron was used in these inductances, and to obtain the frequency range from 50 to 6000 cycles per second three main oscillating coils with suitable coupled coils were built. In order to determine the frequencies given by the oscillator

for different values of the capacity of the variable condenser in the oscillatory circuit, the main oscillatory current was passed through a stretched piano wire passing between the poles of an electromagnet. Resonance vibrations were obtained by suitable adjustment of the length of the wire. With a given tension in the string the distance between two nodes is inversely proportional to the frequency. At the higher frequencies as many as 10 nodes and loops have been obtained. The wire was next adjusted to resonance with a standard tuning fork and the frequency corresponding to any condenser setting calculated for each of the three coils. It was shown by means of a four-plate cathode ray oscillograph that the fields across AB and CD were exactly in phase for all values of the frequency within the range supplied by the oscillator.

The currents to the electrode were measured by means of a Compton electrometer of high sensitivity to charge.

The distances between the gauzes were as follows:—FG = 10 mm., GA = 15 mm., AB = 2 mm., BC = 25 mm., CD = 2 mm.

In a particular case the values of the potential between the plates were:—FG, 150 volts; GA, 270 volts; AB—22 volts; BC, 450 volts; CD—22 volts; D-electrode, 60 volts. Peak value of alternating potential, 60 volts.

In other cases the fields were reduced in the same ratio and in the curves given only the value of the main field is quoted.

With the simple harmonic form of potential pulse the time taken by the ions in crossing the space between the gauzes C and D cannot be calculated accurately. This prevents the method from being used to make accurate measurements of the absolute values of mobility. One of us (C.F.P.) has designed an apparatus giving a square wave pulse of potential,\* which should remove this objection in future experiments. The results given below show, however, that the method is entirely reliable for relative values. The values of mobility cited in the paper are calculated for atmospheric pressure on the assumption that the mobility of negative ions in dry air is 2.1.† No stress, however, is laid on these values as an error of, say, 10 per cent. will have no effect on the general conclusions of the paper.

#### *Experiments with Air.*

Before carrying out experiments in pure gases, determinations of the mobility of ions in dry air at various pressures were made. Langevin's law, namely, that the product of the mobility ( $k$ ) and pressure ( $p$ ) is a constant, has been

\* In the press.

† Tyndall and Grindley, 'Proc. Roy. Soc.,' A, vol. 110, p. 341 (1926).



fully established by the work of previous investigators. We may, therefore, use this fact to test the reliability of the apparatus.

The results are shown in fig. 5 in which the electrometer current is plotted with the product of the frequency ( $\nu$ ) and the pressure. The product is

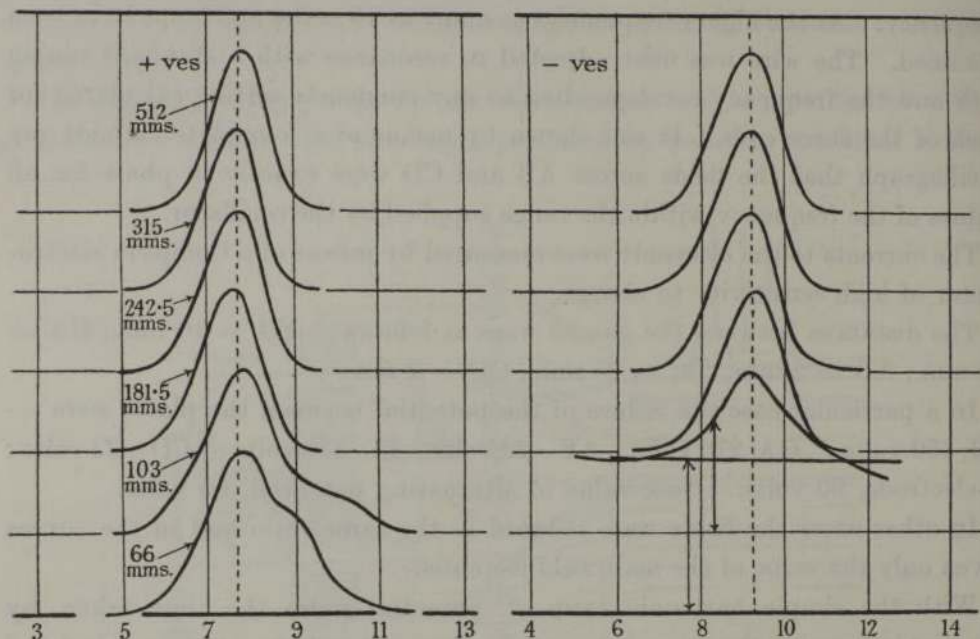


FIG. 5.—Air Frequency  $\times$  Pressure (mm.  $\times 10^{-4}$ ).  
Main Field. 180 volts/cm.

proportional to  $kp$ . The scale of the electrometer current for each pressure is adjusted to make all the peaks of the same height and the curves are displaced vertically in order to exhibit the results in a convenient form.

Considering first the positive ions it will be seen that the maxima of the peaks all appear within experimental error at the same value of " $\nu p$ ." It is exceedingly difficult to explain this result except on the assumptions (a) that Langevin's law holds, and (b) that the calibration of the oscillator is reliable.

Another possible source of error remains. It is conceivable, though highly improbable at the very low current densities employed, that serious contact potential differences may exist. Experiments were made, therefore, in which all the fields were reduced in the same ratio. It was then found that the peaks were exactly of the same form, their maxima occurring at frequencies directly proportional to the field values. It is evident from this that contact potentials play no disturbing part.

At the lowest pressure, 66 mm., there is an indication of a second group of ions of higher mobility which may be attributed to "initial" ions which Erikson originally found to exist in air under certain conditions of age. In dry air it is only at low pressures where the age is of the order of 0.001 second that one would expect "initial" ions to be present in measurable quantity. With negative ions, peaks obeying Langevin's law appear at all pressures except 66 mm. At this pressure there is at all frequencies an electrometer current approximately constant in value. This can only occur if the negative ions are electrons with a mobility which is so high that they shoot through the main field during the duration of a single pulse.

At 103 mm. the curve is the result of a superposition of a peak upon a uniform current. The peak occurs at the same value of " $\nu p$ " as for the other curves and the charge is evidently being carried by a mixture of electrons and "normal" ions. It is noticed also that the width of the "normal" ion peak is approximately the same as that at the higher pressures at which no electrons are present. This suggests that the electrons become attached to neutral molecules only in those regions where they have a relatively small velocity and not in the main field. At this pressure the value of  $E/p$ , where  $E$  is the electric force in volts per centimetre and  $p$  is in millimetres of mercury, was roughly 1.8 in the main field. Lattey\* at pressure up to 29 mm. found electrons in air at much lower values of  $E/p$  provided traces of water vapour were excluded. In the present experiments the presence of water vapour does not appear to be critical, as electrons were found at 103 and 66 mm. whether the air was wet or dry.

At the higher pressures the continuous action of the  $\alpha$ -rays may produce ozone and other products of chemical action in appreciable concentration, and it is not possible to attribute the formation of negative ions to any definite molecule.

#### *Nitrogen.*

The tests in air having proved to be satisfactory the apparatus was filled with purified nitrogen. Two sets of experiments were made. In the first of these the source of the gas was commercial nitrogen from a cylinder and in the second, heated sodium azide. Before generating the gas, the azide was heated for some hours *in vacuo*, at a slightly lower temperature than that necessary to produce decomposition, in order to remove water, carbon dioxide, etc. In both cases the gas was circulated several times over heated copper

\* 'Proc. Roy. Soc.,' A, vol. 84, p. 173 (1910).



oxide and copper filings, and was then passed through liquid air traps into the "baked-out" measuring apparatus.

A selection of the results is shown in figs. 6, A, B and C. Considering first the negative ions, only one curve needs to be shown, namely, that in A (full line), because in every case investigated only electrons were found to be present. For purposes of comparison the type of curve given by the writers and Starr in an earlier communication, and referred to above, is inserted as a dotted line. This curve was obtained with nitrogen originally in a purified state but admitted

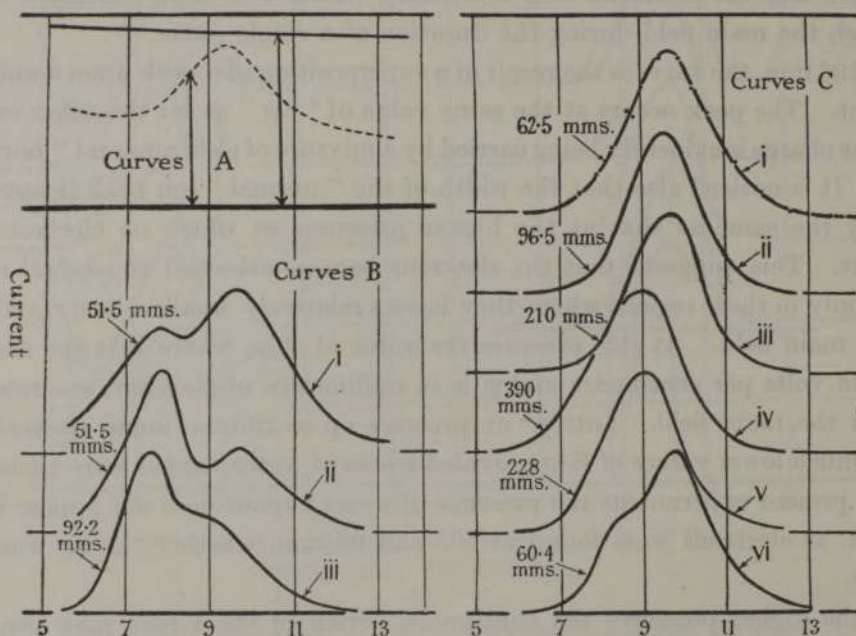


FIG. 6.—Nitrogen Frequency  $\times$  Pressure (mm.  $\times 10^{-4}$ ).  
Main Field. 187 volts/cm.

to an apparatus sealed with wax and not subjected to heat treatment. Taken in conjunction with the present results it shows definitely that the existence of "normal" ions in nitrogen is an indication of the presence of contamination.

That the absence of any "normal" negative ions at these values of  $E/p$  is not a sufficient criterion of purity is, however, shown by the variability of the results obtained with positive ions. The results with cylinder nitrogen as the original source are given in curves B. These curves show two groups of ions varying in proportion even for two samples at the same pressure. Evidently the method of purification was not capable of removing traces of disturbing impurities contained in the cylinder nitrogen. It was for this reason that the

experiments with azide nitrogen were undertaken. The results are shown in curves C.

Curve C (i) at pressure 62.5 mm. was obtained as soon as possible after the gas had been admitted to the baked-out apparatus. The next curve C (ii) at pressure 96.5 mm. was obtained after more nitrogen had been added to the original sample, and similarly for the pressure 210 mm. It will be seen that in these curves only the one group of ions is present. It coincides in position with the group of higher mobility in curves B. Its position is also governed by Langevin's law.

The next addition of nitrogen bringing the pressure up to 390 mm. was not made until a week had elapsed. By this time traces of impurity not removed by the bake-out may well have accumulated in the gas, and there is evidence of this in the displacement of the curve C (iv) to a lower mobility. The subsequent curves at 228 mm. and 60.4 mm. were obtained by pumping off some of the gas. In the latter of these there is evidence of resolution of the peak into two groups and the curve is clearly tending towards the form of that shown in B (i).

The main conclusion to be drawn from these results is the great importance of minute traces of impurity on the mobility of positive ions in nitrogen. Indeed, it is quite possible that even the high mobility 2.1 deduced from C (i) for the sample of greatest probable purity is not the true mobility of a nitrogen positive ion moving through its own gas.

### *Helium.*

The effects of minute traces of contamination are much more striking in the case of helium.

In the first experiments the gas was taken from a cylinder containing helium stated to be of 99 per cent. purity. It was first passed into a tube containing heated copper oxide, then successively into two degassed charcoal tubes immersed in liquid air, a second copper oxide tube and finally into two more charcoal tubes. A liquid air trap was interposed between the apparatus and the last tap. All taps were lubricated with apiezon L.\* In a second series a tube into which sodium was electrolysed in the manner described by Taylor† was inserted after the second copper oxide tube. The purpose of this was to remove residual nitrogen.

\* Burch, 'Proc. Roy. Soc.,' A, vol. 123, p. 271 (1929).

† Taylor, 'J. Sci. Instruments,' vol. 4, p. 78 (1927).



Some typical results for positive ions at a pressure of 359 mm. are shown in fig. 7. The scale of electrometer current is the same for all the curves but they are displaced vertically to exhibit the results in a convenient form.

Curve A, fig. 7, was obtained before the sodium discharge tube had been inserted in the purification plant and spectroscopic examination by electrodeless discharge showed the presence of nitrogen. The curve shows a main peak at mobility 14 and a hump suggesting a peak at a higher mobility of about 17, when reduced to atmospheric pressure. These mobilities are greatly in excess of those obtained for positive ions in helium by previous investigators.

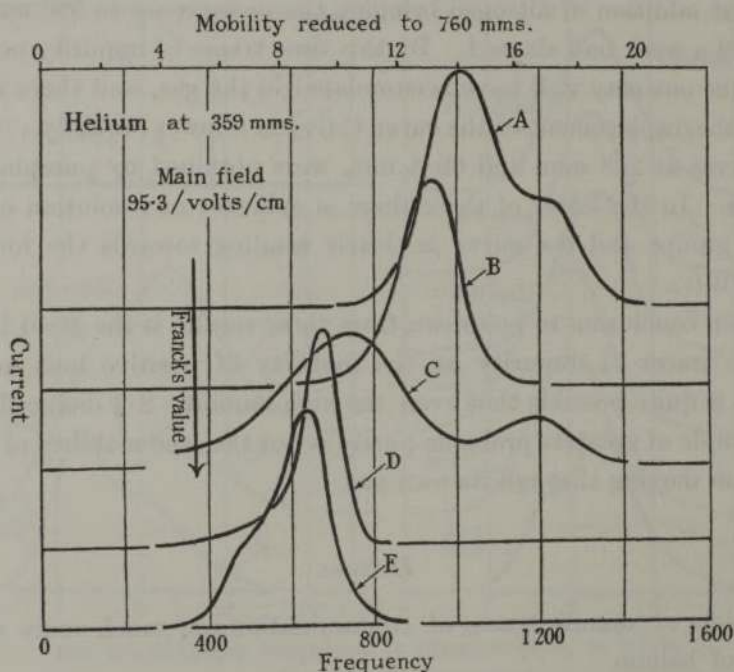


FIG. 7.

Thus Franck and Gellhoff ('Jahrb. Radioact.', vol. 9, S. 250) obtained the value 5.09 whether the gas was "pure" or slightly impure, and Rogers ('Phil. Mag.', ser. 7, vol. 5, p. 895, 1928) gives values ranging from 5.6 to 6.7.

The experiments were then repeated at a pressure of 300 mm. with precisely similar results and in agreement with Langevin's law as far as one could tell for two pressures not very widely different. The stopping power of helium is small and with the present apparatus 300 mm. was the lowest pressure at which it was possible to produce adequate ionisation in the localised region (*i.e.*, the region GF, fig. 3).

To test whether the existence of two peaks was connected with the presence of nitrogen in the helium, the apparatus was baked out again and the gas repurified by the second method described. It was not tested by electrodeless discharge but a spark spectrum showed only helium lines. Though a spark spectrum is not so crucial a test for the presence of impurity as an electrodeless discharge, the gas was presumably purer in this case.

The results were somewhat unexpected because, although only one peak was obtained, it appeared at the somewhat lower mobility of 13. This mobility was shown to be independent of the field by the fact that the peak occurred at half the frequency when the fields were halved. An actual curve is shown in fig. 7, B.

Identical curves were obtained 1, 2 and 3 days later with the apparatus untouched. Ten days later, with liquid air maintained in the traps throughout the whole time, an entirely different curve C was obtained with two peaks, one at mobility 10 and another, a very small one, at one of the original high mobilities, 17.

It will be noticed that the main peak current is now smaller and the curve is spread out over a wide range of mobility. This suggests that the accumulation of impurity not detectable after 3 days had become appreciable in the subsequent week and that the ions were now a composite mixture of various mobilities. Even as it is, the mean mobility of the group is higher than that obtained by previous experimenters.

The next step taken was to remove the liquid air from the last trap so that any impurity which had been condensed in it, such as mercury or vapours from the tap grease vapour, could diffuse into the apparatus. The result is shown in D and it will be seen that the mobility of the ions is now well defined and is still smaller.

Finally, 1 per cent. of pure nitrogen from sodium azide was added to the helium. The result, seen in E, is a slight decrease of mobility which may be attributable to the change in the medium rather than to a change in the nature of the ions. There is a slight indication of the beginnings of a peak at a mobility in the neighbourhood of 7 cm. per second.

Throughout the sequence, experiments on the negative ions gave electrons and no indication of any "normal" ions.

The results for helium are, therefore, even more striking than those for nitrogen in demonstrating the effect of small amounts of impurity on the mobility of positive ions.

If the nature and amount of the traces of foreign gas present were known, it



might have been possible to explain these results in detail on the basis of the principles of electron capture, etc., discussed in the introduction to this paper. This is not possible at present because we have no adequate control of the minute traces of impurity involved, but we believe that it is in this principle that the explanation of the changes we have observed is to be found. That the results are particularly marked in helium is to be expected owing to the small size and mass of the helium ion. A marked decrease in mobility should occur when, by electron capture, the positive charge is transferred to some impurity molecule.

In the first sample of helium an attempt was made, at 300 mm., to apply the method of "clean up" by electrodeless discharge used successfully by Townsend and MacCallum\* in their experiments at lower pressures on sparking potentials in helium and neon. The electrodeless discharge was produced by surrounding a side tube with the main oscillatory coil of a 5 kw. induction furnace. No appreciable change occurred in the mobility curve after  $2\frac{1}{2}$  hours, though at these high pressures the discharge was weak. In the second series of experiments the discharge could not be applied owing to a breakdown in the furnace.

As in the case of nitrogen, we are, therefore, not yet in a position to give a value of the true mobility of helium positive ions in helium. But it is interesting to note that the mobility, 17, of the fastest ion we have observed is roughly three times that previously obtained, and is approaching the value 26.0 deduced by Hassé from the theory of Langevin for a monomolecular helium ion moving in its own gas. This lends support to the view that in the absence of all polar molecules a helium ion does not collect a cluster in its passage through a gas.

Before a value can be assigned to the true mobility of a helium positive ion moving through its own gas the experiments must be repeated under improved conditions. For this purpose it would be desirable to obtain the helium from another source, and, if possible, to redesign the apparatus so that lower pressures may be used. Under these conditions the helium should be neon free. At these lower pressures it should be possible to reduce considerably the chance of a helium ion colliding with an impurity molecule in its passage to the electrode.

The writers propose to continue the investigations on these lines, but the experiments will take time. Meanwhile, the results indicate the conditions necessary for obtaining significant values of the mobility of ions in gases, and

\* 'Phil. Mag.,' vol. 5, p. 695 (1928).

may prevent others from wasting time on experiments in gases of doubtful purity.

*Summary.*

1. A method previously described by the writers and Starr for measuring the mobility of ions in gases has been modified to permit the measurements to be made in an all metal-glass apparatus which can be subjected to a rigorous heat treatment. The method has a high resolving power for ions of different mobility.

2. The apparatus was tested with dry air at various pressures and its reliability shown by the agreement of the results for positive ions with the well established law of Langevin. In dry air at 66 mm. and in a field of 180 volts per centimetre the negative carriers were all electrons. At higher pressures "normal" ions made their appearance.

3. Results in nitrogen emphasised for the first time the very great importance of small traces of impurity on the mobility of positive ions. In every case the negative ions were all electrons; but in spite of this the results with the positive ions were variable. Evidently the absence of "normal" negative ions is not an adequate criterion of purity.

4. The results in helium show even more strikingly the critical effect of traces of impurity on the positive ions. The maximum mobility recorded was of the order of 17. Slight contamination on standing was sufficient to transform the ions into a composite mixture of groups differing widely in mobility with a maximum at 10. After the removal of liquid air from a trap, inserted to prevent the access of mercury or vapours from the tap grease to the gas, the ions had a well-defined mobility of about 9.

5. This marked effect is to be expected from the principle of electron capture discussed by Kallmann and Rosen in a recent paper, according to which a positive ion on impact with a molecule of lower ionisation potential can capture an electron from the neutral molecule with a consequent change in the nature of the ion. At pressures of 100 mm. or more, to ensure that the measured mobility of the positive ion is the true mobility of an ion in its own gas, the residual impurity should be reduced to the order of a few parts in a million. In previous work on this subject nothing approaching this degree of purity has been obtained, and we are led to the conclusion that no significance can be attached to the values recorded in the literature of the mobility of the positive ion in any of the ordinary gases.

6. The highest value that we have so far obtained in helium for the mobility of the positive ion greatly exceeds those obtained by previous investigators;



it is of the same order as the value deduced from classical kinetic theory for the mobility of the positive monatomic helium ion moving through helium.

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*The Absolute Intensities and Internal Conversion Coefficients of the  $\gamma$ -Rays of Radium B and Radium C.*

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§ 1. *Introduction.*

It is well known that with many radioactive bodies the departure of the disintegration particle is followed by the emission of  $\gamma$ -rays. In addition to  $\gamma$ -rays of frequencies  $\nu_1, \nu_2, \dots$ , it is observed that there is an electronic emission consisting of several homogeneous groups whose energies can be written

$$\begin{array}{lll}
 h\nu_1 - K & h\nu_2 - K & \dots\dots\dots \\
 h\nu_1 - L & h\nu_2 - L & \dots\dots\dots \\
 h\nu_1 - M & h\nu_2 - M & \dots\dots\dots \\
 \dots\dots\dots & \dots\dots\dots & \dots\dots\dots
 \end{array}$$

The energies of these groups are identical with those that would be produced by photoelectric absorption in the parent atom of the  $\gamma$ -rays emitted from the nucleus, and this phenomenon is frequently described as the internal conversion of  $\gamma$ -rays. By this is meant that in every case when the nucleus emits energy  $E$  this occurs in the form of radiation of frequency  $E/h$ , but that this does not always escape as such from the atom. In a fraction  $\alpha$  of the cases the radiation is absorbed in the electronic structure and gives rise to a photoelectron, in the remaining fraction  $(1 - \alpha)$  the  $\gamma$ -ray is emitted clear of the atom. The quantity  $\alpha$  is termed the coefficient of internal conversion. Smekal\* and

\* 'Smekal, 'Z. Physik,' vol. 10, p. 275 (1922); Rosseland, *ibid.*, vol. 14, p. 173 (1923).