THE APPLICATION OF POSITIVE RAY ANALYSIS TO IONIZATION PROBLEMS.*

BY

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INTRODUCTION.

ALMOST simultaneously with the appearance of Bohr's first paper on atomic structure, Franck and Hertz, developing an idea of Lenard's, inaugurated a series of experiments which were to prove of great importance to theories of atomic constitution. They undertook to study the effect of collisions between slow electrons and gaseous molecules as a function of the speed of the electrons and the nature of the gas. Other investigators, notably Horton and Davies in England, McLennan in Canada, and Compton, Foote and Mohler in this country, took up the work and soon its direct relation to Bohr's ideas became apparent. It would be an interesting study to trace the mutual reactions of the two lines of investigation through the past decade, the experimental and the theoretical, each helping to solve the other's problems, yet at the same time propounding new ones. Such a discussion, however, is beyond the scope of this paper, which is less concerned with the triumphs of these experimental methods than with their limitations. These can be made evident by a brief presentation of the principles involved and the results obtained up to 1921.

All these experiments on " ionization potentials " are done in gases at low pressures in tubes in which are sources of low speed electrons, usually filaments, and various grids and plates insulated from each other. The general idea is to increase the speeds of the electrons (whose initial speed is small) by applying a known electric field and to study the variation in the currents between electrodes as a function of the applied field. The methods are discussed and references to original papers given in Foote and

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* Communicated by Dr. K. T. Compton, Professor of Physics, Princeton University.

Mohler's recent book.[1] Here, too, the results are given in detail, but for our purpose they may be adequately presented in a few sentences. In monatomic gases and metallic vapors it was found that there were critical speeds which the electron had to attain before it could transfer energy to the atom; that the lowest critical energy corresponded to changing of the outer electron of the atom from its normal orbit to the next possible stationary state and that successive critical energies corresponded to raising the electron to stationary states of higher potential energy until finally it was removed entirely, ionization taking place. These conclusions resulted from the comparison of the experimental observations with spectroscopic data as interpreted by Bohr's theory. Unfortunately, lack of spectroscopic evidence makes this procedure difficult for most substances, and even for the higher degrees of ionization of the metallic vapors. Thus, in the case of polyatomic molecules the complicating factor of dissociation and the meagreness of spectroscopic evidence makes the interpretation of experimental results very uncertain.

The difficulty lies in the limitation of the experimental methods. They detect the occurrence of ionization without giving any evidence as to the nature of the ion produced. Sometimes it is possible by indirect means to distinguish between single and double ionization or between molecular and atomic effects, but clearly it is desirable to get a direct method of analyzing the products of an ionization tube.

The mere word "analyze" at once suggests another type of experimental work, positive ray analysis, originated by J. J. Thomson and so brilliantly developed by Aston and Dempster. Here is a method for determining the ratio of the mass to the charge of an ion, and if it could be combined with the ionizing potential experiments discussed above, it should give the direct evidence desired as to the products of ionization. The difficulties of effecting such a combination are serious, but they have not proved insuperable. Their nature and how they have been overcome will be discussed in the following paragraphs, together with the results obtained by the methods developed and their bearings on ionization problems.

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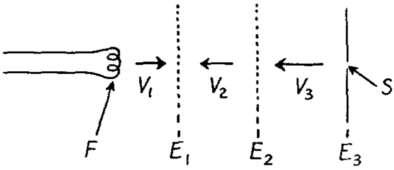
[1] "The Origin of Spectra," 1922, Chap. III.

EXPERIMENTAL METHODS.

The chief difficulty to be overcome becomes apparent when the schematic diagram in Fig. 1 is considered.[2]

This represents an arrangement of a filament and three electrodes such as was used in all the writer's experiments. Electrons are accelerated by the field V_1 toward E_1. In the neighborhood of E_1 they produce ions and are prevented from reaching E_2 by V_2.

FIG. 1.



It is the nature of these ions which is to be investigated. They are accelerated by the fields V_2 and V_3, and some pass through the slit S. After passing S and a second similar slit, the beam of ions so defined is bent by a magnetic field on to a third slit behind which is an insulated plate connected to an electrometer. The magnetic field necessary to bend the ions to the third slit depends on V_2 and V_3 and on the m/e of the ion. However, unless the pressure is so small that the mean free path of the ions is comparable with the distance from E_1 to the third slit, they will either never get through at all or they may lose or gain electrons by collision on the way and so make it impossible to decide what are the primary products of the impact between electrons of speed V_1 and the gas molecules.

On the other hand, there must be enough collisions of electrons and gas molecules between E_1 and E_2 to produce a measurable number of ions. Even with fairly low pressures this may be attained by having the electron density very high. Still it is clearly desirable to have a fair density of gas molecules between E_1 and E_2 and yet practically zero density everywhere else.

When first considering the problem, the writer saw no way of achieving these density variations with substances gaseous at ordinary temperatures, but in the case of the metallic vapors a possibility suggested itself. If a unidirectional stream of vapor

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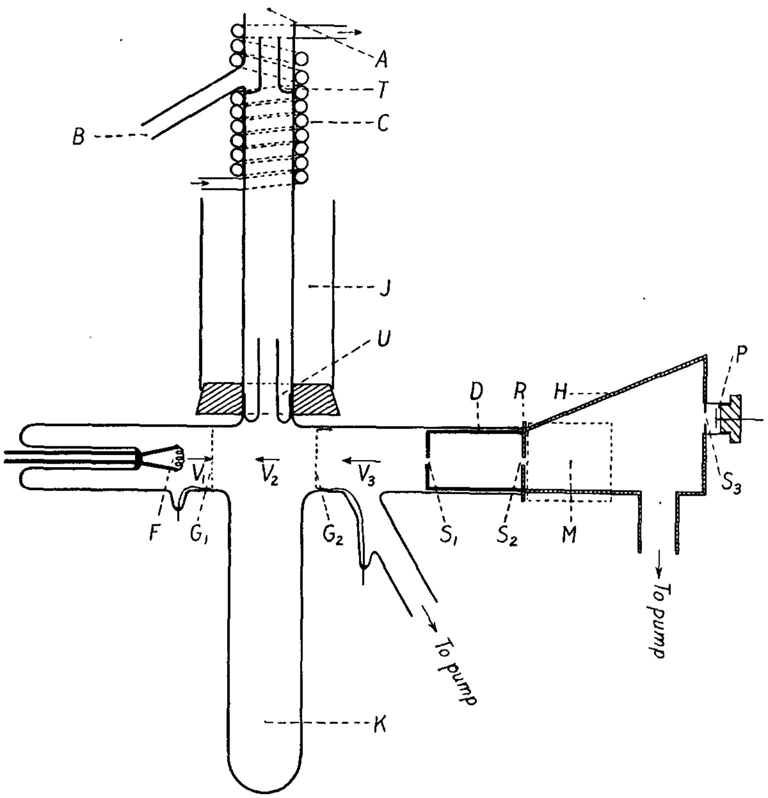
[2] The writer is indebted to the Council of the Royal Society for permission to reproduce the diagrams in this paper.

such as is used in a diffusion pump could be driven across the tube between E_1 and E_2, and then condensed by liquid air, there would be a much larger concentration between E_1 and E_2 than elsewhere in the ionization tube or positive ray box. The successful embodiment of this idea in an apparatus used for mercury vapor will now be described.

EXPERIMENTS ON MERCURY VAPOR.

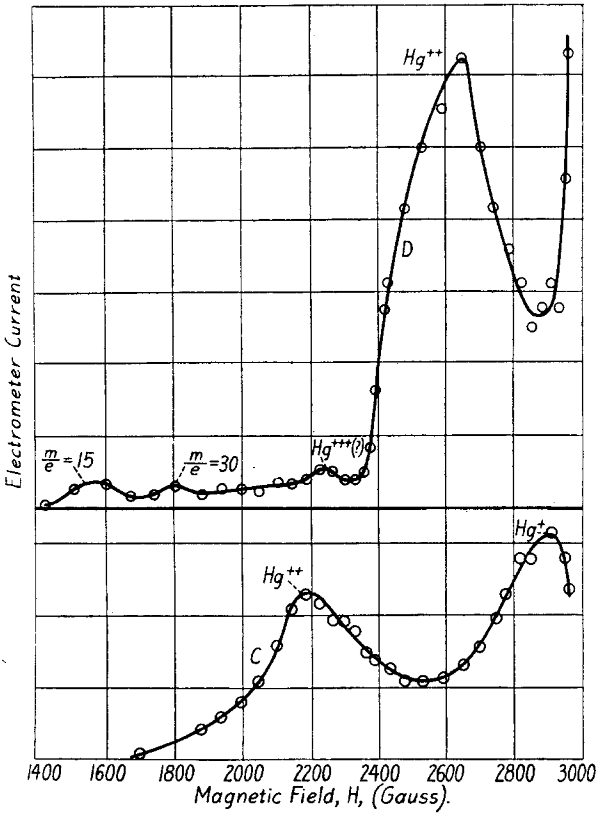
Mercury was chosen as the most favorable substance to study first, chiefly because it lent itself so well to the production of a unidirectional stream and also because its first ionizing potential was so well known that it would serve as a check on the method and a reference point. It was hoped that it would be possible to determine its second ionizing potential and perhaps even higher ones.

FIG. 2.



The apparatus used is shown in Fig. 2. It has been described in detail elsewhere[3] and only a few points will be recalled here. The arrangement of grids and slits corresponds exactly with that already described in the discussion of Fig. 1. Mercury vapor from a hot reservoir is made into a unidirectional stream by the cooling jackets C and J, passes across between the grids G_1 and G_2 and is condensed in K by liquid air.

FIG. 3.



Curve C. $V_1 = -V_2 = 300$ volts. $V_3 = 300$ volts.
Curve D. $V_1 = -V_2 = 175$ volts. $V_3 = 610$ volts.

If this arrangement achieves the varying density conditions required and if V_1 is set at well above the ionizing potential, the current to P observed as a function of V_3 or of the magnetic field between the pole pieces M should show a strong maximum

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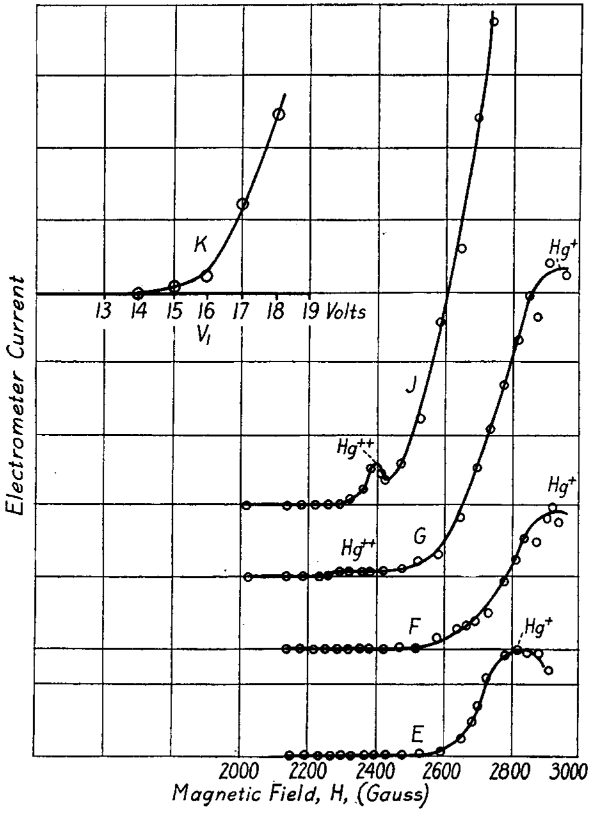
[3] *Proc. Roy. Soc.*, **102**, 283–293, 1922.

corresponding to the value of m/e for Hg^+ and perhaps other maxima assignable to Hg^{++}, etc.

The procedure throughout the work on mercury was to keep all the electrical fields constant and observe the rate of charging of a Compton electrometer connected to P as the current through the magnet was varied. The magnetic field was read from a calibration curve previously obtained with a fluxmeter and coil. Two curves obtained by this procedure are shown in Fig. 3. On account of the different values of $V_2 + V_3$ used, the peaks do not occur at the same values of the magnetic field, H. In both cases

FIG. 4.



Curve E. $V_1 = -V_2 = 13$ (17) volts. $V_3 = 450$ volts.
Curve F. $V_1 = -V_2 = 16$ (20) volts. $V_3 = 490$ volts.
Curve G. $V_1 = -V_2 = 20$ (25) volts. $V_3 = 490$ volts.
Curve J. $V_1 = -V_2 = 25$ (30) volts. $V_3 = 480$ volts.
Curve K. $H = 2820$. $V_3 = 460$. Correction curve for E.
Values of V_1 given are corrected. Uncorrected values in parentheses.

V_1 is so far above the ionizing potential that the Hg^{++} maximum is quite strong. The Hg^{+++} in curve D is doubtful as it was not reproducible. The small maxima at $m/e = 15$ and $m/e = 30$ are attributed to a trace of air. They will be mentioned again in connection with later experiments.

But such curves as these are only the first step towards our goal. The object of the experiment is to determine the critical energies for the formation of the multiply charged ions. At what value of V_1 does the Hg^{++} peak first appear? To determine this, series of runs must be taken at different values of V_1. Such a series is shown in Fig. 4. In order to obtain the effective voltage from the observed, the difference between the observed disappearance voltage for Hg^+ and 10.4 volts, the known ionizing potential, is used as a correction. In the caption of Fig. 4 both corrected and uncorrected values are given and the curve K illustrates the method at arriving at the correction. For further discussion of this point and a detailed consideration of results, reference must again be made to the original paper.

Here it must suffice to state that the critical potential for double ionization of mercury was found to be 19 ± 2 volts. This value agrees with what evidence there is on the enhanced spectrum if it be supposed that the doubly charged ions result from impacts of electrons with atoms which are already singly ionized.

Before going on to the development of the method for gases, it should be mentioned that Kondratjeff and Semenoff[4] have recently used exactly the method described above for studying the ionization of the vapor of $HgCl_2$ and HgI_2. Their paper is a "preliminary communication" but their results show Cl^- and I^- present as products of ionization. Their data, however, are insufficient to throw light on the question of whether or not the critical energies correspond to those calculated by thermochemical equations. Certain aspects of this important question will be discussed in connection with the results of the experiments on gases which will now be presented.

METHOD FOR GASES.

The small maxima in curve D (Fig. 3), apparently due to air, suggested that the application of this mode of attack to gases might not be so difficult as was at first anticipated. By a small

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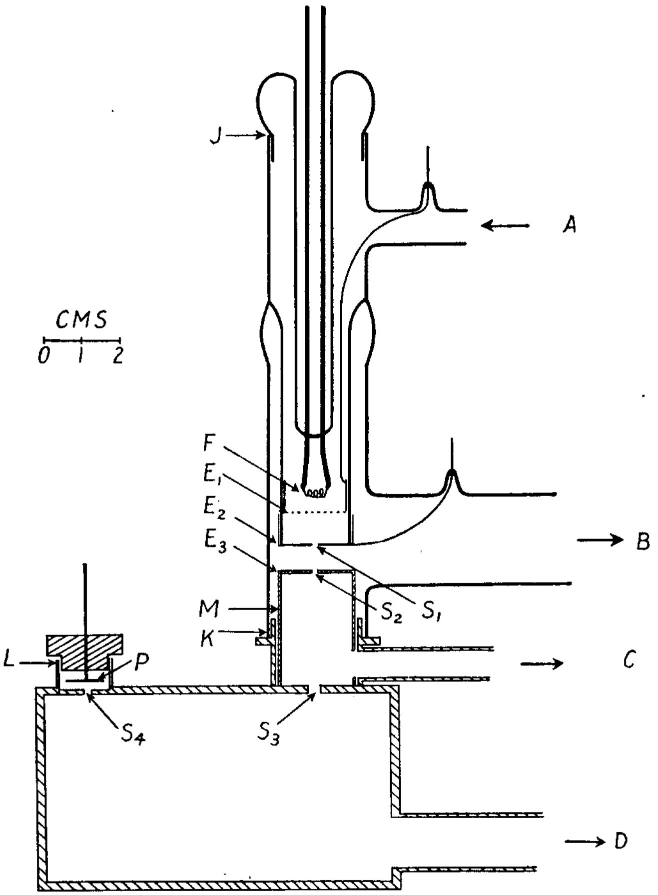
[4] *Zs. f. Physik,* **22,** 1–8, 1924.

modification of the apparatus used for mercury, it was found possible to get fairly sharp maxima for nitrogen, but the results of several months' work were inconclusive though suggestive. An entirely new apparatus, therefore, was designed and set up. It is shown in Fig. 5 and described in detail in a previous paper.[5]

Fig. 5.



It will be seen that the arrangement of electrodes is still the same as in Fig. 1, except that E_2 is now a plate with a single slit instead of a gauze. This change, of course, had to do with the new method used to get varying gas density. The gas to be

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[5] *Proc. Roy. Soc.*, **104**, 121–134, 1923.

studied leaks in slowly at A and is pumped out by one Langmuir pump operating through B and a second through C and D. In this way it is possible to have a fairly high density of gas in the neighborhood of E_1, where the ions are formed, a lower density between E_2 and E_3 and still lower beyond E_3 in the positive ray box.

The positive ray analysis was very much improved by using a larger magnet and bending the rays in a semi-circle to get a focussing effect. The stray field from this powerful magnet caused much trouble and led to an important change in procedure. Whereas previously in a run all the electric fields had been held constant and the electrometer current observed as a function of the magnetic field, from this time on the latter was kept constant and V_3 varied.

We will now consider in some detail what type of curve might be expected. If it be assumed that the ions are formed at E_1 and suffer no collisions between formation and detection at P, then the electrometer currents plotted as ordinates against $\frac{1}{V_2 + V_3}$ as abscissas should give maxima corresponding to the m/e's of the ions produced at E_1. This is obvious from the equations for the effects of electric and magnetic fields on an ion

$$H\rho = m/e \times v \quad \text{and} \quad eV = 1/2\, mv^2$$

which combine to give $m/e = \frac{H^2\rho^2}{2V}$ where ρ is the radius of curvature; v, the velocity; H, the magnetic field, assumed uniform, and V, the potential drop through which the ion has fallen before entering the magnetic field. But in the light of some recent experiments at comparatively high pressures, it is important to consider the situation when the assumption made above is not strictly true; that is, when the ion is not formed exactly at E_1 or else collides somewhere along its path.

First, as to the place of formation, any ions formed on the filament side of E_1 are drawn back toward the filament and need not be considered. Also the electrons will lose their ability to ionize as soon as they have been retarded by such a fraction x of V_2 as is given by

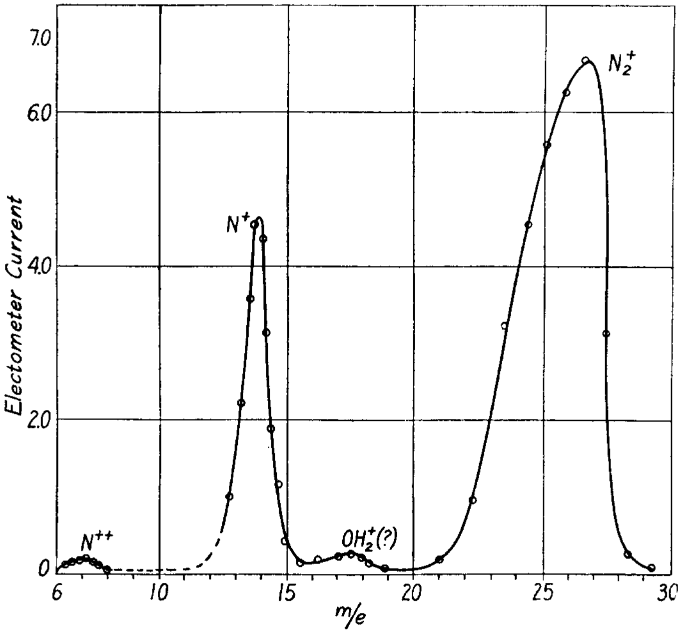
$$xV_2 = V_1 - W$$

where W is the ionizing potential. Clearly the width of the peak is proportional to $\frac{xV_2}{V_2 + V_3}$. Also, since the greatest probability of collision will be near E_1 and taking probability of ionization proportional to $\frac{V - W}{V}$, the greatest number of ions will be produced near E_1 so that the peak will not be symmetrical but will fall off more gradually for higher V_3. This consideration may be modified somewhat by the greater chance of ions produced near E_2 getting through the slit. If the greatest number of ions come from some point between E_1 and E_2, the $\frac{1}{V_2 + V_3}$ scale will give too small a value of m/e and the error will be much greater for peaks where V_3 is of the same order of magnitude as V_2.

Now let us consider secondary effects such as might be caused by production or modification of ions by collision with other ions or molecules. Suppose that the ions formed by the primary electrons are X^+_2 but that they may be converted at any point along their path into $X^+ + X$ by collision with another molecule. If this occurs anywhere between E_1 and E_2, a peak will result at a value of $\frac{1}{V_2 + V_3}$ appropriate to ions of $m/e = X^+_2/2$ and this peak will be nearly as sharp as if the X^+ ions were a primary product, but should be slightly shifted toward larger values of V_3. The same remarks apply to any new ions produced by these secondary collisions. For conversions of X^+_2 to $X^+ + X$ occurring between E_2 and E_3 or for new ions produced there, the V_3 required to give the new ions the necessary radius of curvature in the magnetic field will vary rapidly and continuously so their effect will merely be to increase stray current between peaks. For collisions between S_2 and S_3, on the other hand, the case is different; the X^+_2 ions have now fallen through the entire electric field but do not enter the magnetic field until they pass S_3. If they are to enter at S_2 as X^+_2 and emerge at S_3 as X^+ and yet be bent around to P, they must have fallen through a potential drop $V_2 + V_3$ four times as great as would be necessary for ions which remained X^+_2 throughout, since for the same radius of curvature their velocity must be twice as great. Moreover, since a conversion anywhere between S_2 and S_3 would have the same effect, a peak might be expected at an m/e value 1/4 that for X^+_2. In the above argument the assumption that the velocity is unchanged by the disruption may satisfy both the conditions of conservation of energy and of momentum. Similar reasoning may be applied to conversions of different primary ions and may include secondary associations as well as dissociations if it be remembered that the energy and momentum conditions are more complicated in the case of association.

It may seem absurd to suppose that ions can be disrupted by collision between S_2 and S_3 and yet retain their speed and direction sufficiently to get through S_3 and around to P. A much more natural supposition is that any collision in this region merely scatters the ion out of the beam so that it never gets to P at all, no matter what its velocity on passing S_2. This was the position taken by the writer up to very recently, but in the light of the latest results on hydrogen it seems untenable. It is hoped that the completion of the experiments now under way will clear the matter up. The reason for discussing the point at such length here will become apparent when we come to consider some peculiarities in the results on nitrogen, oxygen and hydrogen which will now be presented.

FIG. 6.

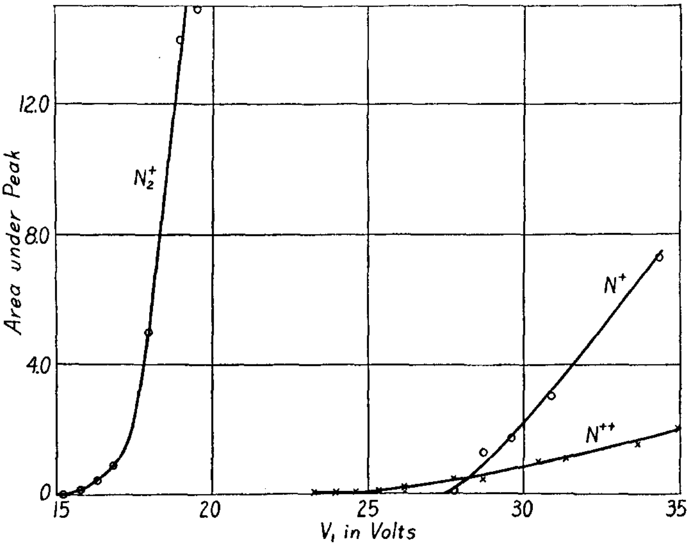


V_1 = 100 volts; V_2 = 40 volts.

RESULTS ON GASES.

Nitrogen and Oxygen.—In Fig. 6 is given a curve which is typical of the results obtained in nitrogen. The *m/e* scale was obtained by assuming the value 14 for the peak marked N^+. It is seen that there are four maxima at *m/e*, 7, 14, 18 and 27. That at eighteen was found due to the presence of water vapor while the other three were due to nitrogen and were attributed to primary ions of the forms N^+_2, N^+ and N^{++} as indicated in the figure. The variation of the intensity of these peaks with V_1, the speed of the impacting electrons, gives curves of the type shown in Fig. 7. Obviously, the dominant product of ionization is the molecular ion, and it is the only product for several volts above the first ionizing potential. This is not altogether unexpected, but the surprising result is that the doubly charged atoms are apparently formed at lower voltages than the singly charged atoms.

FIG. 7.



In oxygen the results were very similar to those in nitrogen, though the peak due to O^{++} was less reproducible and appeared at only slightly lower voltage than the O^+ peak. In both nitrogen and oxygen the critical potential for the molecular ion was identified with that recorded by other observers and values were assumed which were compared with the experimental values to get voltage corrections for the higher critical potentials. These results have been presented and discussed in detail elsewhere.[6] The final values with estimated probable errors are given in Table I.

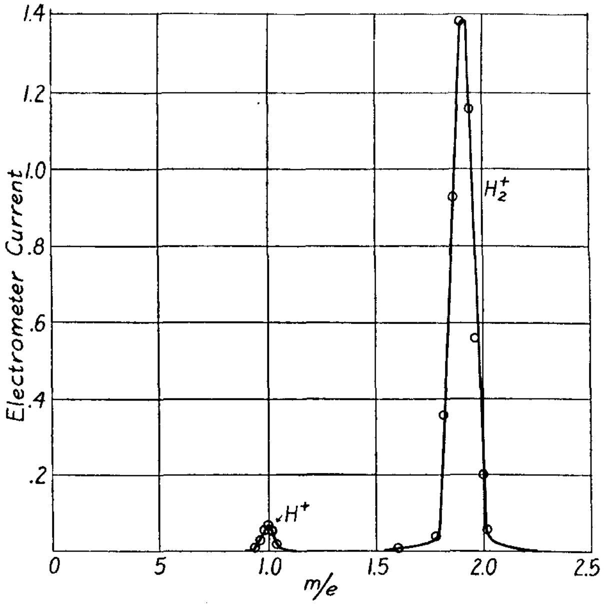
TABLE I.

Type of Ion.	Critical Potential. Nitrogen.	Oxygen.
Singly charged molecule	16.9	15.5
Doubly charged atom	24.1 ± 1.0	22.5 ± 0.6
Singly charged atom	27.7 ± 0.8	23.0 ± 0.3

The possibility that these effects are not all due to primary ionization will become evident when the results on hydrogen are presented.

Before turning to hydrogen, however, it should be mentioned that experiments in nitrogen and oxygen were also done in which values of V_1 as high as 700 volts were used. These indicated a sharp change in the relative intensities of the different ions at

FIG. 8.



$V_1 = 40$; $V_2 = 40$ volts; $H = 1075$ gauss; $i = 655$ microamps; $p = 0.0000 \rightarrow 0.0002$ mm.

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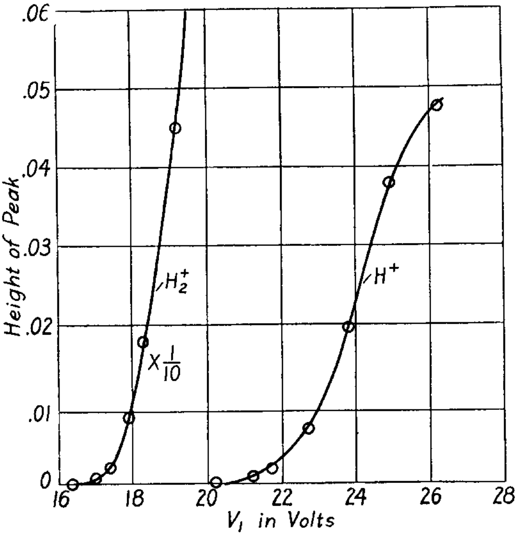
[6] *Proc. Roy. Soc.*, **104**, 121–134, 1923, and **105**, 116–128, 1924.

about 400 volts for nitrogen and somewhat higher for oxygen, though it was impossible to reproduce observations satisfactorily in this region. The number of molecular ions fell off sharply, while at the same time the atomic, particularly the doubly charged atomic, ions increased.

Hydrogen.—As is clear from the typical curve shown in Fig. 8, the molecular ion is even more dominant in hydrogen than in oxygen and nitrogen. Moreover, it was found from curves like that in Fig. 9 that the minimum potential for the detection of atomic ions was about 4.2 volts higher than that for molecular ions, and that the latter point corresponded to the generally observed ionization potential of about 16.5 volts. This is very surprising as the idea has been prevalent that ionization at this potential was accompanied by dissociation. Apparently such a dissociation is a secondary effect, as is shown by the curve in Fig. 10, which was taken at such high pressures that secondary collisions between E_1 and E_2 were probable.[7] Further, at this pressure, the maxima due to H^+ persisted down to the same volt-

FIG. 9.



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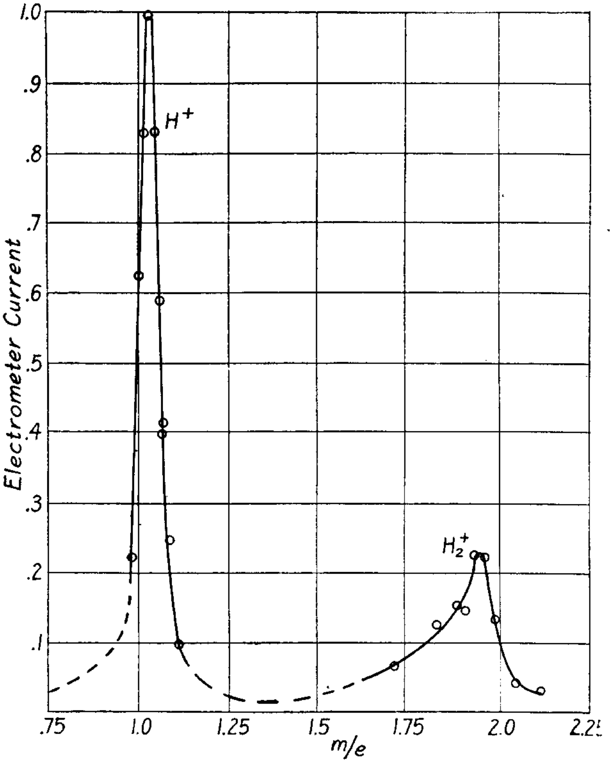
[7] It should have been mentioned in the original report of this work that Dempster observed a similar variation of relative intensity with pressure but was working at eight hundred volts, so that conditions were hardly comparable. (*Phil. Mag.*, **31**, 438–443, 1916.)

age at which the H^+_2 disappeared. This suggested the possibility that the observed disappearance potential for H^+ might not really represent a critical potential but might be due to secondary atomic ions whose numbers first became detectable at this point. The detailed bearing of the results on this question has been considered elsewhere[8] and the point is under investigation once more at the present time. Preliminary results of this new investigation confirm the occurrence of secondary effects at high pressures but indicate that they are more complicated than was supposed. Both atomic ions and triatomic ions occur and increase relative to the H^+_2 with pressure, but in some cases one is much stronger and in some cases the other. The conditions determining which shall predominate are still a mystery at present writing.

FIG. 10.



$V_1 = 20.7$; $V_2 = 20.7$ volts; $H = 800$ gauss; $i = 480$ microamps; $p = 0.0042$ → 0.075 mm.

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[8] *Proc. Roy. Soc.*, **105**, 116–128, 1924.

Another very important new result is the observation of secondary effects due to collisions in the region between S_2 and S_3 such as were discussed in an earlier part of this paper. Small peaks are observed at $m/e = 1/2$ and $m/e = 1/3$ apparently due to the conversion of H^+_2 and H^+_3 to H^+ between S_2 and S_3. So far these secondary effects have been studied only at considerably higher pressures than those used in oxygen and nitrogen. Nevertheless they introduce some element of doubt as to the previous interpretation of the "doubly charged atomic" peaks. It is hoped that further experiment will clear this away.

GENERAL DISCUSSION OF RESULTS.

When the results presented are considered, one important principle emerges. In all three diatomic gases studied, the first ionization potential corresponds to ionization without dissociation. Moreover, if an impacting electron ever causes dissociation simultaneously with ionization, it is first able to do so at such a high voltage that the transition cannot be represented by such a thermochemical equation as

$$X_2 + D + J_{X^+} \longrightarrow X^+ + X$$

where D is the heat of dissociation and J_X the ionizing potential of the atom. It would be possible to explain the critical potential for N^+ by an equation of the form

$$N_2 + D + 2\,J_{N^+} \longrightarrow N^+ + N^+$$

which would be satisfied for $D = 6$ volts and $J = 11$ volts, reasonable values. But in oxygen and hydrogen where we know the values of J and D approximately, there is no agreement whatever. We are forced to the conclusion, therefore, that at least for homopolar compounds it is not possible to apply thermochemical equations to these transitions caused by electron impact. Needless to say, this invalidates any deduction of heats of dissociation from ionization potential experiments.

The evidence on the applicability of thermochemical equations to similar phenomena in heteropolar compounds is conflicting. It is hoped that this problem can be settled by studying such substances with the method described above. Indeed, it is felt that there are many problems to which this method can be applied. For example, the secondary effects just obtained in hydrogen suggest a whole series of experiments on the dissociation and association of ions by molecular impact. Such studies may perhaps throw light on the questions of the mechanism of ionization and of molecular structure which are beginning to have so much fascination and importance at the present time.

Surface Tension of Colloidal Solutions and Dimensions of Certain Organic Molecules. P. LECOMPTE DU NOUY. (*Phil. Mag.*, Aug., 1924.)—He uses an instrument, based on Weinberg's work, that measures the surface tension at short intervals of the same solution and not the property of a layer continuously renewed. "The torsion of a wire controlled by a worm gear is used to counteract the stress of a liquid film adhering to a platinum ring, and as the amount of torsion can be measured by a simple reading on a dial, the surface tension is measured directly. The measurements require only 20 seconds." Thirty-eight thousand measurements were made. Such colloids as blood serum, pure albumin and gold, silver, copper and iron sols show a decrease in surface tension with the passage of time. For example, pure rabbit blood serum drops from 59.5 to 56.0 in seven minutes. The change follows an exponential law and "is due to the adsorption in the surface layer, in function of time, of the molecules in suspension." The decrease amounts to about one dyne during the first minute. It grows larger with the dilution of the solution and reaches a maximum for concentrations between 10^{-4} and 10^{-5}. "Certain colloids, saponin, for instance, do not show any drop at high concentrations, but even a slight increase (10^{-1} to 10^{-3})." Even slight stirring causes the surface tension of the solution to rise though not to its initial value. This result may be obtained several times.

In the case of some organic colloids a study was made of the initial surface tension and of its value two hours later. In every instance there was for some concentration a clearly marked maximum in the decrease observed. For sodium oleate this concentration for maximum change was 1/750,000; for serum 1/10,500. The author gives an explanation of this based on the formation of a monomolecular and oriented layer at the particular concentration corresponding to maximum change. "Should the above assumption of the existence of a homogeneous oriented monolayer at a given concentration be well founded, the rate of evaporation of such a solution should be slower than that of any other concentration. Water molecules would not escape so freely from a solution covered with such a film. At a higher concentration, we have assumed that there is a piling up, and no organization of the molecules. Therefore, the water molecules