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REVIEWS

OF

MODERN PHYSICS

PRODUCTS AND PROCESSES OF IONIZATION BY LOW SPEED ELECTRONS

By H. D. Smyth

Palmer Physical Laboratory, Princeton University

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I. INTRODUCTION

THE progress of an advancing science is a halting irregular affair. Only rarely do theory and experiment move along steadily side by side helping each other in every hazard of the road. The greater the pleasure then in cases where such an ideal is approached, in a case such as is surely found in the early work on stationary states where Bohr's theory was so quickly supported by the experiments on critical potentials. To review this phase in the development of modern physics is always cheering and encouraging. But it is a familiar tale and must not be repeated here. It is mentioned only because our present story starts in one of its few obscure chapters.

The main part of the older tale deals with collisions between low speed electrons and monatomic molecules of gases and vapors. Here theory and experiment ran smoothly along together. But when even the simplest of diatomic molecules was studied both theory and experiment became of dubious reliability. It is only now, at long last, that it is possible to write a fairly thorough and satisfactory account of the collisions between electrons and various polyatomic molecules.* That is the central theme of the present paper though there are some related problems which will also be discussed.

The problem of collisions between electrons and polyatomic molecules simply required for its solution more information than either theory or experiment had to offer ten years ago. It was on the experimental side that progress was first made and it is the development of experimental methods that will be treated first. However, in order to maintain the thread of the narrative, the problem of the ionization of molecular hydrogen will be developed at the same time, since it has been studied by nearly every worker in this field.

Franck and Hertz showed that electrons have to attain a certain minimum speed before they can produce ionization in a gas and that the value of this minimum speed depends on the nature of the gas. The potential difference through which electrons must fall in order to attain this minimum speed is called the ionization potential of the gas. To determine this potential electrons from any source, usually a hot filament, are accelerated by a known variable field between the source and a neighboring grid, pass through the grid and ionize the gas molecules between the grid and a plate electrode. A schematic diagram is given in Fig. 1. The ionization potential is then de-

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* Throughout this paper the term "polyatomic molecule" means a molecule having more than one atom in it, i.e. it includes diatomic molecules. This is contrary to Dennison's recent usage.

tected by a sudden change in the current to the plate *P* as the accelerating field between *F* and *G* is changed. The details of the many modifications of this method may be found described by Franck and Jordan,[1] Compton and Mohler[2] and elsewhere. There is one limitation common to all of them. They measure the energy needed to produce ions but give no indication of the nature of the ions.

But the nature of gaseous ions has been studied extensively by the methods of positive-ray analysis as developed by J. J. Thomson, Wien, Dempster and others.[3,4,5] A combination of the two types of experiment might, therefore, be able to determine the energies required for the production of different types of ion. By such a combination of methods, we might, for instance, be able to find whether the ordinary ionization of hydrogen produces monatomic or diatomic ions.

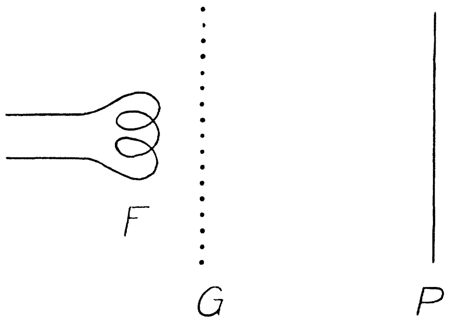

Fig. 1.

We first approached our problem from the point of view of ionization potentials and have given a brief account of the experimental procedure and results in this field. Turning to positive ray analysis which we have now called to our aid, we find a much more highly developed and difficult technique. The principles involved are simple and well-known, merely the deflection of moving charges by electric and magnetic fields; the details of experimental procedure and results have been reviewed in a number of books.[3,4,5] An examination of this older work sheds little light on our particular problem since in nearly every case the conditions of ionization were too complicated to interpret in terms of molecular processes. One exception to this is the work of Dempster on hydrogen published in 1916.

J. J. Thomson had already shown that three types of ion were produced in a hydrogen discharge, H_3^+, H_2^+ and H^+. Dempster[6] by using a Wehnelt cathode as an electron source was able to use much lower voltages than Thomson and to study the effect of varying the pressure while keeping the voltage

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[1] Franck and Jordan, Anregung von Quantensprüngen durch Stösse, 1926.

[2] Compton and Mohler, Critical Potentials, N.R.C. Bulletin, 1924.

[3] J. J. Thomson, Rays of Positive Electricity, 1921.

[4] W. Wien, Kanalstrahlen (Handbuch der Radiologie).

[5] F. W. Aston, Isotopes, 1924.

[6] Dempster, Phil. Mag. **31,** 438–443 (1916).

constant. He discovered that the relative proportions of H_3^+, H_2^+ and H^+ varied greatly with pressure. At high pressures they were all of the same order of magnitude while at low pressures the H_3^+ and H^+ were weak compared to the H_2^+. Perhaps it would be well to quote his summary.

"Electrons of 800 volts speed ionize hydrogen by detaching a single elementary charge from the molecule. They are not able to dissociate the gas.

The positive molecules so formed are able to dissociate the gas. When this occurs this complex H_3 is formed. H_3 cannot be regarded as a stable gas, since it is not present when there is no dissociation of the hydrogen molecule."

Considering that these conclusions stand almost unaltered today it seems strange that this paper should have had so little effect. Perhaps it was because of some inherent weaknesses which later work overcame. In the first place the voltage was too high. Even today the ionization effects of such high speed electrons are difficult of interpretation and results at a single high voltage have little significance; the most important ionization problems of 1916 were concerned with electron speeds of perhaps five to fifty volts. In the second place, in Dempster's apparatus, the positive ions were accelerated by an 800 volt field in the same part of the tube where they were formed, so that increased pressure affected both the formation of the ions and their passage toward the analyzer. Consequently, the interpretation of the observed pressure effects was difficult. This last difficulty persists more or less in the later work but in the experiments which form the principal subject of this report it has been minimized and the electron speed difficulty overcome entirely.

II. Experimental Methods

Objects and Difficulties

In the light of the above criticisms of Dempster's early work we can lay down some general principles which later work must follow. First, let us repeat the statement of the object before us. It is to study the effects of collisions of electrons with gas molecules as a function of the energy of the impacting electrons; more specifically, to find the energy required by an electron to produce single, double or multiple ionization or to cause ionization of varying degree to be accompanied by dissociation. Obviously, the energy of the impacting electrons must be controllable and measurable. Furthermore, the detecting apparatus must be sufficiently sensitive and the ionization sufficiently intense to show an effect as soon as the critical potential has been passed, or at least within a volt or two of such a place.

So much for the formation of the ions, now as to their analysis. The gas density should be such that there is little chance of the ion making a collision between the place where it is formed and the place where it is detected. Yet the gas density must be high for the sake of intensity. Next, the analyzing device must have sufficient resolution to separate all possible products of ionization. Thus, in the analysis of nitrogen for dissociation effects it is only necessary to distinguish between N_2^+ and N^+ whose m/e's differ by a factor of two but in ammonia the ionization products may include N^+, NH^+, NH_2^+ and NH_3^+ so that much higher resolution is necessary. Finally, if the gas studied is at all unstable, there may be spurious effects due to thermal dissociation by the hot filament electron source. Such effects must be reduced as much as possible.

Naturally any given apparatus represents a compromise between these different desiderata. For convenient reference we may list them as follows:

a. Controllable electron energy.
b. Great intensity or sensitivity.
c. No collisions in the analyzer.
d. High resolving power in the analyzer.
e. No thermal dissociation.

The difficulties involved in satisfying requirement (a) are the same that arise in ordinary ionization potential experiments. They are best met by calibrating the apparatus with a gas whose ionization potential is known. This is not particularly difficult though always subject to criticism. It is the last four requirements that are mutually conflicting. Thus, to get great intensity of ionization there must be many collisions, i.e. high gas density, in the ionization chamber, and large slits in the mass spectrograph. But these conditions endanger requirements (c) and (d). Or if we try to increase the number of collisions by using a powerful electron source we get a large hot filament endangering requirement (e).

The degree to which difficulties of this sort have been met can be understood by a detailed consideration of the experimental methods that have actually been used. These fall naturally into three classes, differing in the way in which they meet requirements (b) and (c). It will be convenient to designate them Methods I, II, and III on this basis. They will now be described.

METHOD I. UNIDIRECTIONAL VAPOR STREAM

One obvious way of meeting requirements (b) and (c) is to have a higher density of gas in the region of ionization then in the analyzer. This was done in the author's first experiments by using a unidirectional stream of vapor crossing the ionization tube in front of the filament, as shown in Fig. 2 below.

Mercury vapor from a heated reservoir enters the tube at A and is condensed by liquid air in the trap, K. Electrons from the filament F, are accelerated by the field, V_1, and make ionizing collisions in the space, J. A small reverse field, V_2, draws any ions formed toward G_2 and then a larger accelerating field, V_3, accelerates them to the plate, D. The slits, S_1 and S_2, determine a beam which passes into a transverse magnetic field in the space M. For certain values of e/m, V_3 and H, the ions will be deflected just sufficiently to enter the slit, S_3, and charge up the plate, P, connected to a highly sensitive quadrant electrometer. The current to the electrometer is studied as a function of either H or V_3 at various values of V_1. In this way the relative numbers of ions of different e/m's produced by electrons of different speeds are determined.

This method was developed by the author[7] for the study of mercury vapor

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[7] Smyth, Proc. Roy. Soc. 102A, 283 (1922).

and a little later by Kondratjeff and Semenoff[8] for the study of the vapors of a number of salts. For some years no further development of it was attempted though it is certainly the best for the study of vapors. Recently, Nielsen[9] has applied it to the study of negative ions in mercury vapor, and Ditchburn and Arnott[10] have used it in studying ionization in potassium vapor. The latter work has another feature of great interest. By studying photoionization and ionization by positive ions from a Kunsman source, Ditchburn and Arnott have taken the first step in the application of the general method of positive-ray analysis to processes of ionization other than by electron impact.

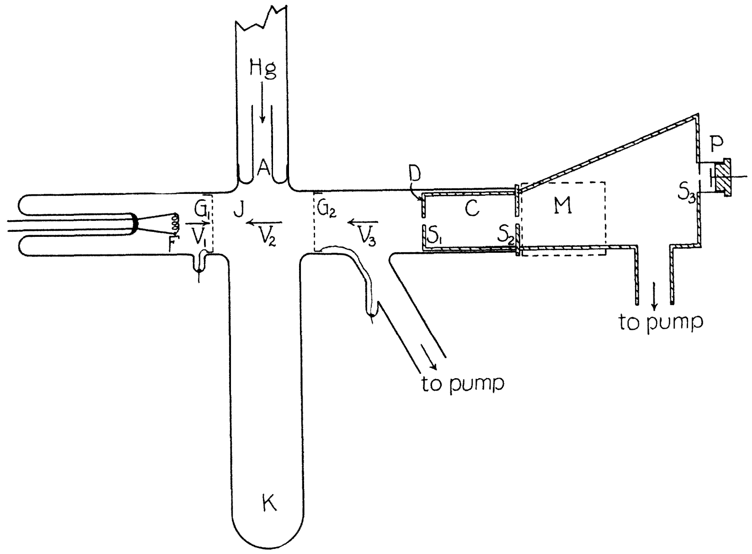

Fig. 2. Method I. Unidirectional vapor stream. (Smyth).

Method II. Differential Pumping

In much of the old work on positive rays it was customary to keep a higher pressure on the discharge side of the cathode than on the analyzing side, a procedure made possible by having the "canal" through the cathode very small indeed. This procedure is also desirable for our purposes to satisfy requirement (c); but requirements (a) and (b) make the problem difficult. Fortunately the initial attack on this problem came shortly after the general introduction of the diffusion pump and the greater control of pressure obtainable by such pumps allowed the construction of an apparatus of the type shown in Fig. 3 below.

In this apparatus, gas flows steadily into the ionization chamber, *J*, and is pumped out from the accelerating space, *A*, the collimating space, *C*, and the magnet space, *M*. In this way a pressure ratio between *J* and *M* is maintained

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[8] Kondratjeff and Semenoff, Zeits. f. Physik **22,** 1 (1924).

[9] Nielsen, Proc. Nat. Acad. **16,** 721 (1930).

[10] Ditchburn and Arnott, Proc. Roy. Soc. **123A,** 516 (1929).

that varies from 10/1 to 1000/1 depending on the particular apparatus and the pressure range.

The arrangement of electric and magnetic fields is practically identical with method I, i.e., V_1, a variable field accelerating electrons from F to E_1, V_2, a small reverse field drawing ions to E_2, V_3, a large variable field accelerating the ions between S_1 and E_2, and H, a transverse magnetic field deflecting the ions to S_3 and the Faraday collector. In the space C there is no electric field and it is shielded from the magnetic field. The magnetic deflection is now through 180° making the positive ray analysis device practically identical with that used by Dempster[11] in his study of isotopes.

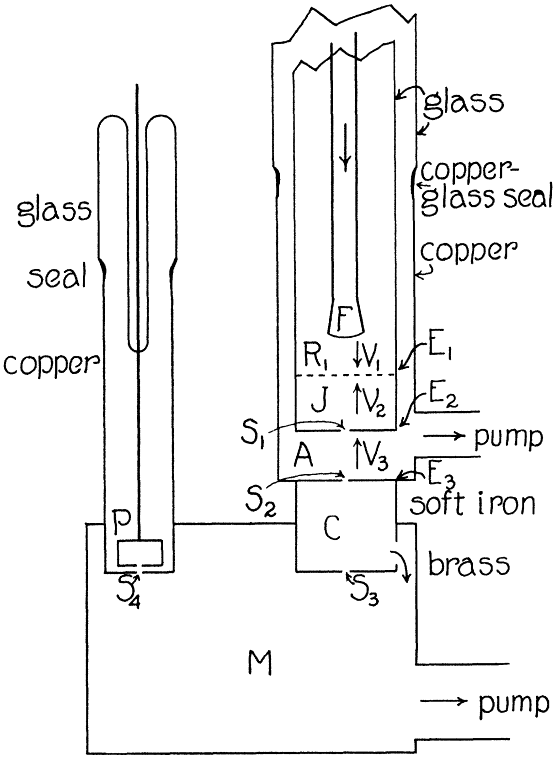

Fig. 3. Method II. Differential pumping. (Smyth).

This method with various minor modifications has been used by the author, Hogness, Kallmann and their coworkers and has given us most of the results obtained. The particular arrangements used need not be discussed in detail. That shown in Fig. 4 was used by Hogness and Lunn.[12] It differs from that of Fig. 3 in two important respects, the ionization chamber, J, is much longer and the collimating space, C, has almost vanished. For details reference may be made to the original paper.

One other particular apparatus may be mentioned since it was directed

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[11] Dempster, Phys. Rev. **11**, 316 (1918).

[12] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

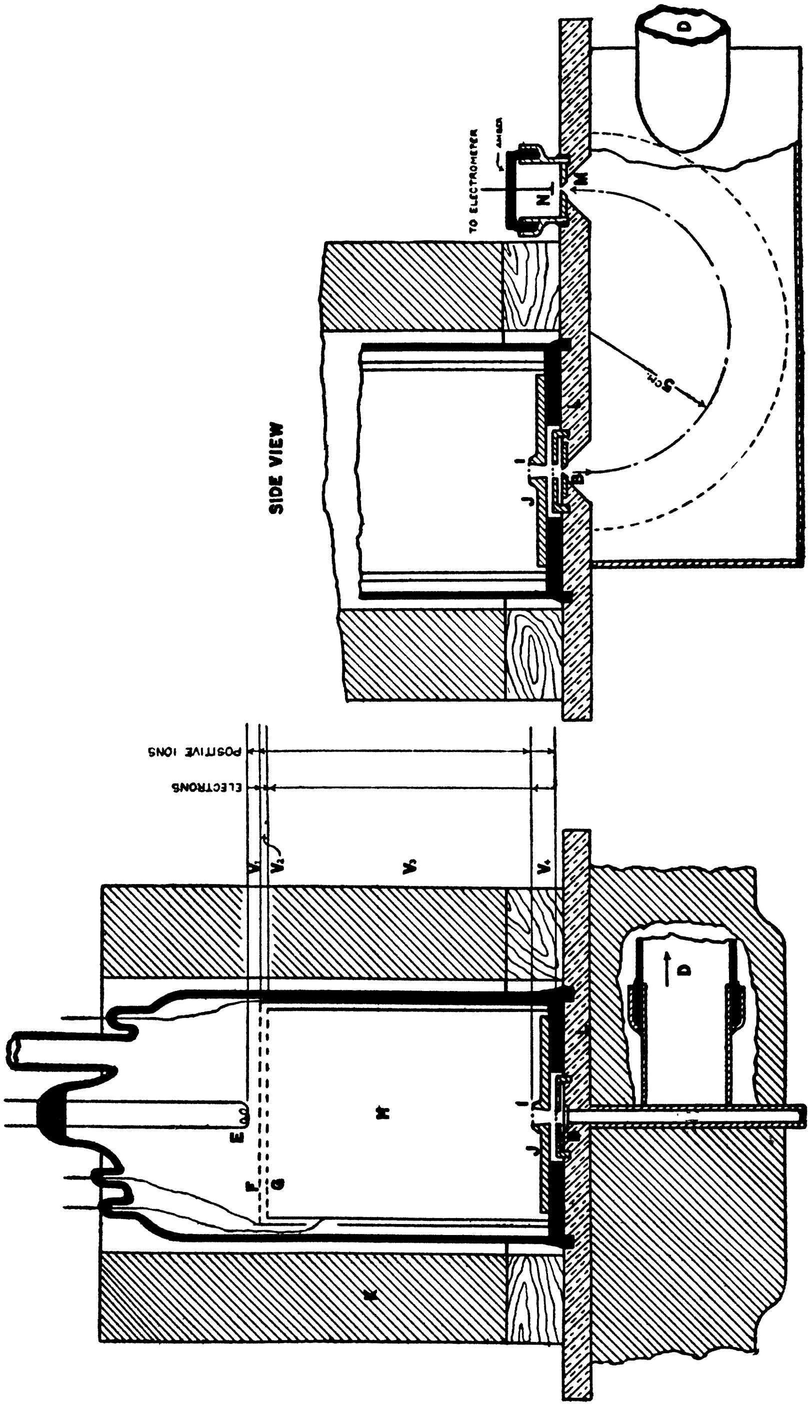

Fig. 4. Method II. Differential pumping. (Hogness and Lunn.)

specifically toward our fifth difficulty (e), thermal dissociation. Smyth and Stueckelberg,[13] working with N_2O and NO_2, were particularly anxious to reduce thermal dissociation. Therefore in addition to using oxide coated filaments that could be run at low temperatures they devised a scheme whereby there was a flow of gas from the ionization chamber J away past the filament as well as out through S_1. Fig. 5 shows their arrangement.

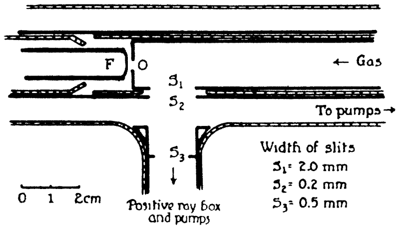

Fig. 5. Method II. Differential pumping.
Special precautions to avoid thermal dissociation. (Smyth and Stueckelberg.)

In a very recent paper Stewart and Olson,[14] working on propane and butane have done very much the same thing, using a narrow slit between their filament chamber and ionization chamber. They were able to maintain a pressure of 10^{-5} mm in the filament chamber when that in the ionization chamber was 10^{-2} mm. They give no ionization potential data, perhaps because their intensities were too small to determine critical potentials.

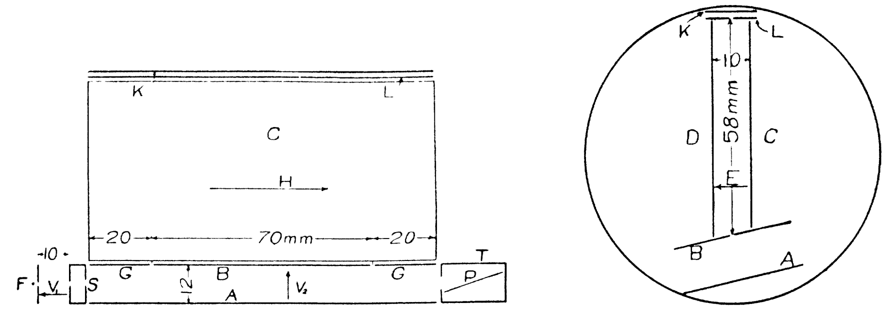

Fig. 6. Side view. Fig. 7. End view.
Method III. Low uniform pressure. (Bleakney.)

Method III. Low Uniform Pressure

In this method, used by Dempster in the work discussed earlier in this paper and recently to great advantage by Bleakney,[15] the pressure throughout the apparatus is kept so low that the mean free path of the ions is greater than their path in the analyzer. In Bleakney's apparatus requirement (b) is met by having a very long region of ionization parallel to the slits which are also long. His analyzer is also of a different type from those used in methods I and II. Diagrams of his apparatus are given in Figs. 6 and 7 below.

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[13] Smyth and Stueckelberg, Phys. Rev. **36**, 472 (1930).
[14] Stewart and Olson, J.A.C.S. **53**, 1236 (1931).
[15] Bleakney, Phys. Rev. **34**, 157 (1929).

The whole of the apparatus is inside a solenoid the field of which keeps the electrons from the electron gun *FS* confined to a narrow ribbon from *S* to *P*. Ions are drawn out by the field, V_2, toward the slit in *B*. In the space between the condenser plates *C* and *D*, they are acted on by the magnetic field, *H*, and the electric field, *E*, which will balance each other if

$$e/m = E^2c^2/VH^2$$

where V is the fraction of V_2 effective in accelerating the ions. Therefore ions of this particular value of e/m reach the collector *K* and the procedure is to study the current to *K* as a function of *E*.

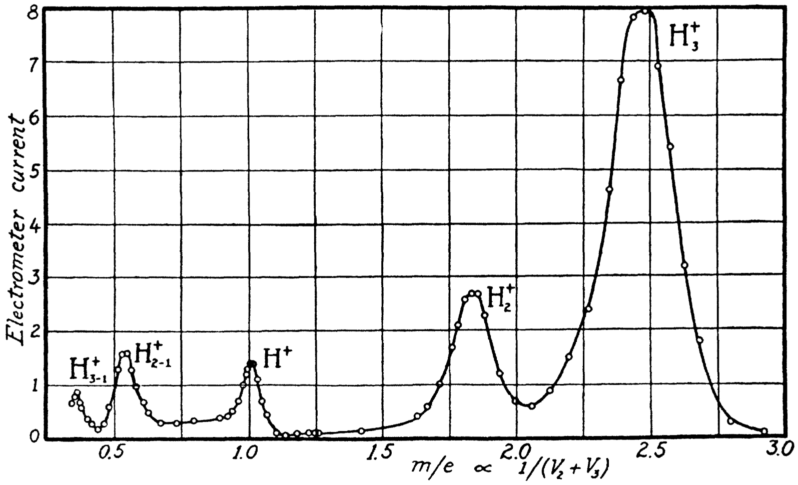

Fig. 8. Typical e/m curve for hydrogen. (Smyth).

Now it is obvious that this particular balancing force analysis arrangement is not necessary to the method but the use of the solenoid is necessary, since very long uniform magnetic fields are required. This imposes a limitation on the magnitude of the magnetic field usable. This fact and the fact that ionizing collisions are so few that even a great length of slit gives small intensities is responsible for the one serious weakness of this method, low resolving power. It seems to the author that no method where uniform pressure is used can escape this difficulty entirely. On the other hand, it should be pointed out that this solenoidal method with long slits might be coupled with differential pumping. It would still be limited however by the magnetic field and probably could not get high resolving power except for very light ions or with specially constructed powerful solenoids.

The three methods we have described vary somewhat in their potentialities and are best used in somewhat different ways and for somewhat different problems but these variations are not so fundamental as to require separate discussions of typical procedure and results.

TYPICAL PROCEDURE AND RESULTS

The steps in this method of study of ionization in a gas are generally these. First to investigate what ions are produced, second, which of them are primary, that is the direct result of an electron impact, and finally, what are the minimum energies required to produce each type of ion. For example, suppose we are studying hydrogen by method II. First an electron speed of perhaps twenty-five or thirty volts and a pressure of 0.05 mm or less are tried and the electrometer current plotted against the ion accelerating field gives the curve shown in Fig. 8. Therefore we know that there are three kinds of ions produced, H_3^+, H_2^+ and H^+ (ignoring the H_{2-1}^+ and H_{3-1}^+ peaks momentarily). But obviously H_3^+ must be some sort of secondary effect and perhaps the H_2^+ or H^+ is also. We try a run at reduced pressure and find H_2^+ relatively much stronger. This suggests that it is produced principally by a primary process. A series of runs at various pressures gives curves like those in Fig. 9 for the relative proportions of the three types of ion at different pressures. Since the extrapolated curves for H^+ and H_3^+ ions both seem to pass through the origin, these ions are evidently produced almost entirely by secondary effects. This may be further confirmed by taking critical potential curves at a reasonably high pressure. Such curves, examples of which are given in Fig. 10, show that the appearance potential is the same for all three types of ion suggesting that they all result from the same primary process, the production of H_2^+.

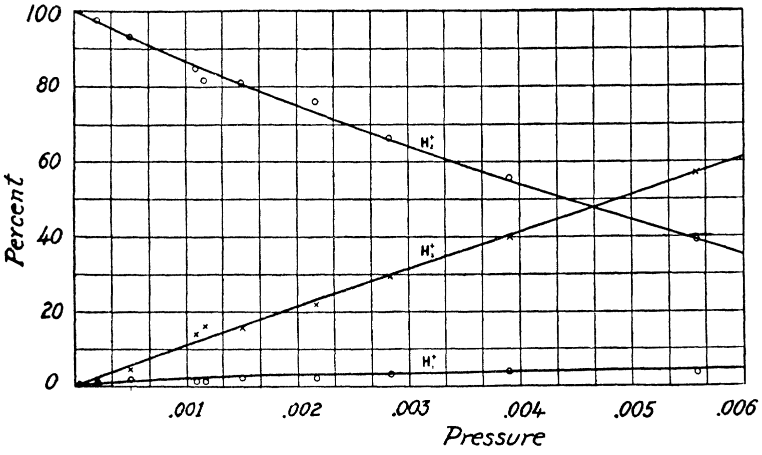

Fig. 9. The relative intensities of different ions in hydrogens as functions of pressure. (Hogness and Lunn.)

Indirect support is also given to this belief by the H_{2-1}^+ and H_{3-1}^+ peaks shown in Fig. 8. These have been shown to be due to ions which pass through the electric field as H_2^+ or H_3^+ but break up into H^+ in the collimating space, *C*, before entering the magnetic field. Their presence indicates that H^+ can be produced by a secondary dissociation of H_2^+. The occurrence of peaks of this type has been discussed in detail by Smyth[16,17] whose apparatus seems to have been particularly favorable to their formation. They have also been observed by Hogness and Kallmann and their coworkers. Their presence in gases other than hydrogen will be cited occasionally in the presentation of results later on.

The preceding paragraphs imply that H_2^+ is a primary product and the only primary product of electron impact in hydrogen. Before accepting this conclusion we must point out several possibilities that have not been excluded. There may be H^+ produced by a primary process of small probability and higher critical potential (as has actually been found to be the case by Bleakney). There may be H_2^+ produced in small quantities as a secondary process. And finally our pressure results may be due chiefly to the different absorption coefficients of the different ions in the magnet space. This last effect has some aspects of sufficient importance to justify its detailed consideration at this point.

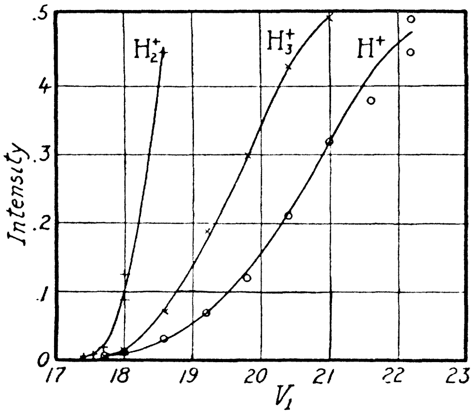

Fig. 10. Ionization potential curves for hydrogen. (Smyth.)

Collisions of the Second Kind and Selective Absorption

In the early work on positive rays, particularly the work of Wien and his school, there is much discussion of "umladung," the gain or loss of charge by an ion. Accounts of these phenomena may be found in Wien's book[4] and in the Handbuch der Physik. Though essentially the same phenomenon with which we are concerned in this section it is difficult to relate the older results with our present theories and observations. So we will start with the results first reported in a letter to Nature by Smyth, Harnwell, Hogness and Lunn.[18]

Harnwell[19] by method II, studied the ions produced in mixtures of the rare gases and found that the relative intensities of the different ions varied with total pressure even though the proportions of the different gases re-

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[16] Smyth, J. of Franklin. Inst. **198,** 795 (1924).

[17] Smyth, Phys. Rev. **25,** 452 (1925).

[18] Smyth, Harnwell, Hogness and Lunn, Nature **119,** 85 (1927).

[19] Harnwell, Phys. Rev. **29,** 683 (1927).

mained unchanged. Hogness and Lunn[19a] found a similar effect in mixtures of argon and NO. These results suggested that the ions of the gas of high ionization potential were neutralizing themselves at the expense of the atoms of lower ionization potential. To be specific consider the curve obtained by Harnwell, shown in Fig. 11, for the relative intensities of Ne^+ and He^+ in a 50-50 mixture of helium and neon. The relative increase of Ne^+ ions is supposed to be due to the reaction

$$He^+ + Ne \rightarrow Ne^+ + He \qquad (1)$$

occurring in the ionization chamber. Harnwell studied exchanges of this type in a number of polyatomic gases as well as in the rare gases. Though in some cases the results were complicated they all appeared to be interpretable on the assumption of an electron interchange

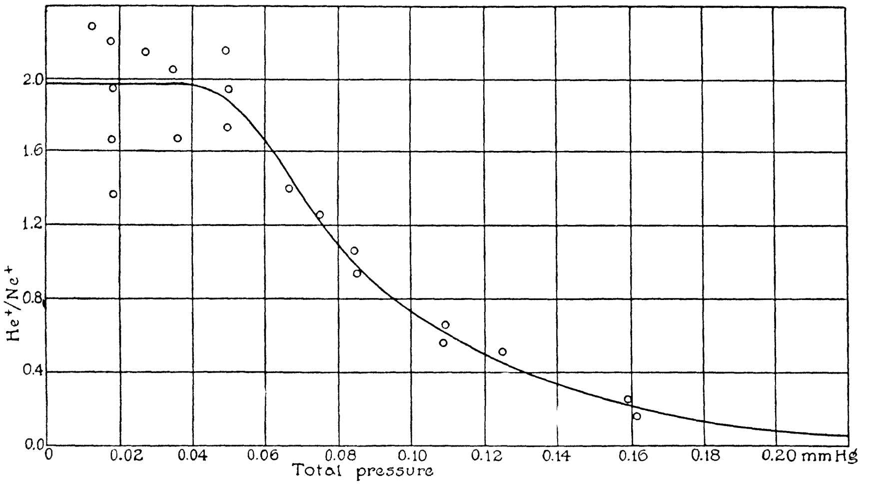

Fig. 11. Ratio of intensities of He^+ to Ne^+ as a function of pressure in a 50–50 mixture. (Harnwell.)

$$A^+ + B \rightarrow B^+ + A. \qquad (2)$$

He further came to the interesting and important conclusion that the probability of such an interchange varies inversely with $I_A - I_B$ if I_A and I_B are the ionization potentials of the molecules concerned.

Recently Kallmann and Rosen [20,21] have extended this work from a somewhat different point of view. In seeking to account for some discrepancies among different authors on the dependence of relative intensities on pressure they began a study of the effect of collisions in the magnet space. Their apparatus (method II) was arranged so that the gases in the magnet space and ionization chamber could be separately controlled.

[19a] Hogness and Lunn, Phys. Rev. **30,** 26 (1927).

[20] Kallmann and Rosen, Zeits. f. Physik **61,** 61 (1930).

[21] Kallmann and Rosen, Zeits. f. Physik **64,** 806 (1930).

Their results show that different ions have widely different probabilities of removal from the beam by collisions in the magnet space. Further, this probability depends both on the nature of the ion and on the nature of the gas in the magnet space. Now removal of an ion from the beam may be the result of loss of velocity, angular scattering, or neutralization. Kallmann and Rosen[20,21] in this work assume that neutralization is the only important factor, or at least the principle one which may be expected to vary with the nature of the absorbing gas. In their later work they have added extra electrodes and gas control in the region of the Faraday box so that they can study the scattering and absorption of ions after they have been separated by the magnetic field. By this method they have shown that angular scattering without loss of charge or energy is very small. They have also shown that slow moving ions are produced in the absorbing gas. These they assume to be the result of collisions of the second kind of the type of Eqs. (1) or (2) above. Probably they are right but it should be pointed out that collisions in which the original ions lost their kinetic energy but retained their charge would give the same results.

With this slight reservation we may accept their explanation of their results by reactions of the type described by Harnwell. In Harnwell's experiments, however, the reaction

$$A^+ + B \rightarrow A + B^+ \tag{2}$$

could only proceed in the direction indicated if $I_A > I_B$ since otherwise the principle of conservation of energy would be violated as the ions have little or no kinetic energy. But in Kallmann and Rosen's experiments the missing energy may be supplied by the kinetic energy acquired by the ions before coming into the magnet space. In fact they conclude from their results that the probability of an interchange like (2) depends only on the absolute value of $(I_A - I_B)$ not on its sign. In agreement with Harnwell's conclusion they find the probability much greater if $I_A - I_B$ is small. Furthermore they show that this is consistent with a quantum mechanical treatment of the collision process wherein the interchange of an electron is a kind of resonance phenomenon.

Besides giving interesting confirmation and generalization of Harnwell's results the experiments of Kallmann and Rosen have an important bearing on the general problem of distinguishing between primary and secondary ions by pressure variations in an apparatus of type II. For without very special precautions it is impossible to keep the pressure in the magnet space from rising when the pressure in the ionization chamber is raised. Suppose then we have two primary ions A^+ and B^+ produced in the ionization chamber from the gas AB but that the probability of the reaction

$$A^+ + AB \rightarrow AB^+ + A \tag{3}$$

is much greater than the probability of the reaction

$$B^+ + AB \rightarrow AB^+ + B, \tag{4}$$

Then as soon as the pressure in the magnet space becomes appreciable the ratio of the intensity of B^+ to A^+ begins to increase. Therefore we get a dependence of relative intensities on pressure just as we would if A^+ were a primary and B^+ a secondary ion.

This fact must certainly be borne in mind in the interpretation of new results and the reconsideration of old. Nevertheless the author believes that a detailed study of particular cases will show that it does not alter many of the conclusions of the older work.

Obviously the phenomena discussed in this section are closely connected with the question of mean free paths of positive ions. A number of physicists have worked on this problem, many of them with positive ray analysis apparatus and the time is ripe for a review of their work. But to discuss it in the present report would lead us far afield and does not seem desirable. Keeping to the problem of ionization there is one further complication to consider before proceeding to a detailed discussion of results obtained in various gases.

EFFECT OF SPACE CHARGE SHEATHS

Gurney and Morse[22] showed that the relative intensities of primary or secondary ions would be influenced by the presence of space charges in the ionization chamber. Though their theory is doubtless correct there arise in practice so few cases where it is exactly applicable and so few cases where any attempt at quantitative interpretation of pressure results can be made that it does not seem worth repeating. Applied to some of Harnwell's results it gave a qualitative explanation of the shape of his pressure-intensity curves. Nielsen[9] in a recent study of negative ions in mercury has found his field distribution so altered by space charge as to prevent entirely the formation of negative ions under certain conditions.

III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

MONATOMIC GASES AND VAPORS

The contribution of the study of ionization in monatomic gases by positive-ray analysis has been chiefly to the problem of probability of ionization. To treat this entire field is quite beyond the scope of the present review. But there are a few other points of interest in the monatomic gases and for the sake of completeness we will give the results briefly.

Mercury

Though not studied as frequently as hydrogen, mercury has been rather a favorite with which to start. The initial work of Smyth has been confirmed and superseded by that of Bleakney[23] who found Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+}, appearing at 30 ± 1, 71 ± 2, 143 ± 3, and 225 ± 5 volts respectively. These ions were all produced as the result of single electron impacts. Bleakney also measured their relative probability. His results are given in Fig. 12 and mark

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[22] Gurney and Morse, Phys. Rev. **33,** 789 (1929).

[23] Bleakney, Phys. Rev. **35,** 139 (1930).

a great step forward in data of this sort as they separate the probabilities of the different types of collision.

Nielsen has recently studied negative ions in mercury and found Hg^- to be fairly intense.

Helium, Neon and Argon.

Using the apparatus built by Smyth for hydrogen, Barton[24] determined the ionization potential of A^{2+} to be 45 ± 1.5 volts. At that time this value was of considerable interest spectroscopically. It has been confirmed by Bleakney[25] who finds A^+, A^{2+}, A^{3+}, A^{4+}, A^{5+}, appearing at 15.7, 44, 88, 258 and less than 500 volts, respectively.

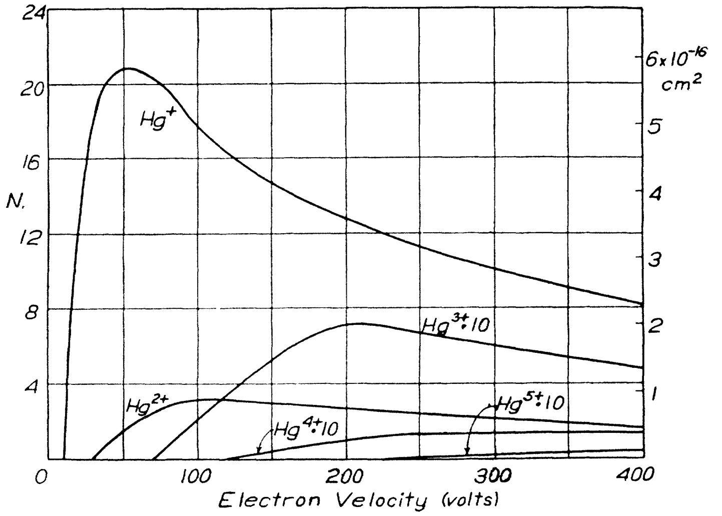

Fig. 12. Ionization probabilities in mercury. (Bleakney.)

Dr. Bleakney has informed the writer that in the light of Smith's work (Phys. Rev. **37**, 808, 1931) the ordinates of these curves are about 25% too large.

In helium Bleakney was able to find only a trace He^{++} and could not study its conditions of formation.

In neon he observed Ne^+, Ne^{2+}, and Ne^{3+}, only and determined their

Table I.

Argon			Neon		
Ion	Obs. I.P.	Spectr. I.P.	Ion	Obs. I.P.	Spectr. I.P.
A^+	15.7 ± 0.1	15.7	Ne^+	21.5 ± 0.1	21.47
A^{2+}	44.0 ± 0.5	43.51	Ne^{2+}	63.0 ± 0.5	62.4
A^{3+}	88 ± 1	84.2	Ne^{3+}	125.0 ± 1.0	125.6
A^{4+}	258 ± 3				
A^{5+}	Less than 500				

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[24] Barton, Phys. Rev. **25**, 469 (1925).

[25] Bleakney, Phys. Rev. **36**, 1303 (1930).

ionization potentials which are given in Table I below together with the spectroscopic values and the corresponding data for argon.

Bleakney also studied ionization probabilities in argon and neon obtaining results similar to those in mercury. The curves analogous to those of Fig. 12 are given in his paper.

POLYATOMIC GASES

Hydrogen (H_2)

Experimental results.

The older results on hydrogen some of which have already been mentioned were summarized and discussed in detail by the author in a paper with Condon[26] in 1928. As to the critical potentials below the ionization potential, there is nothing to add to that discussion save a reference to a recent paper on the continuous spectrum by Finkelnburg and Weizel.[27] But Bleakney's[28] recent results make it desirable to reconsider the ionization processes observed and predicted. First let us quote from the 1928 paper:

"Then at about 15.9 volts strong ionization sets in, which has been shown to be ionization without dissociation. Furthermore, no evidence has been found at this or any higher voltage of the formation of atomic ions from molecules as the immediate result of an electron impact. However, such a process may occur if of small probability, since it might be masked by the large number of atomic ions formed by secondary dissociation of the molecular ions. . . . " This paragraph is quoted to emphasize the fact that Bleakney's most important results are not contradictory to the older conclusions but merely supplement them. He has, in fact, observed the primary production of atomic ions at about 18 volts, an observation made possible by the absence of secondary H^+ ions in his method. Of greater importance and interest is his discovery of high speed atomic ions first produced at 26 ± 1 volts, and becoming quite strong at 30 volts. That there was some sort of critical potential in this neighborhood had been suggested by the results of a number of previous authors but no one had been able to study it in detail. Bleakney found that by reversing the small field V_2 (see Fig. 6) he could reduce his positive ion currents to zero below 26 volts electron energy but that above that a diffuse peak apparently of atomic ions set in. The nature of the peak and an appearance potential run are shown in Fig. 14. Fig. 13 is included to show the sharpness of H_2^+ and H^+ peaks when the ions have no kinetic energy. In comparing Figs. 13, 14 and 15 (below) with Figs. 8, 9 and 10 it must be remembered that secondary effects have now been eliminated. The velocity of the high speed ions has been studied more thoroughly by Lozier[29] in an apparatus expressly designed for this purpose. His results confirm and extend those of Bleakney and are in detailed agreement with the theoretical predictions as we shall show later.

[26] Smyth and Condon, Proc. Nat. Acad. **14,** 871 (1928).

[27] Finkelnburg and Weizel, Zeits. f. Physik **68,** 577 (1931).

[28] Bleakney, Phys. Rev. **35,** 1180 (1930).

[29] Lozier, Phys. Rev. **36,** 1285 (1930).

There is one feature of Bleakney's work which certainly does not fit in with the older results. That is the actual value, 15.4 volts, which he gets for the molecular ionization potential. Although his method appears to be capable of greater accuracy than most of the older ones and although it gives

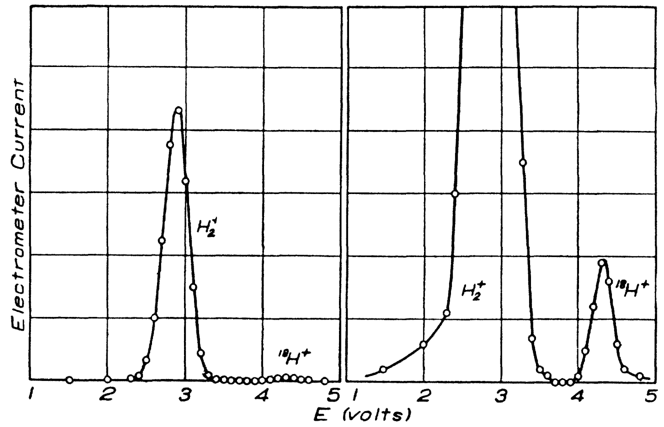

Fig. 13. *e/m* curves for hydrogen. (Bleakney.)

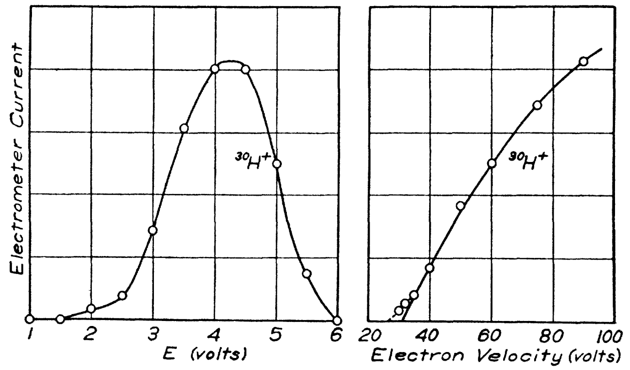

Fig. 14. *e/m* curve and *I.P.* curve for fast H^+. (Bleakney.)

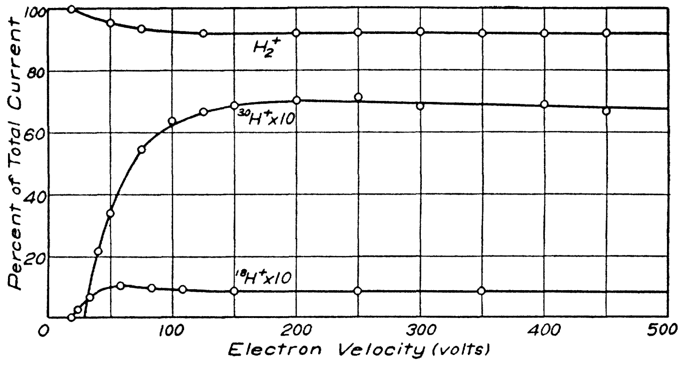

Fig. 15. Ionization probabilities in hydrogen. (Bleakney.)

results that are certainly right for neon and argon the author does not believe that Bleakney's hydrogen result is sufficiently well-based to outweigh the older ones. This belief is the result of conversation with Dr. Bleakney himself and of critical consideration of his paper. There is no apparent flaw in his determinations but they have not been repeated under sufficiently varied conditions to prove themselves independent of pressure, current, impurities, particular tube used, etc. On the other hand the older value of 15.9 ± .2 volts is based on observations of fifteen or twenty investigators under a great variety of conditions. Moreover both the work of Harnwell who found evidence of the transfer

$$H_2^+ + A \rightarrow A^+ + H_2$$

and of Kallmann and Rosen who measured the *I.P.* of H_2 with respect to argon require that the *I.P.* of H_2 be higher than that of argon, spectroscopically determined as 15.69. It is to be hoped that Bleakney will repeat his measurements using argon as the calibrating gas.

The experimental results of Bleakney and previous investigators are summarized in Table II.

TABLE II.

Observed effect	Observed critical potential
(1) Increased "clean up." Radiation	11.5
(2) More radiation Continuous spectrum	12.8
(3) H_2^+ produced	15.9 ± .2 (15.4?)
(4) H^+ produced	18.0 ± .3
(5) Fast H^+ produced	26. ± 1.5
(6) (a) More fast H^+ produced (b) Balmer lines produced	30
(7) More fast H^+ produced	46
Secondary effects	
(8) Plentiful production of H^+ at high pressures	15.9 plus some kinetic energy of ion
(9) Plentiful production of H_3^+ at high pressures	15.9

So far nothing has been said about the relative probability of these events. Only the primary ionizations can be compared quantitatively with the result shown in Fig. 15 reproduced from Bleakney's paper. To this it may be added that effect (1) is fairly strong, (2) weak, 6 (b) fairly strong and (8) and (9) very strong. The high probability of (8) accounts for the previous failure to get definite evidence for (4) or (5) both of which are comparatively weak.

Theoretical interpretation.

When the energy levels and ionization potentials of an atom are known spectroscopically we can predict with reasonable certainty the critical potentials that will be observed in experiments on electron impact. But when polyatomic molecules are concerned the problem is more complicated. The molecule has rotational and vibrational energy as well as electronic energy and all three may be altered by an electron impact. If we graph the possible energy levels of a molecule we get something like that shown in Fig. 16. In general the molecules will be distributed in different vibrational and rotational states according to the temperature though the amounts of energy involved are such that there are very few above the zero vibration state at room temperature.

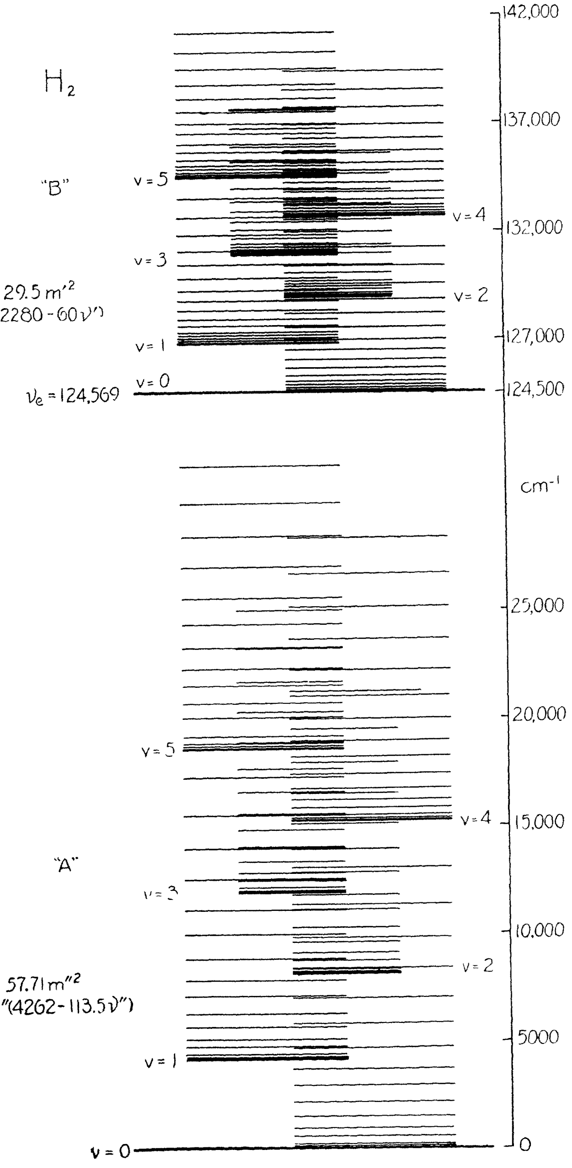

Fig. 16. Rotational and vibrational states of the "*A*" and "*B*" electronic states of the hydrogen molecule. Only fifteen rotational states are shown for each vibrational state and six vibrational states for each electronic state. The distance between the two electronic states has beeen greatly reduced but the levels in each state are to scale.

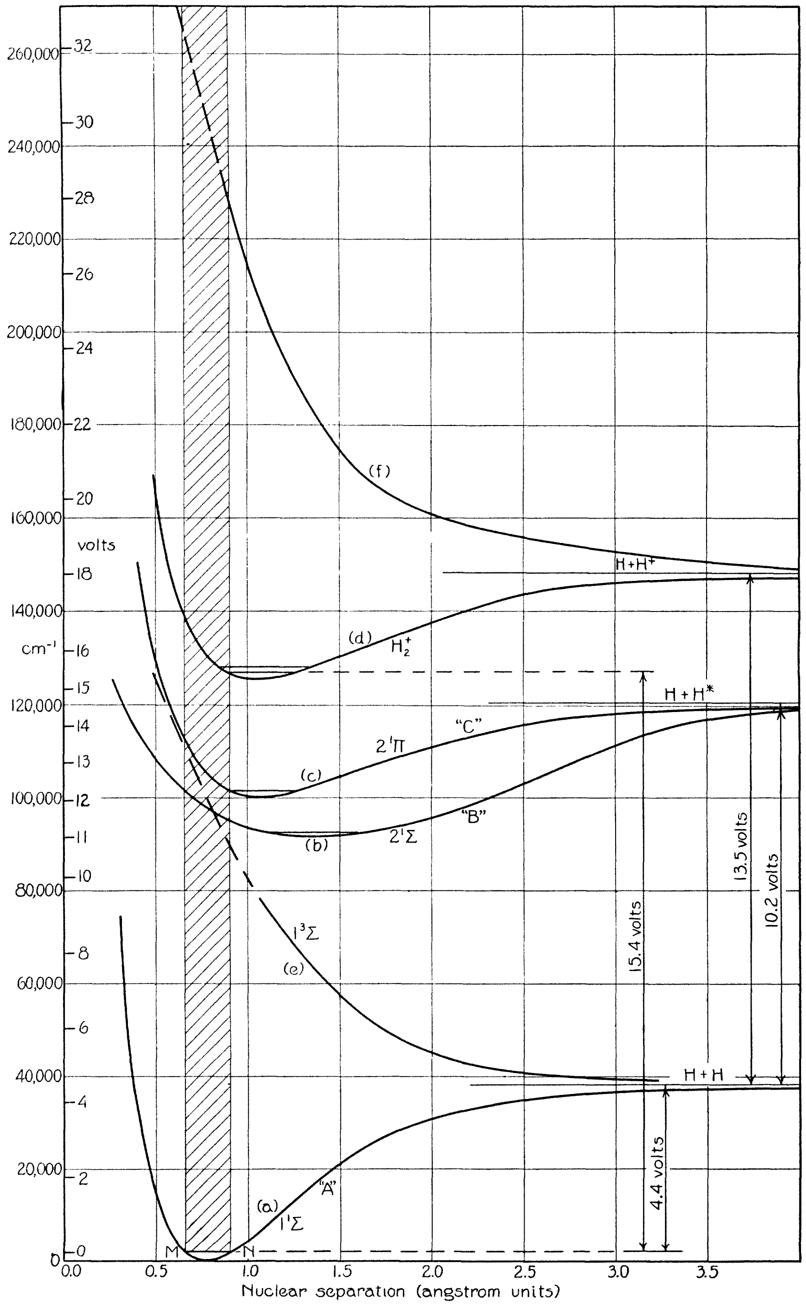

Fig. 17. Potential energy curve for hydrogen drawn as follows, where D_M is the depth of the minimum below the asymptote.

(a) Morse's function[29a] using: $a=1.85$, $r_0=0.76$, $D_M=38{,}200$, $\omega_0=4260$.

(b) Morse's function using: $a=0.7$, $r_0=1.31$, $D_M=28{,}800$, $\omega_0=1337$.

(c) Morse's function using: $a=1.41$, $r_0=1.06$, $D_M=20{,}840$, $\omega_0=2380$.

(d) From Burrau.

(e) From Bleakney's curve.

(f) From Bleakney's curve.

[29a] Morse, Phys. Rev. **34**, 57 (1929).

Now if an impacting electron can raise the molecule from any one of the states A to any one of the states B it is obvious that the amount of energy transferred varies over a considerable range. Nor is there even a definite minimum unless all the molecules are initially in a state of zero vibration and rotation. It is not surprising therefore that experimental determination of ionization and radiation potentials give less precise and reproducible results for polyatomic gases than for monatomic.

Fortunately, the energetically possible transitions resulting from electron impact are not of equal probability. According to the Franck-Condon principle, an electron impact usually does not alter the separation nor relative velocities of the nuclei of a molecule even when it alters the electron configuration. Now for every electron configuration of a diatomic molecule the nuclear binding can be expressed by a "potential energy" curve derived from band spectrum data or by theoretical computation. Such curves are shown in Fig. 17 for several states of the hydrogen molecule. The ordinates represent energy of the system and the abscissas nuclear separation. These curves are of the same type as those given by Bleakney but in some cases have been recalculated as is explained in the caption to the figure. Curves a, b, c, and d have minima and represent stable configurations. Curves e and f represent electron configurations where the resultant force betweenthe atoms is repulsive for all possible nuclear separations and the molecule is therefore unstable. Restating the Franck-Condon principle in terms of these curves we say that an electron impact is likely to cause transitions from a point on a lower curve only to points on upper curves vertically over it, i.e. corresponding to the same nuclear separation.

Transitions to the unstable states are of particular interest. In excitations, energy is absorbed until the molecule is raised to the point on the repulsive curve determined by the Franck-Condon principle; the nuclei then fly apart with kinetic energy corresponding to the heighth of the point of excitation above the asymptote of the curve. Since there are no quantized states of the unstable electronic state and since the nuclear separations of the vibrating molecule in the lower state cover a continuous range, the possible energies absorbed cover a continuous range. Excitation may be either by electron impact or light absorption. Similarly, for emission transitions where the unstable state is lower than the initial electronic state, a continuous spectrum will be emitted, each molecule giving off enough of its energy as radiation to bring it vertically down to a point on the repulsive curve and then giving off the rest as kinetic energy of its disrupting parts. In cases where the disrupting parts are uncharged it is difficult to measure their speed but when they are ions it is comparatively easy.

Now let us consider the case of hydrogen. At ordinary temperatures nearly all the molecules will be in the $v=0$ state, that is will have a half quantum of vibrational energy and will oscillate between the points M and N on curve (a). So if we draw a vertical shaded band with the line MN as base the most probable transitions are to points on the upper curves lying within this band. Actually the probability of a given transition can be calculated from a knowledge of the wave functions of the two states but for our purposes the qualitative application of the Franck-Condon principle is sufficient.

Let us tabulate the probabilities if hydrogen in the zero vibration state be bombarded by electrons of gradually increasing speed and attempt to correlate them with the observed phenomena of Table II.

TABLE III.

Voltage	Probable excited state	Probable reverse transition	Predicted effect	Observed effect	Remarks and references
11.0 c	$1^3\Sigma$	Dissoc.	High speed H atoms	Clean up	
11.5 c	$2^1\Sigma$	$\rightarrow 1^1\Sigma$	U.V. radiation	As predicted	
11.8	$2^3\Sigma$*	$\rightarrow 1^3\Sigma$	Continuous spectrum	As predicted	Finkelnburg and Weizel
12.6	$2^1\Pi$	$1^1\Sigma$	More U.V. radiation	As predicted	Not very strong but reported
15.6	H_2^+	None	Ionization without diss.	As predicted	Experimental I.P. 15.9 ± .3
18.0	H_2^+ excited above diss.	$H^+ + H$	Ionization with diss.	As predicted	Should be and is very weak
28.0 ↓ 40	H_2^+ unstable	$H^+ + H$ + k.e.	Production of fast H^+	As predicted	Experimental value a little lower
46 ↓ 56	H_2^{2+} unstable*	$H^+ + H^+$ + k.e.	Additional fast H^+	As predicted	

* Not included in Fig. 17.

Some features of the above table require further emphasis and explanation.

Fast ions.

In the first place, the most interesting point is probably the prediction and observation of the high speed H^+ ions. The physical reality of the condition represented by the repulsive potential energy curves is here demonstrated beyond question. The explanation of the continuous spectrum is the only other phenomenon for which they are used and has been included in the table for this reason, although no attempt has been made to analyze and include the data on the excitation potentials of different parts of the many line spectrum. Not only has the existence of these high speed ions been demonstrated, but Bleakney and, particularly, Lozier have actually measured their velocities and found them in agreement with the values predicted from the curves.

Ionization potential

Consideration of the potential energy curves shows that it is possible but very improbable that an H_2 molecule should be ionized without raising it to the $v = 1$ vibrational state. It seems most plausible to take 15.6 as the theoretically predicted ionization potential. A very sensitive apparatus might detect ionization at 15.4 but it seems unlikely that this is the explanation of Bleakney's result (see above). The discrepancy between the 15.6 and the best experimental value 15.9 still seems a little large. We have, of course, ignored any possible change in the rotational energy and will continue to do so throughout this paper. To include rotational energies in the present discussion would lead into complications in which the meagre experimental data would be entirely lost. But reference may be made to a paper by Oldenberg[29a] where he shows how the shape of a potential energy curve may be entirely altered by rotation even to the extent of having the minimum eliminated. It is quite possible, therefore, that the discrepancy remaining between the theory and the results presented above may be due to rotational effects, particularly, as these are large in hydrogen on account of its small moment of inertia.

Secondary effects

The temptation to minimize unexplained results is always great. Yet in hydrogen the secondary production of H^+ and H_3^+ is almost the most striking result of all experimentation. Dorsch and Kallmann[30] showed that the H_2^+ ions had to be somewhat accelerated before they could break up, as is consistent with energy required. Smyth showed by a study of the break up of the fast moving ions that collisions increased the probability of break up. But the nature of the mechanism and the degree to which it is spontaneous remains uncertain. No theoretical attack on the problem has been attempted.

The production of H_3^+ also remains a great deal of a mystery. The balance of the evidence suggests that it is produced directly by the process

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$

Several years ago Brasefield[30a] made an attempt to correlate relative intensities in the many line spectrum of hydrogen with relative intensities of H_2^+ and H_3^+ in the discharge. Now that the spectrum has been so well analyzed it might be possible to interpret his results in terms of the states of excitation most favorable to the formation of H_3 or H_3^+.

Negative ions

Lozier[31] reports the observation of negative H^- ions in hydrogen but concludes they were due to water vapor. His results will be discussed in the section on water vapor. So far as the author knows this is the only record of H^- ions appearing in this type of work.

Conclusion

We have seen that the results of experiments on electron impact in hydrogen are many and various but that they are understandable, even predictable, except in a few cases. Such beautiful accord is a great triumph for the quantum mechanics treatment of band spectra and molecular structure. It

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[29a] Oldenberg, Zeits. f. Physik **56,** 563 (1929).

[30] Dorsch and Kallmann, Zeits. f. Physik **53,** 80 (1929).

[30a] Brasefield, Phys. Rev. **31,** 52 (1928).

[31] Lozier, Phys. Rev. **36,** 1417 (L) (1930).

points out clearly the general kind of result we may expect from other gases. Unfortunately, we shall not again be able to set up so complete a theory nor to find such detailed experimental results.

Nitrogen (N_2)

Though nitrogen[32] was the fist polyatomic molecule whose ionization potential was studied by positive-ray analysis, its behavior is not yet perfectly understood. In the first work, Smyth showed that the previously observed ionization potential corresponded to ionization without dissociation and got further strange and curious results at higher voltages. Some of these have been reproduced and interpreted, others have not and may have been spurious. Further work has since been done by Hogness and Lunn,[33] Harnwell,[34] Kallman *et al*,[35] and Lozier.[36] A summary of all this work follows.

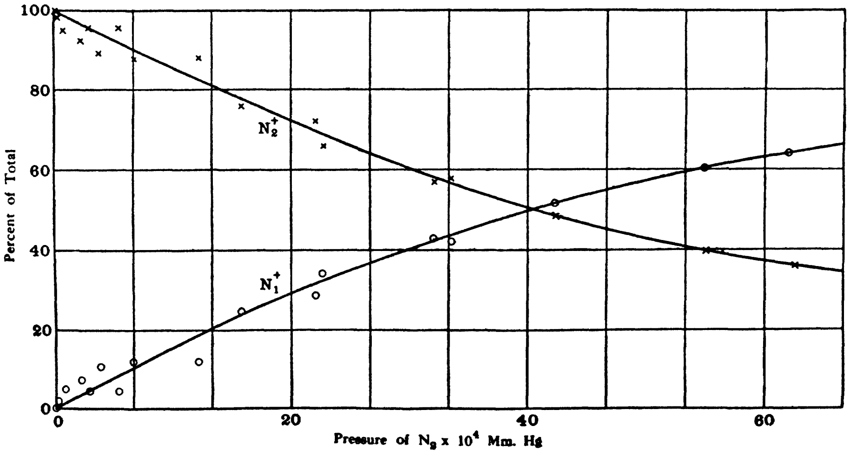

Fig. 18. Relative intensities of different ions in nitrogen as functions of pressure. (Hogness and Lunn.)

Atomic ions and collisions of the second kind

Besides the molecular ions at about 16.5 volts, atomic ions are produced in the neighborhood of 24 volts. Hogness and Lunn observed that the proportion of atomic ions increased rapidly with pressure (Fig. 18) and concluded that they were formed by a secondary dissociation of an unstable or metastable N_2^+ ion requiring 24 volts for its production. Kallmann and Rosen found that in their apparatus the ratio N^+/N_2^+ was independent of the pressure in the ionization chamber if that in the magnet space were kept constant. They believed Hogness and Lunn's result were due to differential absorption in the magnet space. But Hogness and Lunn showed that the N^+/N_2^+

[32] Smyth, Proc. Roy. Soc. **A104,** 121 (1923).

[33] Hogness and Lunn, Phys. Rev. **26,** 786 (1925).

[34] Harnwell, Phys. Rev. **29,** 830 (1927).

[35] Kallmann, *et al,* Zeits. f. Physik **43,** 16 (1927); **44,** 565 (1927); **58,** 52 (1929); **61,** 61 (1930); **64,** 806 (1930).

[36] Lozier, Phys. Rev. **37,** 101A (1931).

ratio increased greatly if the pressure of helium in the apparatus was increased while the partial pressure of nitrogen was kept constant. Kallmann and Rosen did not repeat or discuss this experiment which has no simple explanation on their theory. Furthermore, as will be seen in a later section, selective absorption was hardly noticeable in Hogness and Lunn's work on NO though conditions were just as favorable to it as in nitrogen. Finally in Harnwell's work the suppression of N^+ by the addition of Ne is a result perfectly consistent with the process

$$Ne + N_2^{24+} \rightarrow Ne^+ + N_2$$

which would be probable (the *I.P.* of Ne is 21.5) but quite inconsistent with the process $Ne+N^+ \rightarrow Ne^+ + N$ which is well-nigh impossible since the *I.P.* of N is only 14.5. Harnwell's results in helium and nitrogen are equally well explained by the formation of an N_2^+ at 24 volts which dissociates immediately or one which is metastable. Perhaps this conflict of experimental results is best explained if we assume that the electronic configuration of the ion produced is such that the potential energy curve has a very shallow minimum, then both direct and indirect production of N^+ may be expected and relative intensity of the two effects may be very sensitive to changes in the vibrational or even rotational state of the molecules at the start. This suggestion receives some support from Lozier's results on high speed ions.

High velocity atomic ions. Lozier[36] has now extended his study to nitrogen although his results have not been published in full. According to a private communication he obtains atomic ions beginning at about 24 volts with velocities as low as about two volts and then increasing in velocity up to as much as six volts as the electron velocity is increased. Now the minimum of the normal N_2 potential energy curve is very deep and narrow and the nuclear separation small, so that if excitation were to a repulsive potential energy curve it would almost certainly be to points several volts above the asymptote and therefore all atomic ions produced would probably have greater than two volts kinetic energy. But if the curve had a shallow minimum, lower kinetic energies would be more likely to be present.

Other secondary effects. No other secondary ion has ever been observed but it is interesting to note that Storch and Olsen[37] observed the formation of ammonia setting in sharply at about 23 volts when a mixture of nitrogen and hydrogen was bombarded by electrons. This work has been repeated by Caress and Rideal, and more recently by Brett[38] who found the rate of reaction in a mixture of hydrogen and nitrogen rose sharply at 17.0, 18.5, 20.5, 24.5 and 27.0 volts. Wansbrough-Jones[39] has made similar experiments on mixtures of oxygen and nitrogen. He finds critical voltages for reaction at 17 and 23 volts which he attributes to the nitrogen, concluding that activation of the oxygen plays no part.

One other secondary effect of interest is the N_{2-1}^+ peak observed first

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[37] Storch and Olsen, J.A.C.S. **45**, 1605 (1923).

[38] Caress and Rideal, Proc. Roy. Soc. **115A**, 684 (1927); Brett, Proc. Roy. Soc. **129A**, 319 (1930).

[39] Wansbrough-Jones, Proc. Roy. Soc. **127A**, 511 (1930).

by Smyth and interpreted incorrectly as due to N^{++}. He observed its appearance potential to be about 24 volts. Kallmann and Rosen have studied this peak again and conclude that its appearance potential is the same as that of N_2^+ (about 17). Remembering the cause of peaks of this type* we conclude that there are N_2^+ ions, probably those formed at the first *I.P.* which dissociate on collision after acquiring large kinetic energies.

Negative ions. Both Smyth and Hogness and Lunn observed N_2^- ions but in such small quantities that they were unable to study them. No other negative ions have been observed in nitrogen.

Theoretical interpretation and ionization potentials

The potential energy curves for the normal and several excited states of the molecule and for the normal state and one excited state of the ion are well known. Unfortunately no series limit is known for the electronic terms so that the *I.P.* of the molecule can not be calculated. In tables of energy levels the experimental value of 16.9 is ordinarily used. Until recently there had been no satisfactory determinations of this quantity with the latest technique and it seemed possible that the true value might be as much as half a volt or more lower. Mackay,[40] whose measurements have proved to be remarkably accurate, got 16.3. Smyth and Stueckelberg[41] estimated 16.5 as the most probable value. That this is still too high is suggested by the results of Tate and Smith[42] who report 15.8 as the lowest of a series of ionization potentials. This last value agrees with that of Turner and Samson[43] from the excitation potential of the N_2^+ bands.

As may be seen from Fig. 19 the equilibrium nuclear separations are almost identical for the normal states of N_2 and N_2^+ and the *P.E.* curves similar in shape so that it is not surprising to find no dissociation at the first ionization. Also, the experimental value of the *I.P.* probably corresponds to a transition between $v=0$ vibration states. Only one excited N_2^+ state is known. The minimum of its *P.E.* curve is 3.2 volts above the normal N_2^+ and its asymptote about 3.9 volts[44] higher. Therefore to get an N^+ by excitation to this state, $16.5+7.1=23.6$ volts are needed. Purely from the energy point of view, $9.1+14.5=23.6$ volts, the same value, are needed for the process $N_2 \rightarrow N^+ + N$. This value is remarkably close to that actually observed for this ionization potential. Hogness and Lunn give 24 with no estimate of error but quote Brandt's 24.6 as consistent, Kallmann and Rosen get 24.0, while Harnwell's results show it certainly below the *I.P.* of He at 24.5. The true value is probably about $24.0 \pm .4$ only a half volt above the minimum energy requirement.

Clearly it is possible to explain the observed results by using the known excited N_2^+ state and a considerable deviation from the Franck-Condon

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* See p. 357.

[40] Mackay, Phys. Rev. **24,** 319 (1924).

[41] Smyth and Stueckelberg, Phys. Rev. **36,** 478 (1930).

[42] Tate and Smith, Phys. Rev. **37,** 1705 (A) (1931).

[43] Turner and Samson, Phys. Rev. **34,** 747 (1929).

[44] R. T. Birge, Nature **122,** 842 (1928).

principle. The production of N^+ at 24 would then be exactly analogous to that of H^+ at 18. The N^+ ions would then have velocities down to zero and there would be molecular ions produced in very high and therefore unstable vibrational states. It is not possible to decide yet between this explanation and the previous suggestion of an unknown state with a small minimum in the potential energy curve. Perhaps the unstable molecular ions of Hogness and Lunn come from such a state and the primary atomic ions of Kallmann and Rosen come from the known state.

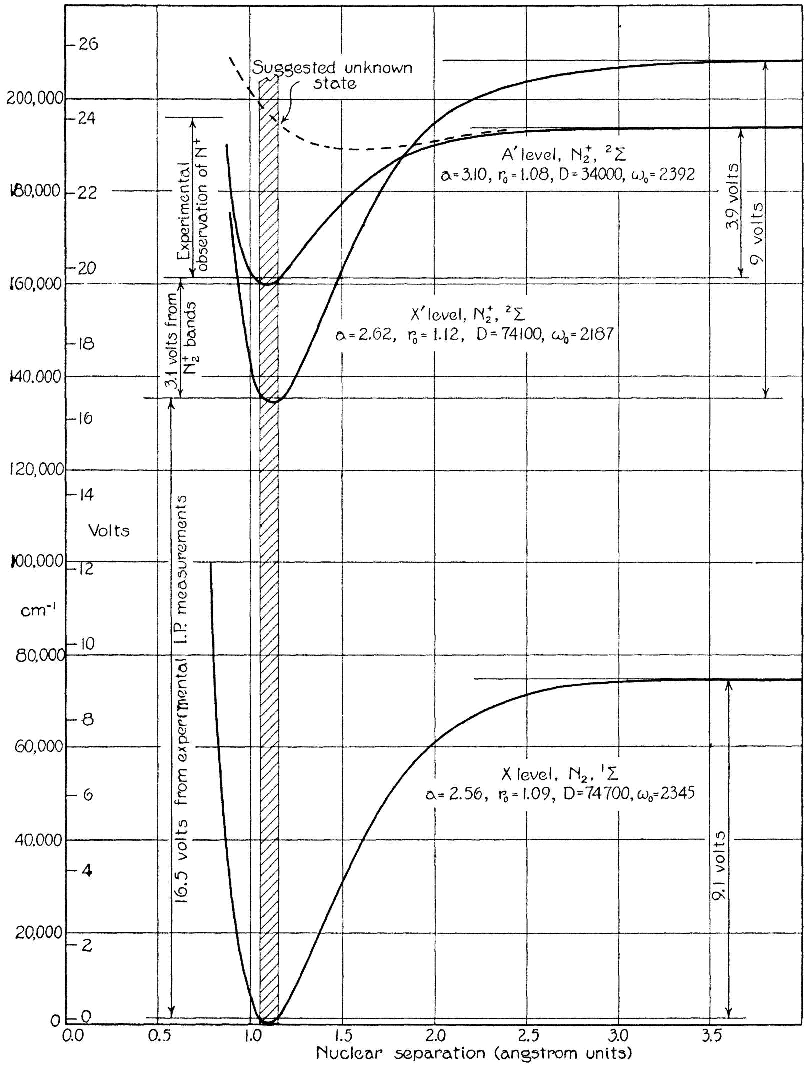

Fig. 19. Potential energy curves for three electronic states of nitrogen. Data for curves are on figure. All were plotted by the use of Morse's function.

Oxygen (O).

In the older work on the first ionization potential of oxygen there were serious discrepancies between the results of different observers, the experimental determinations ranging between 12.6 and 16.1, the values observed by Mackay[40] who was the only author reporting two distinct breaks in the ionization curve. These discrepancies have not been completely explained by the positive ray attack on the problem. Smyth[46] in his first study of the problem observed O_2^+ at about 15.5 volts and O^+ about 7.5 volts higher. He arrived at the absolute value 15.5 by making an estimated correction for potential drop and initial velocity but without any calibrating gas; it is therefore not nearly as significant as the 7.5 volt difference between the two *I.P.*'s. Hogness and Lunn,[45] calibrating with He, obtained 13 and 20 volts values for the two oxygen *I.P.*'s; the difference, seven volts, is in good agreement with the 7.5 volts reported by Smyth.[46] A study of collisions of the second kind by Smyth and Stueckelberg[47] shows the higher *I.P.* definitely below but probably very close to that of Ne, 21.5 volts, since their data indicated that the process $Ne^+ + O_2 \rightarrow O^+ + O + Ne$ was very probable. As to the lower *I.P.* results of a similar sort show that it is probably considerably below that of A, 15.67 and probably below that of water vapor at about 13 volts. It seems likely therefore that the first ionization potential of oxygen is in the neighborhood of 12.5 to 13 volts though it remains probable that there is also a strong higher *I.P.* at 15.5 to 16 volts.

Hogness and Lunn found the ratio O_2^+/O^+ independent of pressure and this was confirmed by Smyth and Stueckelberg so that there is no doubt that O^+ is produced directly by electron impact.

Kallmann and Rosen[48] agree that both processes are primary and give 13 and 19.5 as the appearance potentials. They give neither curves, data, nor estimated error.

Minor and secondary effects

A further point of interest in oxygen is the great intensity of O^+ in both Smyth, and Smyth and Stueckelberg's work compared to that of Hogness and Lunn. Similar discrepancies, though less marked, occur in the data for other molecules. Moreover, changes in the magnetic fields and ion accelerating fields often alter relative intensities. Such effects are very difficult to control and to study; usually they are vaguely explicable in terms of altered distribution and scattering of the ionizing electrons. It occurs to the wrtier that the most uncontrolled and unmeasurable variable in these experiments is the stray magnetic field in the ionization chamber and this may have a direct influence on molecular stability and the nature of electron-molecule collisions.

No O_3^+ nor other secondary ions have been observed in oxygen. Smyth, and Hogness and Lunn both observed a very weak O_{2-1}^+ peak indicating that

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[45] Hogness and Lunn, Phys. Rev. **27,** 732 (1926).

[46] Smyth, Proc. Roy. Soc. **A105,** 116 (1924).

[47] Smyth and Stueckelberg, Phys. Rev. **32,** 779 (1928).

[48] Kallmann and Rosen, Zeits. Physik **61,** 61 (1930).

O_2^+ can be dissociated by a high speed collision but the effect is much weaker than in N_2.

Negative ions

Hogness and lunn observed both O_2^- and O^- but were unable to study the conditions of their formation.

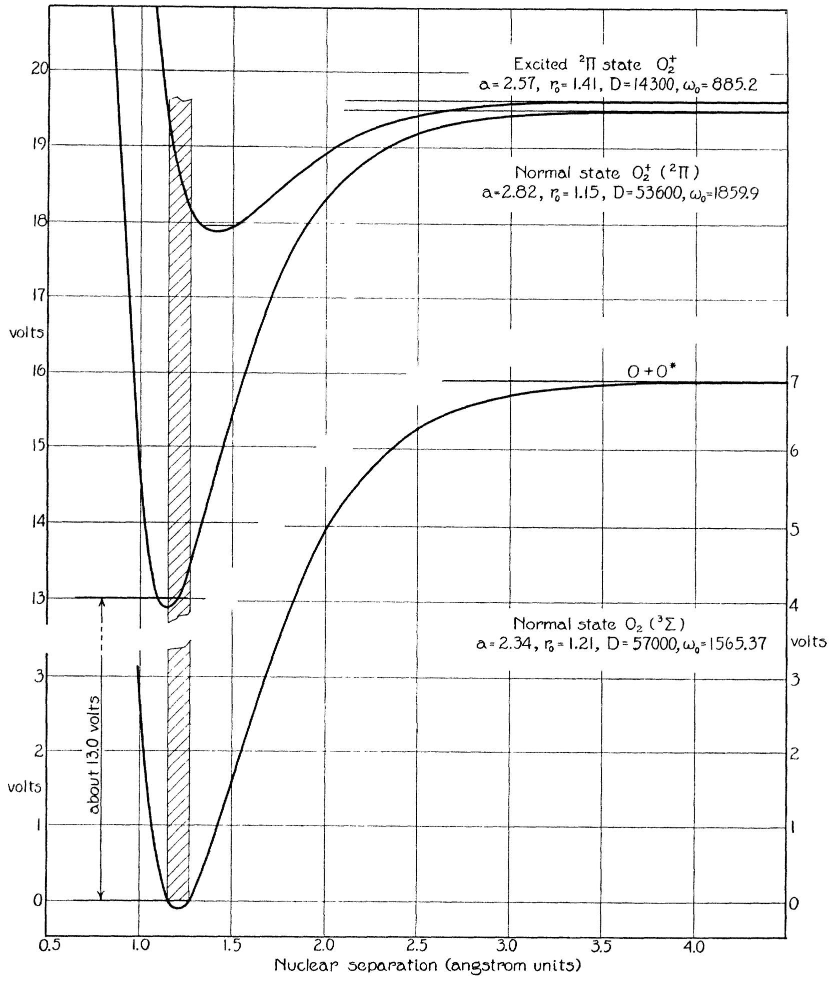

Fig. 20. Potential energy curves for three electronic states of oxygen. Data for curves are on drawing. All were plotted by the use of Morse's function.

Theoretical interpretation

Mulliken[49] and Stueckelberg[50] have both discussed the above results in terms of the electron levels and potential energy curves of oxygen. The potential energy curves for the normal state of both molecule and ion are

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[49] Mulliken, Phys. Rev. **32,** 761 (1928).

[50] Stueckelberg, Phys. Rev. **34,** 65 (1929).

known as well as for several excited states and are shown in Fig. 20 where there is some uncertainty about the r_0 for the ionic states since the rotational structure is unknown.

In their discussions Mulliken and Stueckelberg used the old value 7.05 volts for the heat of dissociation and the experimental value 13.5 volts for the *I.P.* It is now known that 7.05 volts gives dissociation to an excited (^1D) and a normal atom, and that the heat of dissociation to normal atoms is 5.1 volts. Also Mulliken[51] has recently given 11.7 volts as an estimate of the spectroscopic *I.P.*, a value within speaking distance of Mackay's 12.6 and our estimate of something less than 13.

Considering the first ionization it is obvious that the Franck-Condon principle applied to the potential energy curves will give a transition from $v''=0$ to $v'=0$ and therefore the spectroscopic and experimental *I.P.* should agree exactly. The significance of their failure to do so will doubtless be discussed when Mulliken publishes a complete account of his work. Following up the vertical Franck-Condon transition to higher levels we see that we come to the $^2\Pi$ level, which is the initial level of the O_2^+ ultraviolet bands, at a point on the potential energy curve just a little below the asymptote. By assuming small errors in the curves or such deviation from the Franck-Condon principle as is observed in hydrogen we can explain the observed dissociation. Moreover, the asymptote of the excited state is 6.6 volts above the $v=0$ state of the normal ion. This agrees fairly well with our observation that O^+ ions are first observed 7.0–7.5 volts above O_2^+.

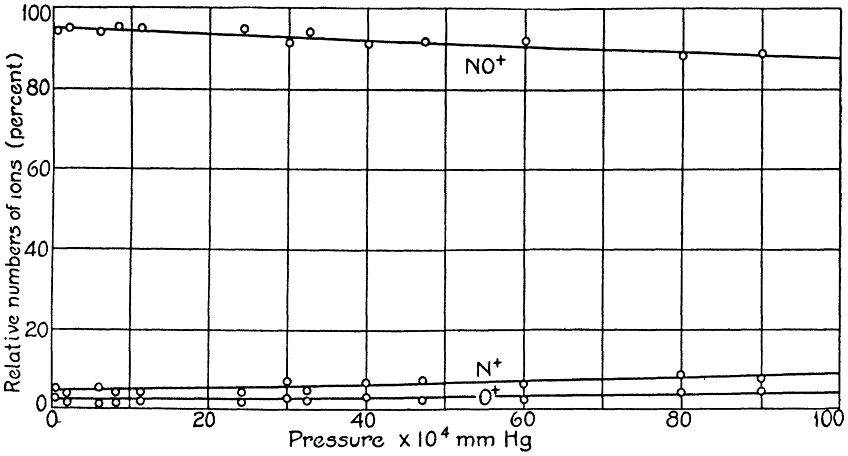

Fig. 21. Relative intensities of different ions in NO as functions of pressure. (Hogness and Lunn.)

Nitric oxide (NO).

The only work that has been done on NO is that of Hogness and Lunn[52] which seems to give quite definite results. They find three primary products

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[51] Mulliken, Phys. Rev. **37**, 1711 (A), (1931).

[52] Hogness and Lunn, Phys. Rev. **30**, 26 (1927).

of ionization, NO^+, O^+ and N^+ appearing at about 9.3,* 21 and 22 volts respectively. Their value for the first ionization potential agrees well with the more accurate values of 9.3 and 9.4 determined previously by Hughes, and Dixon, and Mackay.[40]

Secondary effects and selective absorption

Hogness and Lunn made their customary study of the effect of pressure on the relative intensities of the different ions. Their results are reproduced in Fig. 21. From the fact that the N^+ and O^+ curves extrapolated to zero pressure both have finite ordinates they conclude that both N^+ and O^+ are produced by primary processes. But since NO^+ decreases slightly and O^+ and N^+ increase slightly with pressure they conclude that secondary dissociation of NO^+ also occurs. This is further supported by the observation of a "disruption" peak similar to the H_{2-1}^+ and N_{2-1}^+ peaks already discussed, indicating that high speed NO ions certainly do disintegrate. In the light of Kallmann and Rosen's results the writer feels that the first of the above arguments is inconclusive and that the pressure effect may be due to selective absorption in the magnet chamber.

A further consideration of these results throws some light on the similar results in nitrogen. In NO we have the following processes possible in the magnet space

$$\begin{array}{rcr} & \Delta I & \\ NO_a^+ + NO_b \rightarrow NO_a + NO_b^+ & 0 & (1) \\ N^+ + NO \rightarrow N + NO^+ & 5.2 & (2) \\ O^+ + NO \rightarrow O + NO^+ & 4.2 & (3) \end{array}$$

Since the *I.P.*'s are 9.3, 13.5 and 14.5 for NO, O, and N, respectively, process (1) should be very probable and (2) and (3) very improbable since these probabilities are greater the smaller ΔI.

In nitrogen the similar processes involved were

$$\begin{array}{rcr} & \Delta I & \\ N_2^+ + N_2 \rightarrow N_2 + N_2^+ & 0 & (4) \end{array}$$

and

$$\begin{array}{rcr} N^+ + N_2 \rightarrow N + N_2^+ & 2.0 & (5) \end{array}$$

where the *I.P.*'s are 16.5 and 14.5. We might expect, therefore, that processes (1) and (4) would be about equally probable and that (5) would be much more probable than either (2) or (3). Consequently, selective abosrption in the magnet space should be much more effective in altering relative intensities in NO than in N_2. Yet if we compare the curves in N_2 in Fig. 18 with those for NO given above we see that the effect in N_2 is enormously greater than in NO. Remembering that these curves were taken with the same apparatus and similar conditions, we must conclude that selective absorption is inadequate to explain the results in nitrogen, a conclusion in accord with that previously advanced for other reasons.

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* Hogness and Lunn give 9.0 but this is based on 15.4 instead of 15.7 for the *I.P.* of argon.

Negative ions

Hogness and Lunn report the observation of extremely small amounts of NO^-, N^- and O^- the atomic ions being more numerous, but were unable to make any study of their conditions of formation.

Theoretical interpretation

Since no NO^+ spectrum is known we cannot construct *P.E.* curves for any states of the NO^+ ion. Nor can we calculate an *I.P.* from the known states of NO. Mulliken,[53] however, has discussed Hogness and Lunn's results in terms of probable electron configurations and energy considerations. Confining ourselves to the latter our figures are quite different from Mulliken's due to the use of the revised value (5.1) for the heat of dissociation of O_2 which gives us for the heat of dissociation of NO, 6.1 a value not far from the 6.8 determined approximately from band spectra. We have then $6.1+13.5=19.6$ and $6.1+14.5=20.6$ as the lowest possible potentials for the production of O^+ and N^+ respectively. These values are about 1.5 volts below the observed and suggest that the products of dissociation are either in excited states or have kinetic energy. There are low terms in the O I, O II, and N I spectra of the order of two volts above the normal so that it is impossible at present to make a choice between the two explanations.

Carbon monoxide (CO).

Hogness and Harkness[54] found that there were three primary ionization processes in CO,

(1) $CO \rightarrow CO^+$ at 14.1 volts,
(2) $CO \rightarrow C^+ + O$ at 23.0,
(3) $CO \rightarrow C + O^+$ at about 24 volts.

These results were confirmed by Kallman and Rosen[48,20] who make the curious statement that the assumption that all three processes are primary is contrary to that of Hogness and Harkness. They give slightly different ionization potentials, 14, 21.5 and 25 but without detailed experimental data or statement of probable error. The discrepancies between the two sets of values are probably of the order of the accuracy of each set. The previously accepted value for the first *I.P.* was 14.2. Hogness and Harkness found the CO^+ ion of enormously greater intensity than C^+ or O^+.

Negative and secondary ions

Hogness and Harkness found no trace of negative ions. They thought they had evidence for a secondary effect $CO^+ + CO \rightarrow C^+ + CO_2$.

Theoretical interpretation

Applying the Franck-Condon principle to the potential energy curves shown in Fig. 22 we see that the 14-volt ionization should not be accompanied

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[53] Mulliken, Phys. Rev. **32,** 770 (1928).

[54] Hogness and Harkness, Phys. Rev. **32,** 936 (1928).

by dissociation but that neither should transitions to the other two CO^+ states. However, rather small shifts in the values of r_0 or deviations from the Frank-Condon principle would allow transitions to points above dissociation on any one of the three curves. But the energies necessary are 23.3, 23.8 and 23.8, one of which might account for the highest *I.P.*, that for O^+ at 24 to 25 volts but all seem a little high for the other *I.P.*, that for C^+ at about 22. Our conclusion is then that considerable corrections to the potential energy curves show, both as to r_0 and D are needed to bring theoretical predictions into accord with experimental observations. It is beyond the scope of the present work to discuss the electronic configurations of the different states and their relation to the probable products of dissociation.

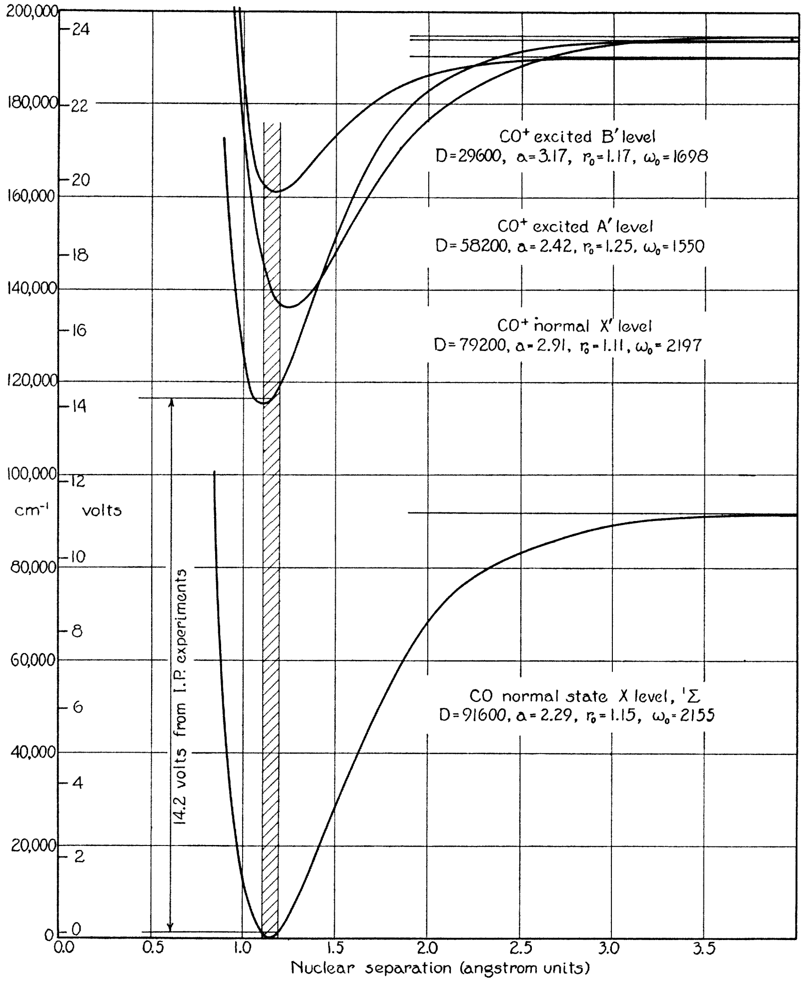

Fig. 22. Potential energy curves for four electronic states of CO. Data for curves are on drawing. All were plotted by the use of Morse's function.

If mere energy considerations be applied, C^+ and O^+ require 21.2 and 23.5 volts respectively for their production. These values are considerably closer to the observations than those obtained above from the potential energy curves.

Hydrogen chloride (HCl).

For a number of years thermo-chemical cycles were constructed on the assumption that the ionization of HCl by electron impact resulted in its dissociation into H^+ and Cl^- ions. The investigation of the truth of this assumption was undertaken by Barton[12] and carried through so thoroughly that no further work has been necessary. He first used the apparatus set up by Smyth for his last work on hydrogen and later an entirely new apparatus with improved resolving power but of similar type. He found that the ordinary first ionization potential at 13.8 volts corresponds to the production of HCl^+ ions and that voltages as high as 78 produced no other primary ions with certainty. He was quite certain that no H^+ ions were so produced. He also observed Cl^+ ions but their intensity seemed to depend on traces of H_2O present and he was not able to determine any critical potential for their production. At high pressures he found a peak due either to $H_2Cl_2^+$ or Cl_2^+ but was unable to study its *I.P.* He observed Cl^- ions produced by very slow electrons either directly or after thermal dissociation of the HCl at the filament.

Since no band spectrum is known for HCl and since no critical potential was observed for any dissociation product no attempt at theoretical interpretation is possible.

Iodine (I_2).

In the interpretation of the results obtained on iodine by Hogness and Harkness[55] the selective absorption effects of Kallmann and Rosen become of major importance for the first time. In this case the relative intensities of both positive and negative ions were studied as functions of pressure and many of the conclusions were drawn from intricate arguments based on such results. It is impossible to correct such arguments by allowing for differential absorption of I^+, I_2^+, I_3^+ in the magnet space; it seems better to state the residuum of definite results and suggest the other possibilities.

Apparently both I_2^+ and I^+ are produced by primary processes at the same potential, 9.5 volts. I_3^+ is produced as a secondary product; no *I.P.* was determined but the probable process is $I_2^+ + I_2 \rightarrow I_3^+ + I$ analogous to the process suggested for the formation of H_3^+. Additional I_2^+ may possibly be formed by a secondary process.

Negative ions

As might be expected from the electronegative character of iodine, negative ions were observed in far greater abundance than in any other gas that has been studied; I^-, I_2^- and I_3^- all occur in quantities comparable to those of the positive ions. Hogness and Harkness believe that only I^- is formed by

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[55] Hogness and Harkness, Phys. Rev. **32,** 784 (1928).

direct electron impact, the electron velocity apparently being immaterial within the range studied (3 to 30 volts). They believe that I_2^- and I_3^- are built up by secondary and tertiary processes. Their reasoning is interesting but not entirely convincing to the present writer.

Theoretical interpretation

Smyth and Compton[56] and, a little later Fruth,[57] showed that the atomic and molecular ionizing potentials were 8.0 and 9.5, respectively, where the absolute values are not very definite but the difference should be accurate to a few tenths of a volt. The spectroscopic heat of dissociation of I_2 is 1.53 volts and the thermochemical 1.6. The agreement between this value and the difference of the *I.P.*'s cited above suggests that ionization in this case may be accompanied by dissociation. We have seen that Hogness and Harkness found that dissociation may take place but does not necessarily do so. No potential energy curve for I_2^+ is available but one may suppose that 9.5 volts represents a transition to a point on the I_2^+ curve very near the dissociation limit.

Potassium vapor (K and K_2).

Ditchburn and Arnott,[10] using method I, studied the ions produced in potassium vapor by three different agencies: (1) photons; (2) electrons; (3) K^+ ions from a Kunsman source. The only stable ion formed by photo-ionization was K^+. Electron impact gave K^+, K^- and probably unstable K_2^+, K_3^+ and K_3^{++} (this last seems very unlikely to the present writer). They determined no appearance potentials but found considerable differences between the results at 36 volts and 100 volts. K^+ ions from a Kunsman source formed stable and unstable K_2^+ ions by attachment.

Carbon dioxide (CO_2).

As soon as we attempt the study of molecules containing more than two atoms our previous difficulties are enhanced. On the expermental side dissociation becomes more probable; on the theoretical side band spectra can offer little assistance. Nevertheless some progress has been made.

Carbon dioxide has been studied by Smyth and Stueckelberg[13] and by Kallmann and Rosen.[48,20] Their results are essentially in agreement and are summarized in Table IV below.

TABLE IV.

Observed product	Appearance potential		Suggested process	Calculated minimum energy required
	K & R	S & S		
CO_2^+	14	14.4	$CO_2 \rightarrow CO_2^+$	
O^+	17	19.6±0.4	$CO_2 \rightarrow CO + O^+$	19.0
CO^+	18*	20.4±0.7	$CO_2 \rightarrow CO^+ + O$	19.7
C^+	29	28.3±1.5	$CO_2 \rightarrow C^+ + O + O$	26.7
(O_2^+)**		20.0±1.0	$CO_2 \rightarrow (CO_2^+ + CO_2) \rightarrow 2CO + O_2^+$	18.9

*Probably direct ionization of CO present from thermal dissociation.
** A secondary product appearing only at high pressure.

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[56] Smyth and Compton, Phys. Rev. **16,** 501 (1920).

[57] H. F. Fruth, Phys. Rev. **31,** 614 (1928).

The values given in the last column are calculated directly from heats of dissociation and ionization potentials. They differ slightly from those given by Smyth and Stueckelberg due to a revision of the heat of dissociation and *I.P.* of oxygen. The values of all such constants used in this paper are collected in Appendices II and III.

Interpretation of results

In spite of the absence of band spectrum data some progress can be made in the interpretation of the above results. We know that carbon dioxide is a straight line molecule with the carbon atom in the middle. It is not surprising, therefore, that we can get CO_2^+, CO^+ and O^+ all at comparatively low potentials but that to get C^+ we must break away both oxygen atoms and ionize the remaining carbon, a process requiring considerably higher energy.

As to the numerical agreement between the observed and calculated values in Table IV it is probably better than we have any right to expect since the experimental errors are estimated and we have made no effort to estimate the error of the calculated values. Since the latter are only minima a downward revision of the constants on which they are based would not be in conflict with these results but any large upward revision could hardly be accepted.

The value calculated for the secondary production of O_2^+ postulates as an intermediate process the formation of an excited CO_2^+ ion. If this is correct it means that CO_2^+ has an energy level, perhaps a metastable one, at 4.5 volts above the normal. The corresponding wave-length is 2750 A. Possibly it is significant that there are strong carbon dioxide bands in this region and that they are very probably due to CO_2^+.

To summarize, it is clear that we have a fairly extensive knowledge of the effects of electron impact on CO_2 and that the observed ionization potentials agree remarkably closely with those calculated from energy considerations.

Nitrous oxide (N_2O) and Nitrogen dioxide (NO_2).

In studying these gases Smyth and Stueckelberg[41] were very much bothered by dissociation, so much so that pressure effects could not be studied and the real origin of some types of ion was in doubt. Nevertheless a number of the possible processes of ionization were observed and their critical potentials measured with reasonable certainty. Without considering the detailed arguments necessary to establish many of the conclusions we will quote them in Table V, below:

The values of the *I.P.*'s given are of accuracy varying between about one volt for those in parentheses to 0.5 volts or better for the others. As in the case of CO_2 the calculated values have been revised since the original paper was written. They are based on heats of formation from Landolt-Börnstein, and the heats of dissociation of N_2, O_2 and NO. They have been checked independently from Mecke's[59] paper using the revised value for O_2.

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[59] Mecke, Zeits. f. Phys. Chem. **B7**, 108 129 (1930).

TABLE V.

Process	Calculated minimum energy required	Observed appearance potential	Remarks
$NO_2 \rightarrow NO_2^+$		(11.)	
$NO_2 \rightarrow NO^+ + O$	12.7		Obscured by $NO \rightarrow NO^+$
$NO_2 \rightarrow NO + O^+$	16.9	(17.7)	
$NO_2 \rightarrow N + O_2^+$	17.4		O_2^+ present but I.P. obscured by NO^+.
$NO_2 \rightarrow N^+ + O_2$	18.9	(20.8)	Perhaps due to NO
$N_2O \rightarrow N_2O^+$		12.9	
$N_2O \rightarrow N_2 + O^+$	15.2	(16.3)	Quite certain
$N_2O \rightarrow N_2^+ + O$	18.2		Obscured by $N_2 \rightarrow N_2^+$
$N_2O \rightarrow NO^+ + N$	14.0	15.3	Reasonably certain
$N_2O \rightarrow NO + N^+$	19.2	21.4	Reasonably certain

It seems that in every case where a definite conclusion can be drawn it is that the process to be expected does occur and at nearly the minimum possible energy. Perhaps the most interesting processes are $NO_2 \rightarrow N^+ + O_2$ and $N_2O \rightarrow N_2 + O^+$ which evidently do occur although the corresponding process $CO_2 \rightarrow C^+ + O_2$ does not. This is in perfect accord with the idea that N_2O and NO_2 are triangular molecules while CO_2 is linear

Water vapor (H_2O).

Peaks due to ions from water vapor have been observed in nearly every positive-ray apparatus ever set up but they have usually been unwanted and have been studied systematically only by Barton and Barlett,[60] Bleakney, and Lozier.[61] As usual, the most common ion is undissociated, the H_2O^+ ion. It is always accompanied by HO^+ and H_3O^+. The ionization potential for the H_2O^+ is about 13 volts but due to imperfect resolution Barton and Bartlett were uncertain of the appearance potentials of HO^+ and H_3O^+ though they thought that of HO^+ was about 13 volts. Recent incomplete and unpublished data of Smyth and Mueller suggest 17.3 volts for this ion and about 13.0 volts for H_3O^+ which is probably a secondary product. H_2^+ and H^+ are also observed and the appearance potential of H^+ has been determined as 19.2 volts by Bleakney; this result is confirmed by Smyth and Mueller's preliminary data. All of these ions are present in quantities small compared to that of H_2O^+ but varying considerably in the experiments of different investigators.

Assuming equal binding energy for the first and second H's in H_2O Mecke gives a value of 4.8 volts for the $H_2O \rightarrow OH + H$ dissociation energy. Using this value for calculation the energy required for the ionization process $H_2O \rightarrow OH + H^+$ is 18.2, one volt lower than the experimental value. Applying a similar argument in reverse to the observed value for the process $H_2O \rightarrow OH^+ + H$ we can calculate the *I.P.* of OH as about twelve volts.

Negative ions

H^- ions have been studied by Bleakney and Lozier[61] with very curious results. They find the electron velocity has to be exactly 6.6 or 8.8 volts for the

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[60] Barton and Bartlett, Phys. Rev. **31**, 822 (1928).

[61] Lozier, Phys. Rev. **36**, 1410 (1930).

H^- ions to appear.* This is in contrast to all other negative ions so far observed including OH^- from H_2O (observed by Smyth and Mueller). The significance of this remarkable result is not yet clear.

A curious effect was observed by Smyth and Stueckelberg[47] who found that the presence of argon, however carefully dried, always brought out the H_2O^+ peak as the pressure was raised. This is presumably due to a collision of the second kind

$$A^+ + H_2O \rightarrow A + H_2O^+$$

and suggests the presence of a higher *I.P.* for water at about 15 volts.

Hydrogen sulphide (H_2S).

With the same apparatus as used by Barton for HCl, Bartlett[62] found H_2S^+, HS^+ and S^+ all formed from H_2S by primary processes at potentials of 10.4 (assumed from Mackay), 16.9 ± 1.5 and 15.8 ± 1.5 respectively. No S_2^+, nor hydrogen ions were reported.

Taking the value 49.9 kg. cal (Landolt-Börnstein) for the heat of the reaction $(S_1)+(H_2)\rightarrow(H_2S)$ and 10.3 (Russell) for the *I.P.* of sulphur we can calculate the energy, 12.5 volts, for the process $H_2S\rightarrow H_2+S^+$ or 16.9, for the process $H_2S\rightarrow H+H+S^+$. It is hard to identify the experimental value 15.8 with either.

If we take the value 19.6 kg. cal for $\frac{1}{2}(S_2)+(H_2)\rightarrow H_2S$ from the L.B. Ergänz. Bd 1. and $S_2\rightarrow S+S$, 90 kg. cal from L.B. vol. II, p. 1585, we get

$$H_2S + 64.6 \rightarrow H_2 + S$$

or in volts, 2.8, and we get

$$H_2S \rightarrow H_2 + S^+ \rightarrow 13.1 \text{ volts} \tag{1}$$

and

$$H + H + S^+ \rightarrow 17.5 \text{ volts} \tag{2}$$

which suggest that the observed process is (1). We cannot calculate any minimum energy for either of the other two ionizations.

Cyanogen C_2N_2

Dorsch and Kallmann[63] studied $(CN)_2$ because they thought it might show a greater degree of dissociation than the diatomic gases they had worked on previously. This proved not to be the case. They found the ions C^+, C_2^+, CN^+, $C_2N_2^+$ in the proportions of 1.5:1:2:12 all produced by primary processes. Using 18.5 volts for the heat of dissociation,

$$C_2N_2 \rightarrow 2C + 2N,$$

8.1 and between 6 and 7, for the heats of dissociation of CN and C_2, respectively, they get theoretical values for some of their observed ionizations. Table VI is taken from their paper.

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* Note added in proof: This effect has been confirmed by Smyth and Mueller.

[62] Bartlett, Phys. Rev. **33,** 169 (1929).

[63] Dorsch and Kallmann, Zeits. f. Physik. **60,** 376 (1930).

TABLE VI.

Process	Calculated minimum energy required	Appearance potential
$C_2N_2 \rightarrow C_2N_2^+$	$J_{C_2N_2}$	13.5
$C_2N_2 \rightarrow CN + CN^+$	$J_{CN} + 2.3$	18
$C_2N_2 \rightarrow C_2^+ + N_2$	$J_{C_2} + 3$	17
$C_2N_2 \rightarrow C_2 + N_2^+$	19	Not observed
$C_2N_2 \rightarrow C^+ + C + N_2$	20.7	22.5
$C_2N_2 \rightarrow C_2 + N + N^+$	26.5	Not observed

They consider the 13.5 volt value the most accurate of their observations but give no estimate of probable error. Their other values they consider probably one or two volts too high. Making this correction to the observed values estimates of 14 and 12 volts can be made for the *I.P.*'s of CN and C_2 from the second and third processes in Table VI.

In a later paper, Kallmann and Rosen[64] study the differential absorption of the different ions from C_2N_2 by filling the magnet space successively with cyanogen, argon, oxygen and ammonia. In using their results to get relative values of ionizing potentials, they assume that strong absorption of an ion occurs if the *I.P.* of the ion is equal to or greater than that of the absorbing gas.* If the ions had no kinetic energy this assumption would be valid. (See the work of Harnwell or of Smyth and Stueckelberg on oxygen) but when the ions have large kinetic energies, as in this case, it is presumably the absolute difference of the *I.P.*'s which determines the probability of a collision of the second kind. That this is the case had previously been maintained by Kallmann and Rosen[20] themselves both on theoretical and on experimental grounds. In polyatomic molecules the possibility of exciting vibration may, in effect, favor the collisions where the *I.P.* of the ion is greater but, even so, we can hardly accept the statement quoted above without qualification. With reservations then, we can give Kallmann and Rosen's list of ionization potentials derived from these experiments

$$J_{NH_3} < 11.2 < J_{C_2} < J_{O_2} < J_{(CN_2)} < J_{CN} < 15.5$$

Assuming J_{O_2} to be about 13.0 these results are in agreement with those already given in Table VI and the subsequent discussion.

Ammonia (NH).

Working with the apparatus used by Barton on HCl, Bartlett[62] found three ions produced in ammonia, namely NH_3^+, NH_2^+ and NH^+ appearing at potentials of 11.2 ± 1.5, 12.0 ± 1.5 and 11.2 ± 1.5. From pressure effects he concluded that only NH_3^+ and NH_2^+ were primary products and NH^+ secondary. Reconsideration of his evidence in the light of Kallmann and Rosen's results on differential absorption makes it less certain that NH^+ is secondary but still probable. No negative and few if any hydrogen ions were observed.

It is interesting to note that the intensity for NH_2^+ is approximately the

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[64] Kallmann and Rosen, Zeits. f. Physik, **61**, 332 (1930).

* "... dass die Ionisierungsarbeit dies Moleküle gleich oder grösser als die des absorbierenden Gases ist."

same as for NH_3^+ grouping ammonia with methane, butane and propane as the only gases where a process involving dissociation has been shown to be as probable as one involving only ionization.

Methane (CH_4).

Hogness and Kvalnes[65] undertook the study of methane in the hope of obtaining the binding energy between the CH_3 radical and the hydrogen atom. Though they failed in this their results are of considerable interest. They found two and only two products of ionization, CH_4^+ and CH_3^+; each was produced by a primary process; they were of about equal intensity; and their appearance potentials were 14.5 volts for CH_4^+ and 15.5 volts for CH_3^+. No negative ions were found.

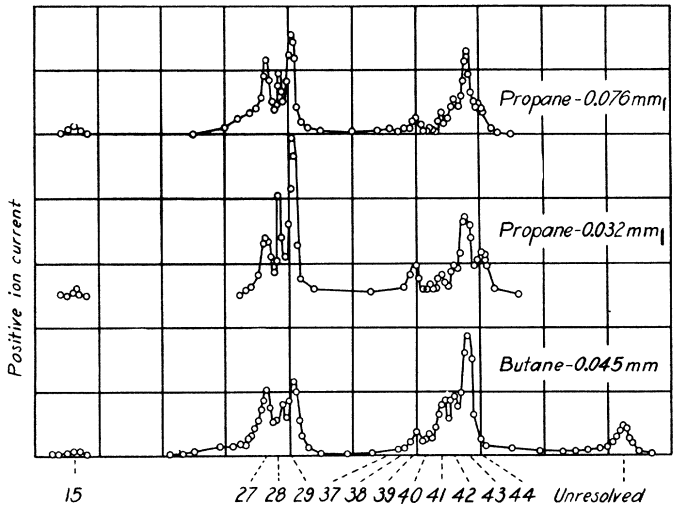

Fig. 23. *e/m* curves for propane and butane. (Stewart and Olson.)

Methane is a symmetrical molecule with the carbon atom in the center and behaves in many respects like a rare gas. It is interesting that the two ionization potentials are so nearly the same but we have no means of calculating them. Of particular interest, too, is the result that the two types of ion-are equally probable. In every other gas studied except propane, butane and ammonia, ionization without dissociation is by far the most probable process.

Propane (C_3H_8) and Butane (C_4H_{10}).

Stewart and Olson[13] have recently studied propane and butane with an apparatus like that of Hogness and Lunn except that they took special precautions to avoid thermal dissociation. They apparently made no appearance potential runs and in fact do not even state at what electron velocity their data were taken. But they found many primary processes of ionization in each case and often those which involved dissociation were as probable or more so than the simple ionization of the molecule. It may be seen from their

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[65] Hogness and Kvalnes, Phys. Rev. **32**, 942 (1928).

curves reproduced in Fig. 23 that it is possible to produce almost any kind of lighter hydrocarbon ion from either propane or butane. But it is interesting to note that they found no hydrogen ions, a result in agreement with that of Hogness and Kvalnes on methane.

IV. General Conclusion

The object of the group of experiments which have been described was to determine the energies required for the production of different types of ion by electron impact. This has been accomplished in a number of cases so that a good deal of light has been shed on the general problem of processes of ionization by electron impact at low voltages. One outstanding result is the infrequency with which dissociation accompanies ionization. For even at the higher potentials where dissociation products are observed they are usually small in numbers compared to the undissociated ion. In no case is the undissociated ion missing and in only one case, iodine, does the atomic ion appear as well as the molecular ion at the lowest ionization potential. Dissociation appears most probable in ammonia and the hydrocarbons.

A second result of great interest is the observation of high speed ions. That high speed atoms are produced by analogous excitation processes seems certain though they have not been directly observed. Such processes must be of tremendous importance in raising the average temperature of gases in discharges or in any phenomena involving the dissipation of the energy of high speed electrons in a gas. For molecular structure, too, these high speed ions have importance. Their study may be of great help in establishing unstable states and explaining continuous spectra.

The theoretical interpretation of the various ionization potentials is fairly satisfactory as far as it goes. Unfortunately there are few cases where data are available for definite theoretical predictions. Apparently the Franck-Condon principle holds pretty well in cases where the potential energy curves are known. But really the situation seems simpler than might be anticipated, for the appearance potentials are approximately those calculated merely from energy considerations. In molecules of more than two atoms this is of greatest importance since no spectroscopic data are available or likely to be so in the near future.

Considering possible future work along this same general line the writer feels that the emphasis should be greatly changed. There are not many more molecules that can be studied in the way we have described without getting into hopeless complications. The future value of this type of work lies rather in the study of fast ions, ionization probabilities and ionization by means other than electron impact or, perhaps, in the study of such negative ions as the H^- observed only at a particular potential in water vapor, and certainly the most interesting of all recent results. Unforeseen theoretical developments might, of course, focus attention on some other phase of the experiments.

APPENDIX I

PRIMARY IONIZATION PROCESSES IN POLYATOMIC MOLECULES.

Gas	Ion observed	Appearance pot.	Probable process	Calculated minimum energy required
H_2	H_2^+	15.9	$H_2 \rightarrow H_2^+$	15.6
	H^+	18.0	$H_2 \rightarrow H^+ + H$	18.
	H_f^+	26.0	$H_2 \rightarrow H^+ + H + \text{k.e.}$	28.
	H_f^+	46.	$H_2 \rightarrow H^+ + H^+ + \text{k.e.}$	46.
N_2	N_2^+	16.5	$N_2 \rightarrow N_2^+$	—
		(15.8)		
	N_2^+ u.s. N^+	24.0	$N_2 \rightarrow N_2^+ \rightarrow N^+ + N$ $N_2 \rightarrow N^+ + N$	23.5
O_2	O_2^+	13. ?	$O_2 \rightarrow O_2^+$	—
	O^+	20.5	$O_2 \rightarrow O^+ + O$	18.6
CO	CO^+	14.1	$CO \rightarrow CO^+$	—
	C^+	23	$CO \rightarrow C^+ + O$	21.2
	O^+	24	$CO \rightarrow C + O^+$	23.5
NO	NO^+	9.3	$NO \rightarrow NO^+$	—
	O^+	21	$NO \rightarrow N + O^+$	19.6
	N^+	22	$NO \rightarrow N^+ + O$	20.6
HCl	HCl^+	13.8	$HCl \rightarrow HCl^+$	
I_2	I_2^+	9.5	$I_2 \rightarrow I_2^+$	
	I^+	9.5	$I_2 \rightarrow I^+ + I$	
	I^-		$I_2 \rightarrow I^- + I$	
K_2 or K	K^+	—	—	—
	K_2^+	—	—	—
	K^-	—	—	—
CO_2	CO_2^+	14.4	$CO_2 \rightarrow CO_2^+$	
	O^+	19.6	$CO_2 \rightarrow CO + O^+$	19.0
	CO^+	20.4	$CO_2 \rightarrow CO^+ + O$	19.7
	C^+	28.3	$CO_2 \rightarrow C^+ + O + O$	26.7
NO_2	NO_2^+	11.	$NO_2 \rightarrow NO_2^+$	
	NO^+	?	$NO_2 \rightarrow NO^+ + O$	12.7
	O^+	17.7	$NO_2 \rightarrow NO + O^+$	16.9
	O_2^+	?	$NO_2 \rightarrow N + O_2^+$	17.4
	N^+	20.8	$NO_2 \rightarrow N^+ + O_2$	18.9
N_2O	N_2O^+	12.9	$N_2O \rightarrow N_2O^+$	
	O^+	16.3	$N_2O \rightarrow N_2 + O^+$	15.2
	N_2^+	?	$N_2O \rightarrow N_2^+ + O$	18.2
	NO^+	15.3	$N_2O \rightarrow NO^+ + N$	14.0
	N^+	21.4	$N_2O \rightarrow NO + N^+$	19.2
H_2O	H_2O^+	13.0	$H_2O \rightarrow H_2O^+$	
	HO^+	17.3	$H_2O \rightarrow OH^+ + H$	
	H^+	19.2	$H_2O \rightarrow OH + H^+$	18.2
	H^-	6.6	—	
		8.8		
	OH^-	—	—	
H_2S	H_2S^+	10.4	$H_2S \rightarrow H_2S^+$	
	HS^+	16.9	?	
	S^+	15.8	?	

Gas	Ion observed	Appearance pot.	Probable process	Calculated minimum energy required
C_2N_2	$C_2N_2^+$	13.5	$C_2N_2 \rightarrow C_2N_2^+$	—
	CN^+	18.	$C_2N_2 \rightarrow CN + CN^+$	—
	C_2^+	17	$C_2N_2 \rightarrow C_2^+ + N_2$	—
	C^+	22.5	$C_2N_2 \rightarrow C^+ + C + N_2$	20.7
NH_3	NH_3^+	11.2	$NH_3 \rightarrow NH_3^+$	—
	NH_2^+	12.0	$NH_3 \rightarrow NH_2^+ + H$	—
	NH^+	11.2	(Secondary?)	
CH_4	CH_4^+	14.5	$CH_4 \rightarrow CH_4^+$	
	CH_3^+	15.5	$CH_4 \rightarrow CH_3 + H$	
C_3H_8	Almost all lighter hydrocarbons but no hydrogen.			
C_4H_{10}	Almost all lighter hydrocarbons but no hydrogen.			

Appendix II

ATOMIC IONIZATION POTENTIALS

Atom	I. P.	Atom	I. P.
H	13.5	O	13.5
He	24.5	N	14.5
A	15.7	C	11.2
Ne	21.5	S	10.3
Hg	10.4		

All values are taken from Russell, Astrophys. J. **70,** 16 (1929) except O which is from Frerichs, Phys. Rev. **34,** 1239 (1929) and H which is from Birge, Table of Physical Constants, Phys. Rev. Sup. **1,** 1 (1929). The values are taken only to the nearest tenth of a volt though in most cases they are known more accurately.

Appendix III

A. HEATS OF REACTION FROM THERMOCHEMICAL DATA (LANDOLT-BÖRNSTEIN)

	Process	Energy Absorbed (in volts)
1.	$[C]^* \rightarrow C$	6.1
2.	$[C] + \frac{1}{2}O_2 \rightarrow CO$	−1.3
3.	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	−3.0
4.	$2[C] + N_2 \rightarrow C_2N_2$	2.9
5.	$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$	.94
6.	$N_2 + \frac{1}{2}O_2 \rightarrow N_2O$	.77
7.	$N_2 + 2O_2 \rightarrow 2NO_2$	.33
8.	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	−2.5
9.	$H_2 + S \rightarrow H_2S$	−2.2
10	$\frac{1}{2}S_2 + H_2 \rightarrow H_2S$	− .85
11.	$S_2 \rightarrow S + S$	3.9

B. MOLECULAR DISSOCIATION

Process	Energy Required	Basis of Calculation
A. $H_2 \rightarrow H+H$	4.4 volts	Band spectra
B. $N_2 \rightarrow N+N$	9.1	" "
C. $O_2 \rightarrow O+O$	5.1	" "
(a) $CO \rightarrow C+O$	10.0	1,2,C
	(11.2)	Band spectra
(b) $NO \rightarrow N+O$	6.1	5,B,C
	(6.8)	Band spectra
(c) $CO_2 \rightarrow CO+O$	5.5	3
(d) $\rightarrow C+O+O$	15.5	c,a
(e) $NO_2 \rightarrow NO+O$	3.4	7,B,C,b
(f) $\rightarrow N+O_2$	4.4	7,B,C
(g) $N_2O \rightarrow N_2+O$	1.7	6,B,C
(h) $\rightarrow NO+N$	4.7	6,B,C,b
(i) $H_2O \rightarrow OH+H$	4.7	8,A,C and assumption of equal binding
	(4.8)	Mecke's value
(j) $C_2N_2 \rightarrow 2C+2N$	18.4	1,4,B
(k) $C_2 \rightarrow 2C$	6.7	Band spectra
(l) $CN \rightarrow C+N$	8.1	" "

* [ ] indicates solid state. All others refer to gaseous state.

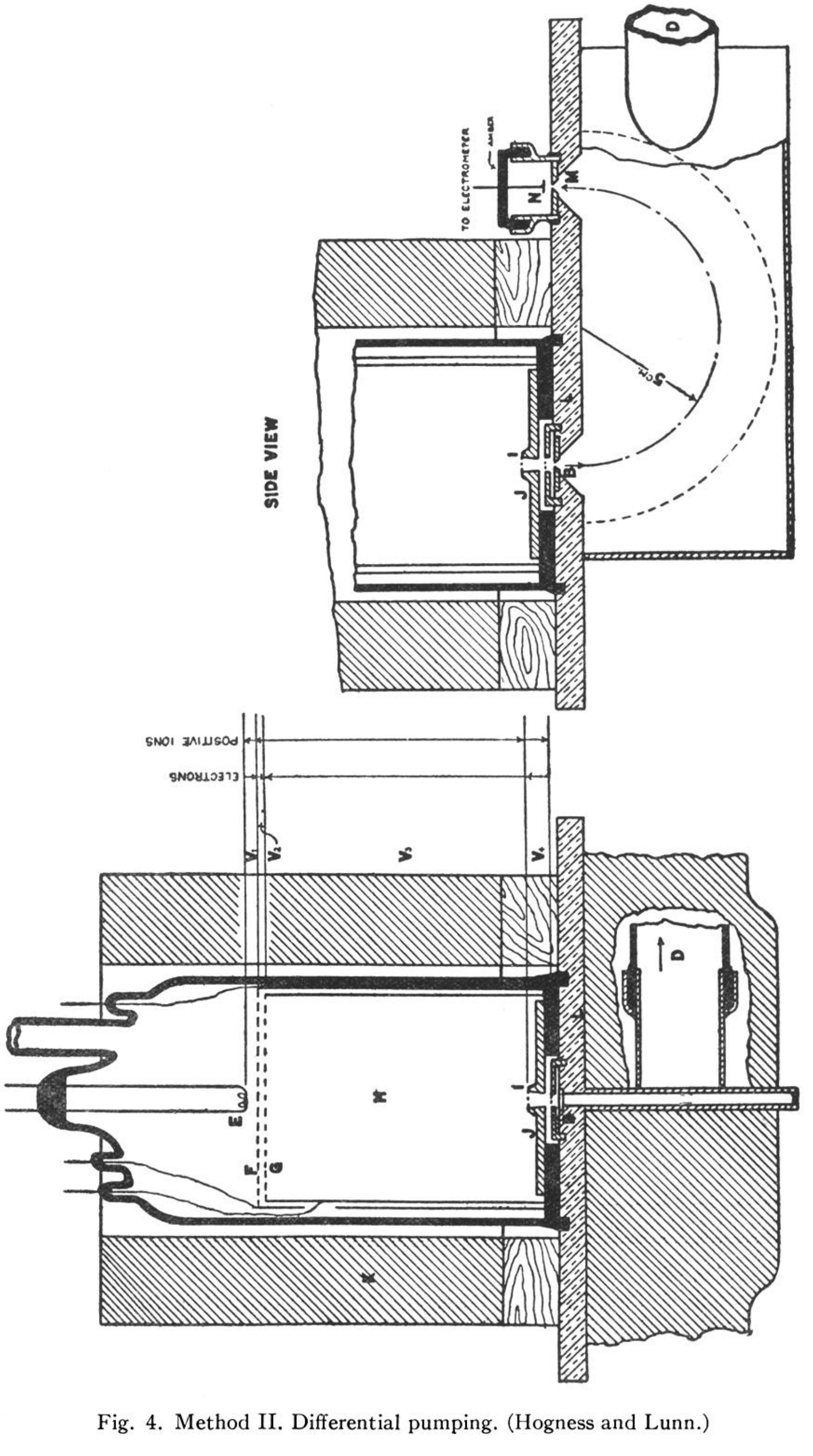

Fig. 4. Method II. Differential pumping. (Hogness and Lunn.)