THE IONIZATION OF NITROGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS

By T. R. Hogness and E. G. Lunn

Abstract

Using an apparatus previously described in which ions formed by impact of electrons of energy (V_1+V_2), or by secondary processes, are pulled from the ionization chamber by the field V_3 and then analyzed magnetically by Dempster's method, the relative numbers of ions of type N_1^+ and N_2^+ are measured for various pressures and voltages. At low pressures (less than 10^{-5} mm) only N_2^+ was observed; as the pressure was increased the percentage of N_1^+ increased regularly and reached 60 at .006 mm. The percentage of N_1^+ was markedly greater when helium at a relatively high partial pressure was present. Below 24 volts, no N_1^+ ions were produced, although N_2^+ ions appeared with (V_1+V_2) greater than 17 volts. These N_2^+ ions must therefore be stable toward collisions, while above 24 volts N_2^+ ions are produced which may be disrupted on collision to form N_1^+ ions. The critical potentials for nitrogen of 16.95 and 24.6, then, correspond to the formation of N_2^+ (stable) and N_2^+ (unstable). N_1^+ ions are therefore produced only by dissociation of unstable N_2^+ ions. The percentage of N_1^+ was found to be independent of the field V_3 from 2.7 to 27 volts, hence the dissociation of an unstable N_2^+ ion is independent of its speed over this range. N_1^{++} ions are not produced at all below 500 volts. The N_2^- ions found by Smyth were present but too weak to be studied. A diagrammatic representation of the electrons distributed in the two types of N_2^+ ion is suggested in accordance with the ideas of G. N. Lewis. Correlation with spectroscopic evidence indicates that the negative bands are emitted by the stable ions.

THE method for the positive ray analysis of the products of electron-impact ionization of gases previously described[1,2] in its application to hydrogen is here used to study the ionization of nitrogen.

Apparatus and method. Electrons from the oxide-coated platinum filament E (Fig. 1) are accelerated by the field (V_1+V_2) into the ionization chamber H. The ions formed there by the primary process of electron impact and by secondary processes, are accelerated by the small field V_3, then by the large analyzing[3] field V_4. Those that pass through the slit B enter the analyzing magnetic field where they are bent through the arc of a circle; the ion beam is focused on to the slit M and the electrometer collecting plate by varying either V_4 or the magnetic field.

[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10,** 398 (1924).
[2] Hogness and Lunn, Phys. Rev. **26,** 44 (1925).
[3] Dempster, Phys. Rev. **11,** 316 (1918).

The nitrogen was prepared by the action of bromine-water on aqueous ammonia and was purified with solid potassium hydroxide, liquid air, and phosphorus pentoxide.

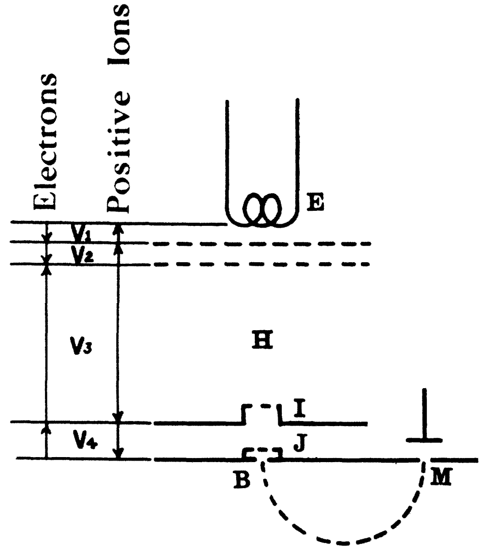

Fig. 1. Diagram showing method of analysis of ions.

Positive ions. N_2^+ and N_1^+ were the only positive ions found. It may be recalled that in the ionization of hydrogen by electron impact the

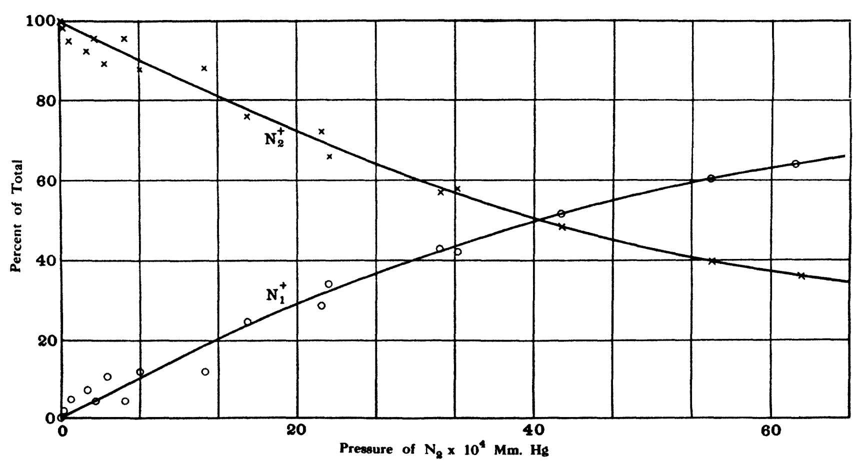

Fig. 2. Percentage of N_1^+ and of N_2^+ as a function of pressure.

formation of the singly-charged molecular ion is the primary process.[4,5,2] That, analogously, the formation of N_2^+ is the primary process and that

[4] Dempster, Phil. Mag. **31,** 438 (1916); Phys. Rev. **6,** 651 (1916).

[5] Smyth, Phys. Rev. **25,** 452 (1925), and references there cited.

N_1^+ is formed by collision of unstable N_2^+ with gas molecules, is shown by Figs. 2 and 3. In Fig. 2 the percentage of N_1^+ and N_2^+ as measured by the relative peak intensities is plotted against the pressure of nitrogen. It is evident that the percentage of N_1^+ extrapolates to zero at zero pressure; N_1^+ can therefore be formed only by secondary collision. Confirmatory experiments failed to show any trace of N_1^+ at pressures of less than 10^{-5} mm, although the intensity of N_2^+ was still large.

The conclusion that N_1^+ is formed by collision is further confirmed by the results of a study of the relative ionic intensities in mixtures of helium and nitrogen. The intensity peaks N_1^+ and N_2^+ were first obtained for a low pressure (Fig. 3A); helium was then mixed with the nitrogen in the reservoir, the partial pressure of the latter being therefore the same

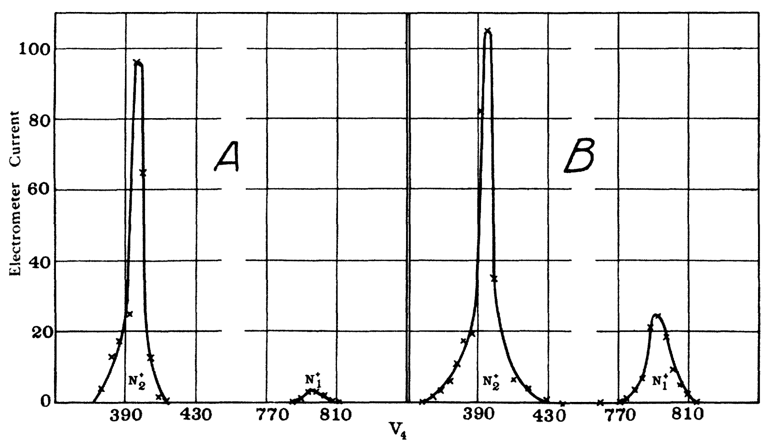

Fig. 3. Peaks obtained (A) with pure nitrogen, (B) with a mixture of nitrogen and helium.

as its previous total pressure, and the intensity peaks were again measured with other conditions the same. The percentage of N_1^+ was appreciably greater (Fig. 3B). The presence of the helium increased the chance of collision of the unstable N_2^+ and its consequent disruption:

$$N_2^+ = N_1^+ + N.$$

The experiments of Figs. 2 and 3 were made with 84-volt electrons.

Now consider, however, the experimental results presented in Fig. 4 in which the percentage of N_1^+ and N_2^+ is plotted against the corrected voltage of the impact electron (V_1+V_2). (The smaller figure relates to another experiment extending to higher voltages.) From 17-24 volts no N_1^+ ions were formed. Similarly, Fig. 5A shows the results of an intensity-peak experiment made with 23-volt electrons at a high pressure, which normally favors the formation of N_1^+, yet no evidence thereof is shown. Fig. 5B was obtained with 84-volt electrons under the same conditions, except that the filament current was reduced to make the N_2^+ intensity

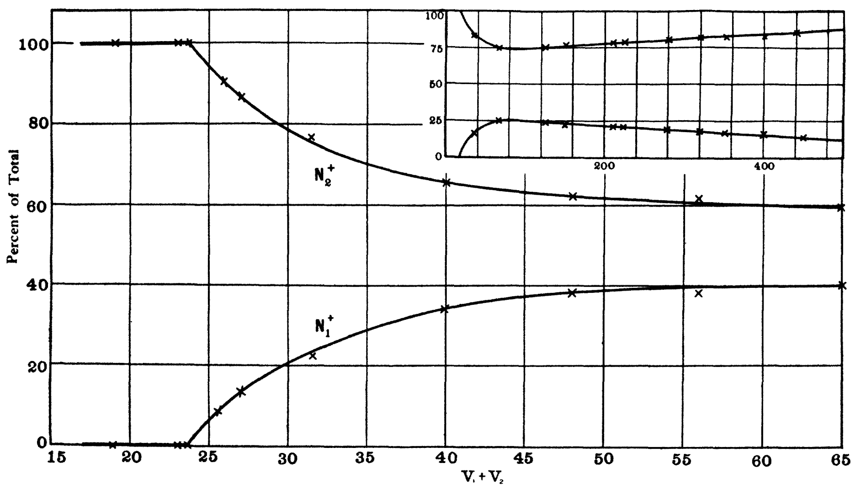

Fig. 4. Variation in the relative numbers of N_1^+ and N_2^+ ions with energy of impact electrons.

comparable with that in Fig. 5A. Now, Figs. 2 and 3 give evidence that N_1^+ is formed only by collision of N_2^+ with gas molecules; Figs. 4 and 5

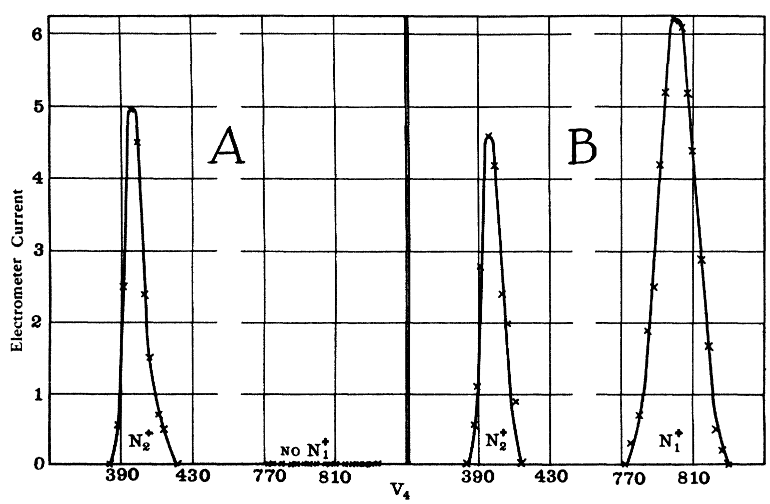

Fig. 5. Peaks obtained (A) with 23-volt and (B) with 84-volt impact electrons.

give evidence that N_1^+ is not formed below 24 volts. There are, therefore, two kinds of N_2^+ ions: the unstable form, which is produced by impact electrons of energy greater than 24 volts and is disrupted on collision with gas molecules; the stable modification, which has energy equivalent to 17-volt electrons and is not disrupted by such collision. The critical potentials of 17 and 24 volts for the formation of the stable and unstable N_2^+ ions respectively are the means of six determinations made in essentially the manner previously described[2] for hydrogen with the use of helium as the calibrating gas. The disappearing-potential curves N_1^+, N_2^+ and He^+ (Fig. 6) when extended to higher voltages approach the same "saturation" intensity; this, as was previously shown, is a necessary condition for the more accurate determination of ionization potentials by this method.

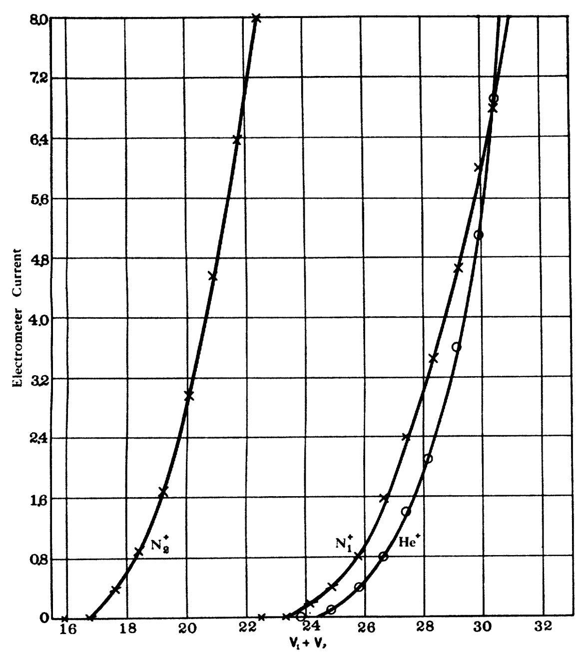

Fig. 6. Variation of intensity of peaks N_2^+, N_1^+ and He^+ with energy of impact electrons.

Study of the relative intensities of N_1^+ and N_2^+ as a function of V_3 showed that over a range of 2.7 to 27 volts the percentage of N_1^+ is independent of V_3. The dissociation of the unstable N_2^+ ion is therefore independent of its speed over this range.

Negative ions. N_2^- was the only negative ion detected. Under all conditions of pressure, filament current, etc., studied, its intensity was very small—too small to make feasible a study of its origin.

Discussion

The principal conclusions of Smyth[6] from his study of the ionization of nitrogen may be briefly summarized as follows: (1) The ions N_2^+, N_1^+ and N^{++} are formed as the result of primary ionization by impact electrons at ionization potentials of (16.9), 27.7 ± 0.8 and 24.1 ± 1.0 volts, respectively; (2) the percentage of N_1^+ and N^{++} ions increases sharply at 350-400 volts; and (3) negatively charged molecular ions are formed. Smyth's conclusion that N_1^+ is formed directly by electron impact is made untenable by the facts presented above. In the light of his subsequent work on hydrogen[5] it seems probable that the ion of apparent $m/e = 7$ which Smyth ascribed to N^{++} is one of the type N_{2-1}^+, namely, an ion N_2^+ which dissociated after it had fallen through the full analyzing field V_4. This view he has since hinted at.[7] The ionization potentials attributed by him to the formation of N_1^+ and N^{++} should have been the same according to this view. Smyth's value of 27.7 ± 0.8 volts should then be considered as spurious, while the 24.1 value agrees with that found by us, within experimental error. Traces of an ion having an apparent $m/e = 7$ were found also in the present work, but only at the highest pressures employed. They could be formed by disruption of N_2^+ ions in the region between the gauge J and the slit B (Fig. 1). The insert of Fig. 4 shows no evidence of the abrupt increase in the percentage of N_1^+ at 350-400 volts found by Smyth.

The several determinations of the critical potentials of nitrogen[8] all show a critical point near 17 volts. The accurate measurements of Brandt[9] gave 16.95 volts as its value, and in addition show two higher potentials of 24.6 and 29.9 volts. In the light of the present work the 16.95 and 24.6 volt potentials are those for the formation of the N_2^+ (stable) and N_2^+ (unstable) respectively.

In studying the synthesis of ammonia from nitrogen and hydrogen in the low-voltage arc, Storch and Olson[10] found an abrupt increase in the amount of ammonia with 23-volt impact electrons. The approximate coincidence of this critical potential with that found above suggests that the sharp increase is due to the formation and disruption of the unstable N_2^+ ion.

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

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

[8] For a summary of these see Compton and Mohler, Bull. Nat. Res. Council, vol. 9, part 1, Critical Potentials.

[9] Brandt, Zeits. f. Physik **8,** 32 (1921). See also Franck, ibid. **11,** 155 (1922).

[10] Storch and Olson, J. Am. Chem. Soc. **45,** 1605 (1923).

Studies of the excitation of the spectra of nitrogen by impact electrons have shown that the negative bands appear at about 20 volts,[11] and that the line spectrum does not appear much below 30 volts.[12] Presumably, then, these negative bands are due to the stable configuration of the N_2^+ ion. The critical voltage of 30 for the appearance of the line-spectrum is in reasonable agreement with the ionization potential for the formation of the unstable N_2^+ ion when the question of spectroscopic intensity is considered.

The effect of helium in increasing the percentage of N_1^+ as noted above is in agreement with the observations of Merton and Pilley[13] on the effect of helium on the spectrum of nitrogen. The difference between the effects of argon and helium in exciting the line spectrum may be ascribed to the

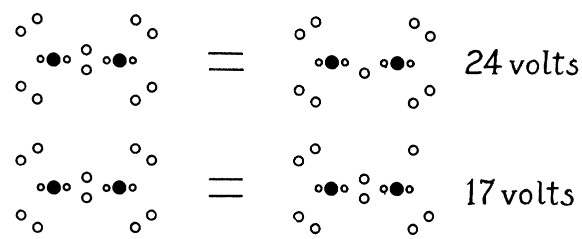

Fig. 7. Diagrammatic representation of the ionization of the two types of N_2^+ ions, in accordance with the ideas of G. N. Lewis.

relatively lower ionization potential of argon and to collisions of the second kind[14] in which argon is ionized by the N_2^+ (unstable) ion

$$N_2^+(\text{unstable}) + A = A^+ + N_2.$$

A probable explanation of the two kinds of N_2^+ ions is that two types of electrons are concerned in the ionization processes here studied. The electron removed at 17 volts is a non-bonding electron, and the N_2^+ ion formed by its removal is stable; the electron removed by impact electrons of greater than 24 volts is, by analogy with the H_2^+ ion, a bonding one, the removal of which forms the unstable N_2^+ ion. Adopting the general scheme of the two-electron bond and the pairing of electrons proposed by G. N. Lewis,[15] the formation of the two types of N_2^+ ions may be represented by the diagrammatic equations given in Fig. 7 where there are

[11] L. Bloch and F. Bloch, Compt. Rend. **170,** 1380 (1920); **173,** 225 (1921); Duffendack, Astro. J. **61,** 209 (1925).

[12] Duffendack, Phys. Rev. **20,** 665 (1922). Duffendack and Duncan, ibid. **23,** 295 (1924).

[13] Merton and Pilley, Proc. Roy. Soc. **107A**, 411 (1925).

[14] Klein and Rosseland, Zeits. f. Physik **4,** 46 (1921); Franck, ibid. **9,** 259 (1922).

[15] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923.

four non-bonding electrons for eachatom in the molecule, all of which are at the same energy level. Any difference of energy in the two pairs in each atom as proposed by Stoner[16] would be too slight to be detected by the present method.

Studies of the dissociation of nitrogen[17,12,18] confirm the chemical evidence as to its stability. Langmuir's experiments on the dissociation of nitrogen by incandescent tungsten led him to estimate the heat of dissociation as greater than 10 volts. This fact, together with the great chemical stability, precludes the possibility of the N_2^+ ion formed at 17 volts dissociating unless the ionization potential of the nitrogen atom is very low. Eucken[19] has recently calculated the heat of dissociation of nitrogen to be 19.1 volts, a value higher than that indicated by the present experiments.

The similarity in the ionization of nitrogen and oxygen found by Smyth[20] naturally suggests that the processes of ionization are similar. Experiments to investigate this are in progress.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA.
September 5, 1925.

[16] Stoner, Phil. Mag. **48,** 719 (1924); also Smith, Chem. and Ind. **43,** 323 (1924).

[17] Langmuir, J. Am. Chem. Soc. **34,** 860 (1912); Langmuir and Mackay, ibid. **36,** 1708 (1914); Langmuir, ibid. **37,** 417 (1915).

[18] Duffendack and Compton, Phys. Rev. **23,** 583 (1924).

[19] Eucken, Ann. der Chem. **440,** 111 (1924).

[20] Smyth, Proc. Roy. Soc. **105A,** 116 (1924).