A MASS SPECTRAL INVESTIGATION OF NITROGEN AFTERGLOW

Thesis

by

Donald Stanley Jackson

Submitted to the Faculty of Graduate
Studies and Research in partial
fulfilment of the requirements for
the degree of Doctor of Philosophy

McGill University

August 1954

ACKNOWLEDGEMENT

The author would like to thank Dr. H.I. Schiff under whose direction the present investigation was undertaken for his most generous assistance and encouragement.

Acknowledgement is also made to Canadian Industries Limited for Fellowships held during the sessions 1951-1952 and 1952-1953.

TABLE OF CONTENTS

DETERMINATION OF THE APPEARANCE POTENTIAL OF THE NEW SPECIES

INTRODUCTION

If a condenser with a capacity of several microfarads is charged to a voltage sufficient to break down the dielectric insulation of nitrogen gas, the resulting discharge causes the gas to glow with a yellow phosphorescence which persists even after the cessation of discharge. This phenomenon, first noted by E. P. Lewis, (62) is called the nitrogen afterglow. One method of producing nitrogen afterglow is to incorporate a cold cathode discharge tube through which nitrogen gas is flowing at a pressure of about one millimeter of mercury as a circuit element in a relaxation oscillator so that a condenser will discharge through the gas at a rate of about ten times per second.

While condensed discharge develops the afterglow with maximum intensity it is also possible to generate nitrogen afterglow using ring discharge produced by electo-magnetic induction when the pressure of nitrogen is appropriately adjusted (94).

Examination of current-voltage relationships for cold cathode discharge tubes containing gases under conditions of normal (that is, non condensed) discharge indicates that nitrogen seems to behave as most other gases. It is not to discharge theory therefore that one must turn for an explanation of the nitrogen afterglow phenomenon.

PROPERTIES OF NITROGEN AFTERGLOW

The yellow phosphorescence of the afterglow dies away only slowly with time. Lord Rayleigh (82) found that when the walls of the vessel were 'poisoned' with metaphosphoric or sulfuric acid the afterglow persisted for 5½ hours.

Effect of Temperature Local heating of a tube through which the afterglow is streaming destroys the afterglow which reappears in a cooler part of the tube below the heated area (58). Reinecke (87) has observed that the afterglow is enhanced by cooling to -70°C but is destroyed on lowering the temperature still further to -180°C.

Effect of Oxygen Oxygen in small amounts exerts a promoting effect on the afterglow. This was first noted by Compte (19) and confirmed (101)(3)(2) in spite of the strong objections of Strutt (98). Later workers have shown however that large amounts (greater than about 0.1%) tend to destroy the afterglow. (81)(45)(115).

Effect of Pressure Several workers have found that sudden increases in pressure increase the brightness of the afterglow but decrease the lifetime (56)(84). From experiments on the effect of pressure on the lifetime of the aftergow Rayleigh concluded that the decay of the afterglow followed a bimolecular law. However Willey (114) has obtained evidence favoring a ternary process.

Spectrum Emitted by the Afterglow The spectrum emitted by nitrogen afterglow is characterized principally by a selection of bands from the first positive system (100). These bands involve transitions from the $B^3\Pi g.$ molecular state, in the 6th, 11th and 12th vibrational levels mainly, to the $A^3\Sigma_u$ state in the 7th and 8th vibrational levels.

Reactivity of Nitrogen Afterglow The glowing gas has been found to react with metals to form nitrides (98) (109) (112) and with hydrocarbons to give mainly hydrogen cyanide along with lesser amounts of other hydrocarbons (93)(96)(97)(38)(10)(102)(105). The reactive nature of the gas has given rise to the term 'active nitrogen'.

THEORIES OF THE NATURE OF 'ACTIVE NITROGEN'

The touchstone of success for any theory of 'active nitrogen' is its ability to explain those properties outlined above. Three main theories have been presented by various workers over the past fifty years.

Ionization in Nitrogen Afterglow and the Molecular Ion Theory

On the basis of experiments in which the afterglow was passed unchanged through highly charged screens Burke (12) concluded that charged particles were not responsible for the afterglow. On the other hand Strutt

(95, 96) detected large currents when the afterglow was passed between parallel metal plates across which a potential difference was applied. He expressed the opinion that the number of charged particles present could not have been generated in the discharge itself but must have originated later as the result of changes occurring in the glowing nitrogen.

Mitra (68)(69)(70)(71) maintained that the energy of active nitrogen resided in molecular ions formed in the discharge, in spite of the general observation that the removal of charged particles from the afterglow does not affect either the rate of decay, the reactivity or the spectrum emitted (95)(116)(117)(85). In the original statement of his theory it was supposed that discharge produces molecular ions in the A' state and that these ions convert to the X' state by radiation of the negative bands of nitrogen. Neutralization of the molecular ions in the X' state may occur through collision with the walls or by three body collisions with electrons and ground state molecules. If neutralization by collision with the walls was prevented by some "poisoning" agent then the three body process might proceed sufficiently slowly to account for the long lifetime of the afterglow. The promoting effect of small amounts of oxygen on the afterglow could be accounted for by the strong electron affinity of oxygen and the increased probability of collisions between positive molecular ions of nitrogen and negative ions of oxygen. Neutralization would presumably produce excited nitrogen molecules in the $C^3\Pi$ molecular level which would then, by emitting the observed second positive bands of nitrogen, revert to the $B^3\Pi g$ level from which the first positive bands originate. Mitra estimated that decay by a three body collision of the type outlined would require that 32.5 seconds would elapse before the glow fell to one tenth of its initial intensity.

Lord Rayleigh (84)(86) showed from experiments in which gold foils were heated by the action of nitrogen afterglow that as much as 12.9ev of energy could be recovered as thermal energy for each nitrogen molecule that passed through the exciter. This work was taken by Mitra (71) as confirming the molecular ion recombination hypothesis since recombination might liberate this amount of energy. However Benson (5) under apparently similar conditions was only able to recover about 0.27ev/molecule of nitrogen and Cyzan (21) has offered an explanation of the large amount of thermal energy reported by Rayleigh based on the existence of a condenser field in the system, electron activation of nitrogen in the vicinity of the foil and energy transfer to to the foil by electrons.

Worley (119) in a study of adsorption by nitrogen afterglow failed to discover the 0-0 band of the molecular ion thus showing that the unexcited ion is not a primary carrier of energy. Mitra then modified his theory by assuming that recombination only occurred when the molecular ion was in some vibrational level other than the lowest. Recent work by Biondi and Brown (6) has shown that the recombination coefficient of the molecular ion is about 13 x 10^7 ions/cc x sec. at a pressure below 5 mm. of Hg. Thus the lifetime of the molecular ion is far too short to account for the relatively long lifetime of the afterglow.

While the original molecular ion theory proposed by Mitra is now generally discredited the work of Kubo and Hamada (59) suggests that the production of molecular ions is essential to the formation of active nitrogen. They found the production of 'active nitrogen' increases suddenly when nitrogen molecules are bombarded with electrons with energies greater than 16 volts. The formation of N_2 from molecular nitrogen requires electrons with energies of 15.5 ev. This led Willey (118) to speculate that molecular ions are the precursors of active nitrogen. Mitra (72) then postulated that dissociative recombination of molecular ions with electrons leads to the formation of molecules in the $B^3\Pi g$ and $A^3\Sigma_u$ states. He later modified this theory by assuming that the process of dissociative recombination leads to the formation of nitrogen atoms in the ^2D and ^2P states (73).

P. A. Constantinides (20) and also Willey and Stringfellow (117) have ascribed the conductivity observed when the afterglow is passed between parallel metal plates to secondary emission of electrons due to the action of the afterglow on the electrodes. Ion traps were used in these experiments in order to eliminate the possibility that discharge plasma might cause interference.

Modern work has confirmed the presence of free electrons in nitrogen afterglow produced by condensed discharge. Benson (5) determined their density from the shift in frequency of a resonant microwave cavity through which the afterglow was flowing. At a distance of twelve inches from the exciter he found one free electron for each 2.5×10^8 molecules in the stream. He found no evidence for the presence of positive ions. Chao and Chang (16) studied the distribution of electron energies along a tube containing nitrogen afterglow and found electrons with energies in excess of twenty volts.

Thus it appears that although ions are undoubtedly present in the discharge region and may even be involved in the formation of 'active nitrogen' they are not likely to be found in the long lived afterglow.

Metastable Molecule Theory

Saha and Sur (91) found that when 'active nitrogen' transferred energy to admixed gases by collisions of the second kind no spectral lines requiring more than 8.5 volts for their production were excited. Since this amount of energy falls short of that which might be recovered from the recombination of two nitrogen atoms it was speculated that active nitrogen was a molecular species in a metastable state whose lifetime was very long. This conclusion was supported by Foote, Ruark and Chenault (29) on the same basis. Further evidence seemed to come from the work of Willey and Rideal (110). They measured the heat liberated in a calorimeter where the afterglow was destroyed by reaction with NO. The mechanism assumed for the reaction was

$$N_2(\text{active}) + NO \rightarrow NO(\text{active}) + N_2(\text{inert})$$

$$NO(\text{active}) + NO(\text{inert}) \rightarrow N_2 + O_2$$

and $2NO + O_2 \rightarrow 2NO_2$

One NO is assumed to be excited per active nitrogen molecule. The amount of NO_2 formed was taken as a measure of the amount of 'active nitrogen'. They concluded that 43.1 Kcal. was recovered per mole of reactive species present in the gas. In view of the assumptions used this can hardly be considered a reliable estimate of the energy of 'active nitrogen'.

The results of these workers were soon shown to be in error. In a later paper Foote et al. (30) disagreed with their former results and gave the energy liberated by 'active nitrogen' as 10 eV. They suggested that these results were more in harmony with the hypothesis that 'active nitrogen' was atomic nitrogen. R. C. Johnson (53) objected to the work of Willey and Rideal since their figure of 43 Kcal/g mole could not be reconciled until the ability of 'active nitrogen' to excite the 2061 line in the iodine spectrum, the excitation of which requires 150 Kcal/mole. This view was supported by Easson and Armour (24) who found that active nitrogen dissociates I_2 and raises it to the 8.4 eV energy level. Willey in a letter to Nature (111) criticized Johnson on the basis that his evidence is only inferred from the ability of active nitrogen to excite other spectra.

Fowler and Strutt (31) found no afterglow when the discharge was such as to emit only the line spectrum of nitrogen, that is, when atoms were definitely present in the discharge tube. They concluded that the concept of a metastable molecular species must be invoked to account for the long lifetime of 'active nitrogen'.

The metastable molecule hypothesis was also supported by Birge (7)(8) and Strutt (99) on the grounds that the spectrum emitted by the afterglow was characteristic only of molecular specis. Birge (9) later withdrew this opinion when Dr. Sponer showed on theoretical grounds that there are objections to the metastability of a molecule with a high vibrational quantum number.

Mulliken in 1924 (74) suggested on theoretical grounds that the $A^3\Sigma_u$ state might be metastable. Kaplan (54) believed he had direct proof of the existence of metastable $A^3\Sigma_u$ molecules in the afterglow. He discovered the (0,6) and (0,5) bands of a new system $A^3\Sigma_u - X^1\Sigma_g$, the so called Vegard-Kaplan system. Muschlitz and Goodman (75) found by direct measurement that the $A^3\Sigma_u$ state had a lifetime of 10^{-4} seconds, which is insufficient to explain the lifetime of the afterglow. In addition Frost and Oldenberg (32) could find no adsorption by metastable molecules in the afterglow.

R. W. Nicholls (76) has indicated a possible process whereby $B^3\Pi_g$. molecules are produced by electron bombardment. He points out that the multiplicity change involved in a direct excitation of the triplet levels from the singlet ground state makes such a transition forbidden.

It is suggested that the primary excitation by collisions between ground state molecules and electrons results in population of the singlet levels $a'\Pi$ and b. Population of the triplet levels can come about by intercombination collisions of the second kind between slow electrons and the molecules in the excited singlet states. Herzberg (46) has proposed 'g' symmetry for the $a'\Pi$ level rendering it metastable, thus raising the excitation life time and making collisions of the second kind more probable.

Atomic Nitrogen Hypothesis

Angerer (1) and Rudy (90) found that the decay of the afterglow follows a bimolecular law. Kneser (56), measuring the decay of the phosphorescence, found that his results agreed with the hypothesis that deactivation occurred by means of collisions between two active atoms and a non reactive particle. Willey (113) suggested that the decay of the afterglow went by a slow three-body collision ($N + N + N_2 \rightarrow N_2'$) followed by two rapid binary impacts. This theory was able to explain the negative temperature coefficient of the afterglow. He suggested that atoms were responsible for the afterglow and were present in proportion 10^{-7} of chemically active molecular nitrogen. B. Lewis (61) found that active nitrogen would only react with atomic hydrogen to give ammonia and claimed this to be evidence that the reactive species in the afterglow was atomic nitrogen. Wrede, (120) using his differential diffusion gauge found that atomic nitrogen was present in the nitrogen afterglow to the extent of about 2 %. Jackson and Broadway (52) using the Stern Gerloch technique found indications of ${}^2P_{\frac{1}{2}}$ atoms. This work has been criticized by Herzberg on the basis that ${}^2P_{\frac{3}{2}}$ and ${}^4S$ atoms should also have been present but were not found.

The idea that the union of nitrogen atoms might account for the duration and reactivity of the afterglow was put forward by Lord Rayleigh in 1911 and developed by Sponer (92) and Bay and Steiner (4). Cario and Kaplan (14) and Cario (13) considered that active nitrogen contains not only normal atoms in the ${}^4S$ state but also atoms in metastable ${}^2D$ and ${}^2P$ states (2.37 and 3.54 volts above the ${}^4S$ ground state respectively) and metastable nitrogen molecules in the $A^3\Sigma_u$ state. Excitation of the visible afterglow was supposed to be due to a collision of the second kind between a molecule in the $A^3\Sigma_u$ state and an atom in the ${}^2P$ state. Theories based on the supposed presence of a metastable $A^3\Sigma_u$ state may be considered untenable on the basis of the recent work by Muschlitz and Goodman on the lifetime of this state.

This theory was also criticized by Helb and Sponer (42) and Herman (44) on the grounds that it violates the Frank Condon principle. These authors proposed a new theory in which the energy of the afterglow is stored partly as energy of dissociation of nitrogen into normal atoms and partly as the excitation energy of metastable ^2D atoms. A ^2D atom is supposed to recombine with a normal atom in the presence of a third body directly into the $B^3\Pi g$ molecular state. Oldenberg (79) has criticized theories of active nitrogen which claim that resonance gives preference to a process whereby the total energy of recombination is converted to electronic energy of a third body such as

$$N + N + N_2 \rightarrow N_2 + N_2\ (B^3\Pi g.)$$

He points out that in certain cases impacts of a second kind show a preferred probability which Frank has attributed to resonance. Resonance is important in the transfer of electronic into electronic energy (Hg + Na) and of electronic into a small amount of vibrational (Hg + various molecules). However the energy of recombination of a colliding pair like N + N is not readily transformed by resonance to electronic excitation of a third body but is more probably distributed over the various degrees of freedom in the collision complex.

Kaplan (55) has proposed a new mechanism whereby a collision between an electron and a molecular ion in the X' level produces two atoms in the ^2P state

$$N_2^+(X') + e \rightarrow N(^2P) + N(^2P)$$

A further reaction involving deactivation by electron bombardment is postulated

$$N(^2P) + e \rightarrow N(^2S)$$

This reaction produces electrons with sufficient energy to excite a molecule in the postulated metastable $A^3\Sigma_u$ state to v = 11 or 12 of the $B^3\Pi g$. state. Aside from the use of the metastable $A^3\Sigma_u$ state the plausability of Kaplan's theory rests on the value taken for the heat of dissociation of nitrogen. In equation (i) the energy available is the ionization energy of nitrogen which is 15.6 volts. If the heat of dissociation of nitrogen is taken to be 7.38 volts then the energy requirement for the process is 14.5 volts. However if it is 9.76 eV the requirement is 16.9 volts and this process becomes implausable.

A. Van de Ziel (104) summarized the various possibilities as to the heat of dissociation of nitrogen and concluded that either 7.35 or 6.33 eV was the correct value. Hagstrum (40) favors the value 7.38 but other modern workers (35)(36)(23) have concluded that the value

9.76 as proposed by Gaydon (33) on spectroscopic grounds is correct.

Cario and Reinecke (15)have proposed a theory in which the value of 9.76 is accepted as the dissociation energy of nitrogen and the recombination of two normal atoms (^4S) in the presence of a third body is considered responsible for delivering the energy of the afterglow of nitrogen. This is similar to a theory proposed by Mitra (73).

Gaydon (34) has found metastability in the $\nu\,{}^1\Sigma$ lower state of the fifth positive band and proposes that the union of two normal atoms might lead to this metastable molecular state which would act as a reservoir for the B level. The conditions for the formation of the $v\,{}^1\Sigma$ lower state are similar to those in the formation of active nitrogen, that is, condensed discharge.

Recently Oldenberg (80) has proposed a mechanism based on the collision of metastable ^2D or ^2P atoms with molecules in the $A^3\Sigma_u$ state to produce molecules in the appropriate $B^3\Pi g$. levels.

A somewhat different mechanism using atoms has been proposed by Reinecke (87). Aware of Oldenberg's objection to ordinary three body collision processes he proposes that the first step is the attachement of a nitrogen atom to a molecule in the ground state to form a 'quasi molecule'. This slightly stable species may then either dissociate or be struck by a second nitrogen atom. Recombination of the two nitrogen atoms would occur in the immediate vicinity of the $N_2(X)$ molecule which could either carry away no energy in which case a $B^3\Pi g$ molecule in the 12th vibrational level would result or it could carry away sufficient energy to give rise to a $B^3\Pi g$. molecule in the 6th vibrational level.

No direct experimental evidence for the presence of nitrogen atoms in the afterglow has yet been found. Kubo and Hamada (57) found no evidence of resonance enhancements that would be expected from collisions of the second kind between metastable nitrogen atoms and foreign gases. Herbert, Herzberg and Mills (43) (See also Discussions of the Faraday Soc. #14 127 (1953)) searched spectroscopically for evidence of the presence of metastable atoms but could find no appreciable amount. This together with a complete lack of any evidence for a metastable molecular state suggested that a direct experimental analysis of the afterglow by a fundamentally different technique should be undertaken. It was therefore decided to explore the possibility of using the Mass Spectrometer to determine the composition of active nitrogen.

MASS SPECTROMETRY

Mass Spectrometry is a method for the analysis of positive ions. There are two main branches to the field, mass spectroscopy and mass spectrometry.

In 1910 J. J. Thompson separated different mass components of a given element on a photographic plate by subjecting positively charged particles produced from the element in a discharge tube to the combined action of parallel electrostatic and magnetic fields. Mass Spectroscopes of this type were further developed by Aston, Bainbridge and others for the accurate determination of isotopic mass. Such instruments are not suited to accurate measurement of the relative abundance of different mass components in a chemical mixture.

At about the time (1919) that Aston was engaged in developing his first mass spectrograph Dempster (22), employing a method first used in 1907 by Classen (17)(18), produced a new type of positive ray apparatus which was well suited to making ion abundance measurements. While Aston's method involved subjecting ions to simultaneous electrostatic and magnetic deflections, Classen's method consisted of obtaining an ion beam having mono-energetic particles and then focusing them through a system of slits around a semi-circular path by means of a magnetic field. Instruments of the type developed by Dempster are called mass spectrometers. During the next twenty years the development and application of the mass spectrometer was spasmodic, although by 1940 several new and improved designs had been published. Up to this time most of the technical advances leading to more reliable instruments had been due to Bleakney. Modern development is chiefly indebted to A. O. Nier who, from 1936 onwards, has introduced many refinements and simplifications. The resulting instruments have found a wide range of application not only in analyses of gases and isotopic abundance measurements but also in the field of kinetics. Of considerable interest is the recent application of mass spectrometry to the study of free radicals.

APPLICATION OF THE MASS SPECTROMETER TO FREE RADICAL STUDIES

A free radical (R) present in a reaction mixture can often be identified by determination of its mass alone. The radical must be introduced into the electron beam in the ion source of the mass spectrometer along a practically collision free path. It is then ionized by electron impact

$$R + e \longrightarrow R^{+} + 2e$$

this process occurring when the kinetic energy of the electrons exceeds the ionization potential of the free radical.

In an extensive exploratory study of reaction intermediates by means of a mass spectrometer Eltenton (25)(26)(27) first pointed out that if atoms or radicals are already present in consequence of thermal or chemical dissociation of the parent molecule, it is possible to select for each radical a value of the electron bombarding energy sufficient for ionization of the radical but insufficient for ionization and dissociation of the parent molecule. Hipple and Stevenson (47) used a mass spectrometer to measure the ionization potential of methyl radicals produced by the thermal decomposition of $Pb(CH_3)$. Robertson (88) using a mass spectrometer of low resolving power and high sensitivity was able to detect methyl and ethyl radicals in the pyrolysis of hdyrocarbons on a hot filament. In all these cases the investigators produced ions by bombarding the free radicals with electrons having energies above the ionization potential of the free radical being studied but below the appearance potential of the ionized radical from the parent molecule.

Measurements using this technique involve working at low sensitivities. Moreover if theenergy spread of the electrons in the ionization chamber is greater than the dissociation energy of the parent molecule adequate sensitivity in distinguishing between free radical ions and similar ions produced by dissociation of parent molecules may not be attainable. Robertson (89) has discussed these limitations in detail. The method is of limited use in the quantitative determination of free radical concentration since little is known about ionization probabilities at low electron energies. Lossing and Tickner (64) have described a technique for measuring methyl radical concentrations using ionizing electrons of about 50 volts as is customary for the usual gas analysis. Later publications (49)(50)(63)(51) showed the applicability of the machine and the technique to the determination and characterization of a variety of free radicals and thus encouraged the belief that a definitive examination of nitrogen afterglow could be undertaken using similar techniques.

EXPERIMENTAL PROCEDURE

APPARATUS

Mass Spectrometer

A 90° sector type mass spectrometer having an analyzer with a 15.0 cm. radius of curvature was used in this work. The ion source was similar in design to that described by Nier (77) but used a drawing-out potential rather than a repelling potential to remove the ions from the electron beam. The pumping arrangement was modified according to Lossing (65) in order to decrease the diffusion into the ionizing chamber of radicals formed by thermal dissociation on the filament. This was done by enclosing the filament chamber completely except for a number of small holes in the plate forming the bottom of the chamber. A number of corresponding but larger holes were made in each succeeding plate down the stack forming a pumping path which ended in the analyzing tube. Each plate of the source was spaced from its neighbors by a single cylindrical glass ring ground to the required height. In this manner the filament chamber could be pumped out directly and maintained at a pressure lower than that of the ionizing chamber itself.

Ions impinging on the collector plate after traversing the analyzing tube of the mass spectrometer were neutralized by electrons drawn from ground across a 10^{11} ohm resistor. The potential difference created across this resistor was then impressed between cathode and grid of a 954 acorn pentode operated as an electrometer tube. This circuit gave a voltage gain of slightly less than unity but considerable current amplification. Further amplification was accomplished by means of a high current gain, negative feedback, D.C. amplifier, the output of which was fed to the Leeds and Northrup Model G Speedomax recorder. This recorder had a 0.8 second time constant for full deflection across its 10 millivolt scale. An Ayrton shunt arrangement allowed a change in sensitivity. The maximum sensitivity of the instrument was such that an ion current of 10^{-14} amperes at the collector produced a deflection of about one centimeter on the chart.

Magnetic scanning was used, the ion accelerating voltage being kept constant at about 2000 volts with a regulation of ± 0.01%. The slits of the ion source and the collector were of such a size as to provide a mass resolution of one part in two hundred. A repeller potential of 45 volts was applied to the collector end for improved peak shape.

Most of the electronic controls were similar to those described by Graham Harkness and Thode (37).

We are indebted to Dr. F. P. Lossing and Mr. G. Ensell for the construction of the leak used in this work. The leak was made in a quartz thimble whose tip was blown out to a thickness of 10-20 microns. The open end of the thimble was blown on to a graded seal and finally sealed to a pyrex tube to form the flow assembly shown in Fig.II. By means of a pair of sharp metal points and a high frequency tesla coil a hole was sparked through the thin tip. The hole, 30 microns in diameter, appeared to be almost perfectly circular with fire polished edges. The distance from the leak to the electron beam was 1.5 cm. By this arrangement the gas could be sampled from the flow system under conditions of low pressure with few collisions.

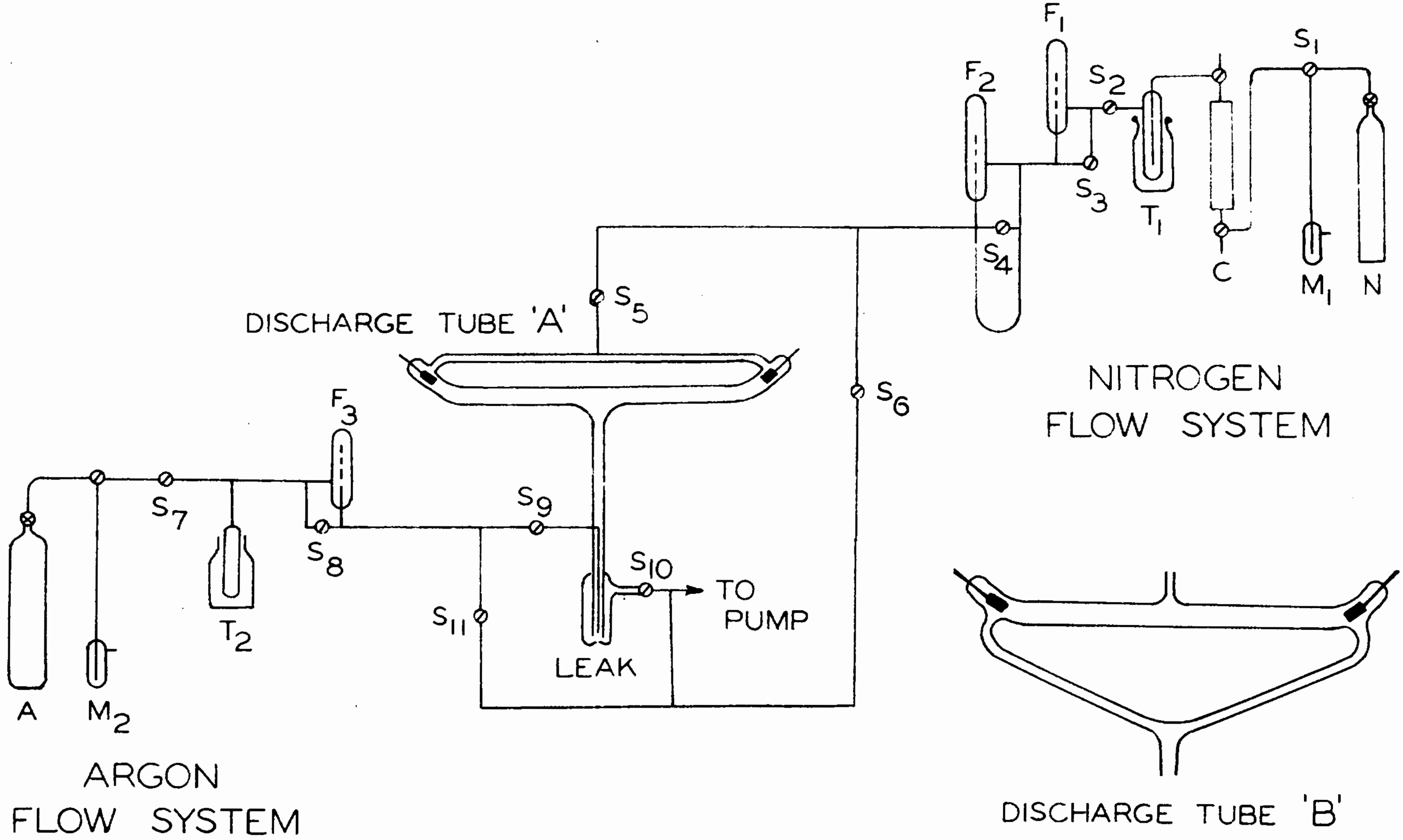
Flow System

The flow system is shown schematically in Fig.I.

Commercial, water pumped nitrogen was drawn from cylinder N and maintained at atmospheric pressure by means of the "blow-off" manostat M. It was purified by passage at 440°C over copper turnings that had been oxidised and then freshly reduced with hydrogen. The turnings were packed in a pyrex tube, 60 cms. in length and 3.5 cms. in diameter, which was encased by the furnace C. The nitrogen then flowed through trap T_1

<u>Figure I</u>

Flow System For Nitrogen And Argon


F$_1$
S$_1$
F$_2$
S$_2$
S$_3$
T$_1$
S$_4$
C
M$_1$
N
S$_5$
DISCHARGE TUBE 'A'
S$_6$
NITROGEN FLOW SYSTEM
F$_3$
S$_9$
S$_7$
S$_8$
S$_{10}$
TO PUMP
S$_{11}$
T$_2$
LEAK
A
M$_2$
ARGON FLOW SYSTEM
DISCHARGE TUBE 'B'

which was cooled with a dry ice-acetone mixture to remove water and traces of organic material. Capillary F_1 served to reduce the pressure from atmospheric to about one or two millimeters of mercury. A change in the size of this capillary varied the pressure and the flow rate of the nitrogen simultaneously. The flow rate was measured by the capillary flowmeter F_2. The nitrogen passed into the discharge tube over the electrodes. After being subjected to discharge the gas flowed down a tube 50 cms. in length and 1.3 cms. in diameter, over the pin-hole leak and thence to the pump. In this way a small central portion of the gas stream could be continuously sampled into the mass spectrometer. A Welch 1405 B Duo-Seal pump was used, which provided a flow rate of 1.03×10^{-5} moles of nitrogen per second when F_1 was adjusted to give a pressure of one millimeter of mercury in the discharge tube.

Also shown in Fig.I is the flow system used for introducing Argon into the mass spectrometer during appearance potential measurements. A sample of welding grade argon was frozen into trap T_2 from the cylinder A. Stopcock S_7 was then closed and air removed from the argon by pumping. The argon pressure could be reduced from its vapour pressure at liquid nitrogen temperature of 13 mm. of mercury to the desired value by means of capillary F_3. It was introduced into the apparatus directly over the leak in order to avoid any spurious effects which might have resulted from its presence in the discharge.

The apparatus from the discharge tube inlet to the mass spectrometer leak and ion source arrangement is shown in greater detail in Fig.II. The glass tubing shown in this part of the apparatus was "poisoned" by drawing up a 10% solution of metaphosphoric acid in such a way that the aluminium electrodes remained dry. It will be noted that the discharge tubes in Figs. I and II are somewhat different in design for reasons which will be discussed in the following section.

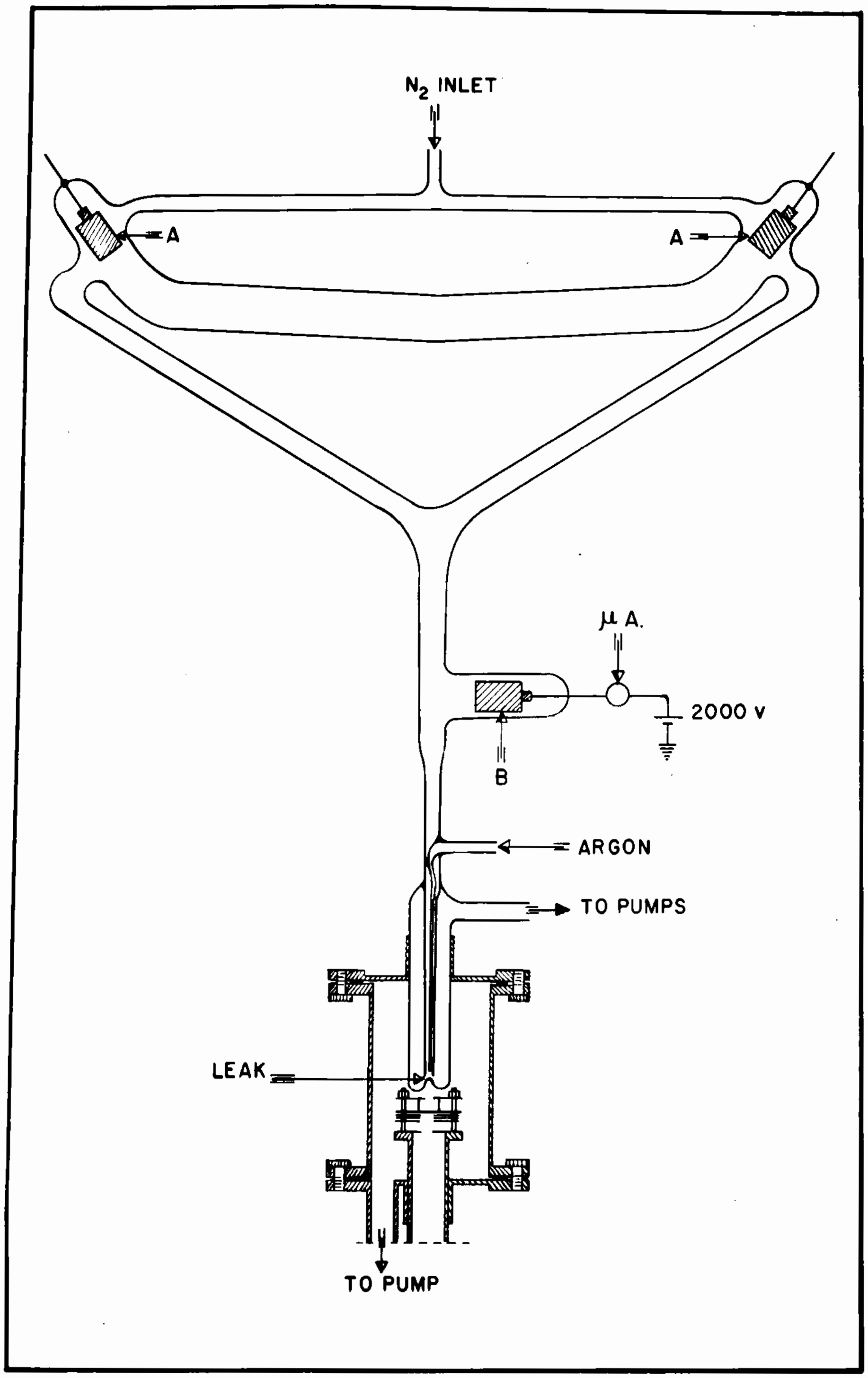
Discharge Tube and Circuit

The electrical circuit used to excite the nitrogen is shown in Fig.III and is identical to that described by Greenblat and Winkler (38), with the omission of the spark gap.

The original discharge tube, shown as 'A' in Fig.I, is essentially of the Wood-Bonhoeffer type (11). When this tube was used, two types of electrical interference were encountered between the discharge circuit and the mass spectrometer. First there was an increase in the background noise of the amplifier. This noise could be reduced to less than twice its normal value by shielding the discharge tube power supply and keeping

Figure II

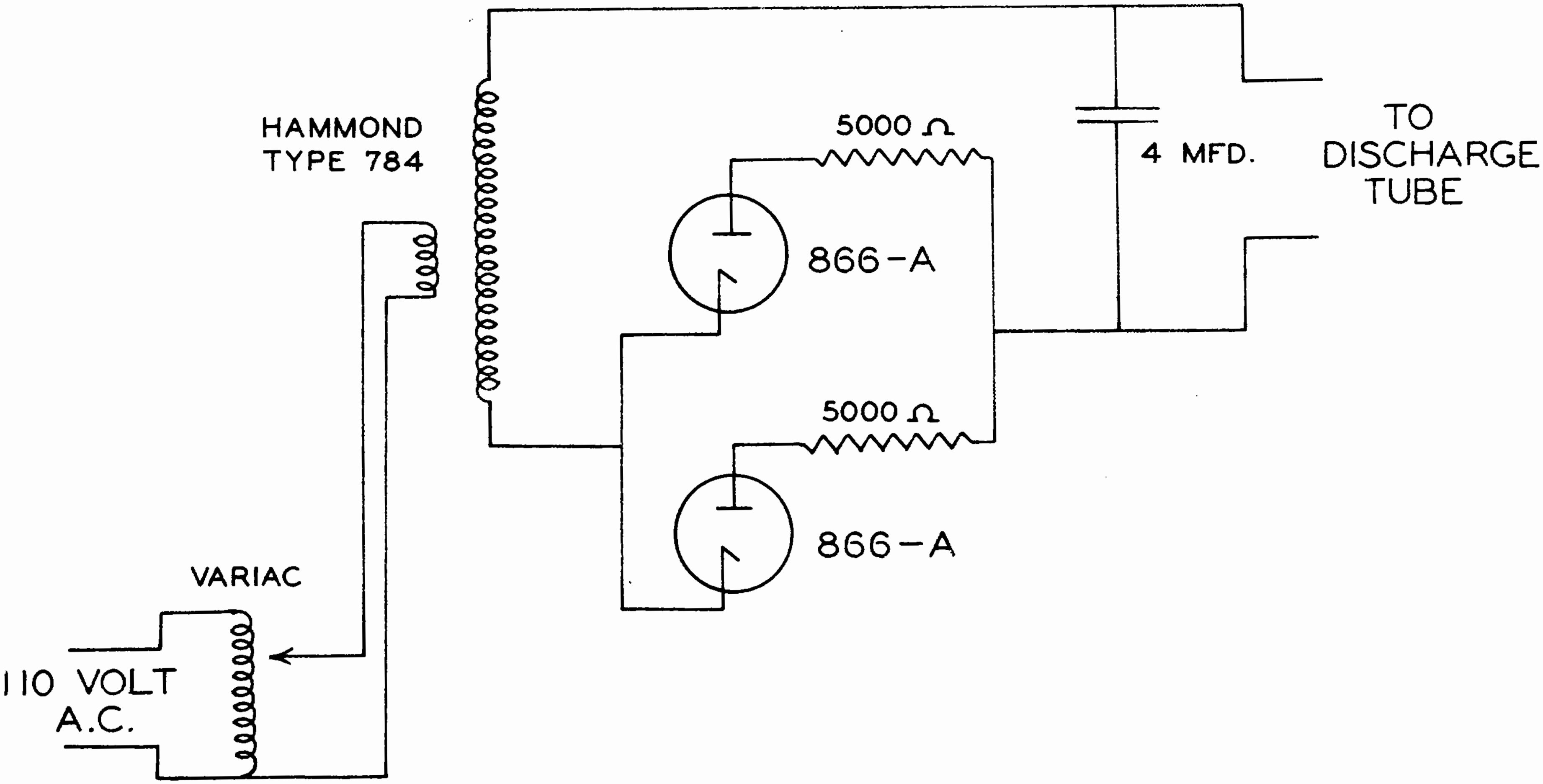
Detail of Pumping Line to Mass Spectrometer



N_2 INLET
A
A
μ A.
2000 v
B
ARGON
TO PUMPS
LEAK
TO PUMP

<u>Figure III</u>

Power Supply For Discharge Tube


HAMMOND
TYPE 784
5000 Ω
4 MFD.
TO
DISCHARGE
TUBE
866-A
5000 Ω
866-A
VARIAC
110 VOLT
A.C.

it at a distance from the mass spectrometer collector plate. There remained however, a distinct instability when the mass spectrometer was focussed on an ion peak, which indicated interference with the high potential on the ion source. In addition, the quartz leak was found to increase in size and to be actually punctured on several occasions. Both these observations suggested that charged particles in the gas stream, presumably originating in the discharge, were being accelerated through the leak to the top plate of the ion source which was 2000 volts above ground potential.

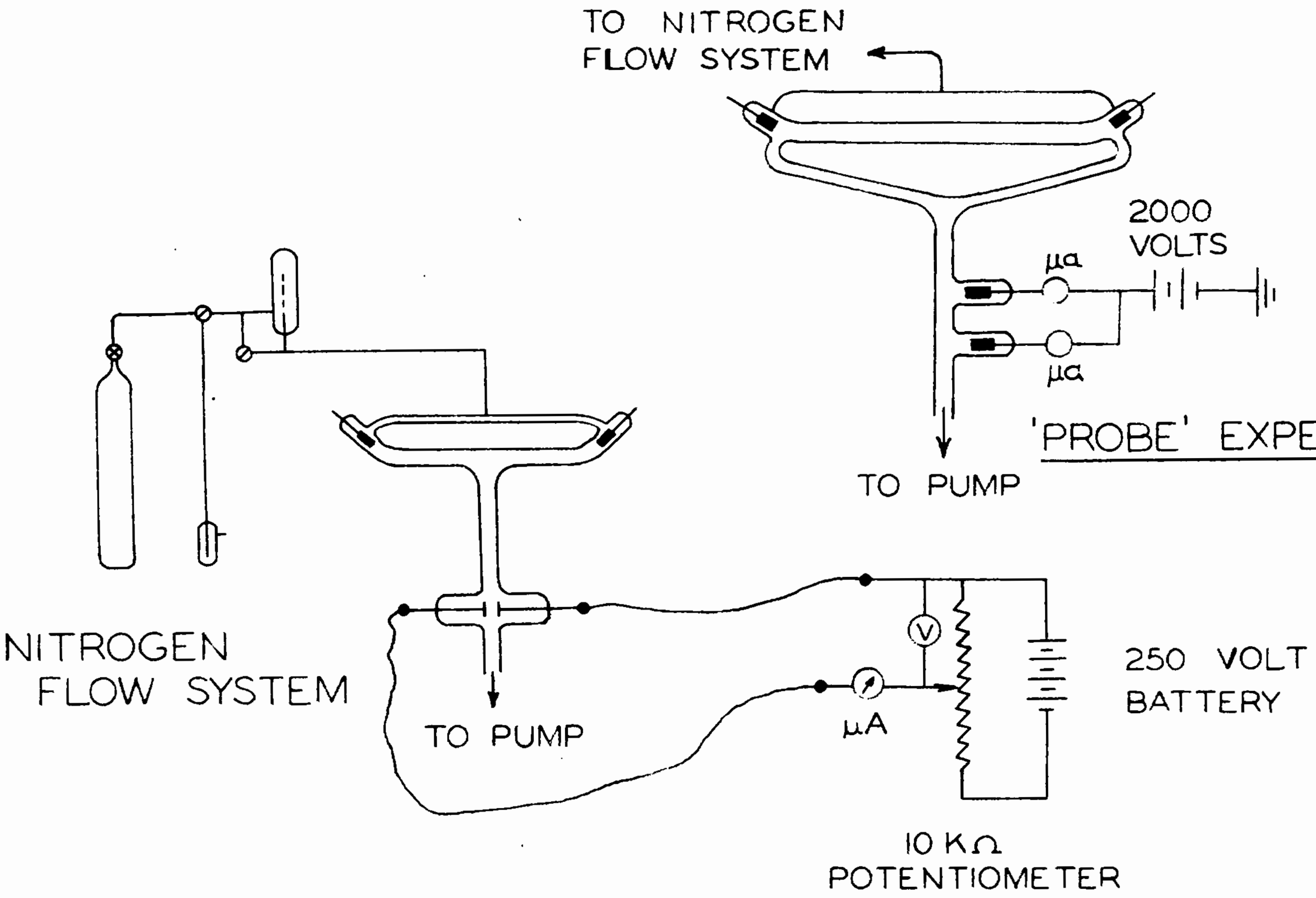
Such electrical interference could not be tolerated if differences between the ion intensities of normal and active nitrogen were to be detected. For this reason experiments were undertaken to detect and determine the nature of any charged particles in the gas stream below the discharge.

CONDUCTIVITY OF NITROGEN AFTERGLOW

A discharge tube of type A shown in Fig.I was connected by means of glass tubing 2.5 cm. in diameter and 18 inches in length to a chamber containing circular plane parallel electrodes 3.5 cm. in diameter and 1.0 cm. apart. The arrangement is shown in Fig.IV. The electrodes of the conductivity cell were made from aluminium

Figure IV

Apparatus For Conductivity Experiments



'PROBE' EXPERIMENT

CONDUCTIVITY APPARATUS

ELECTRICAL CIRCUIT

sheet one millimeter thick and fastened by press seals to tungsten leads which were fused through the walls of the chamber. The discharge tube and pumping line to the chamber were poisoned with metaphosphoric acid.

The nitrogen flow system which was a simplified version of that already described is evident from the diagram. The pressure and flow rate were about one millimeter of mercury and 1×10^{-4} moles per second respectively.

Various voltages drawn from a battery-powered potentiometer were applied between the two electrodes and the resulting current was measured by a microammeter.

In order to determine whether the observed conductivity of the nitrogen afterglow was a property of the afterglow itself, argon gas under similar flow conditions and at the same pressure was passed through the discharge tube. Since argon does not exhibit a long lived afterglow any conductivity observed could be ascribed to electrons originating in the discharge tube. The results are given in Table I and Fig.V.

The current-voltage characteristics of a cold cathode discharge tube depends markedly on whether or not an external source of electrons or ions is present. In the absence of charged particles no current passes

Table I

Current As A Function Of Impressed Voltage In
Conductivity Cell

Figure V

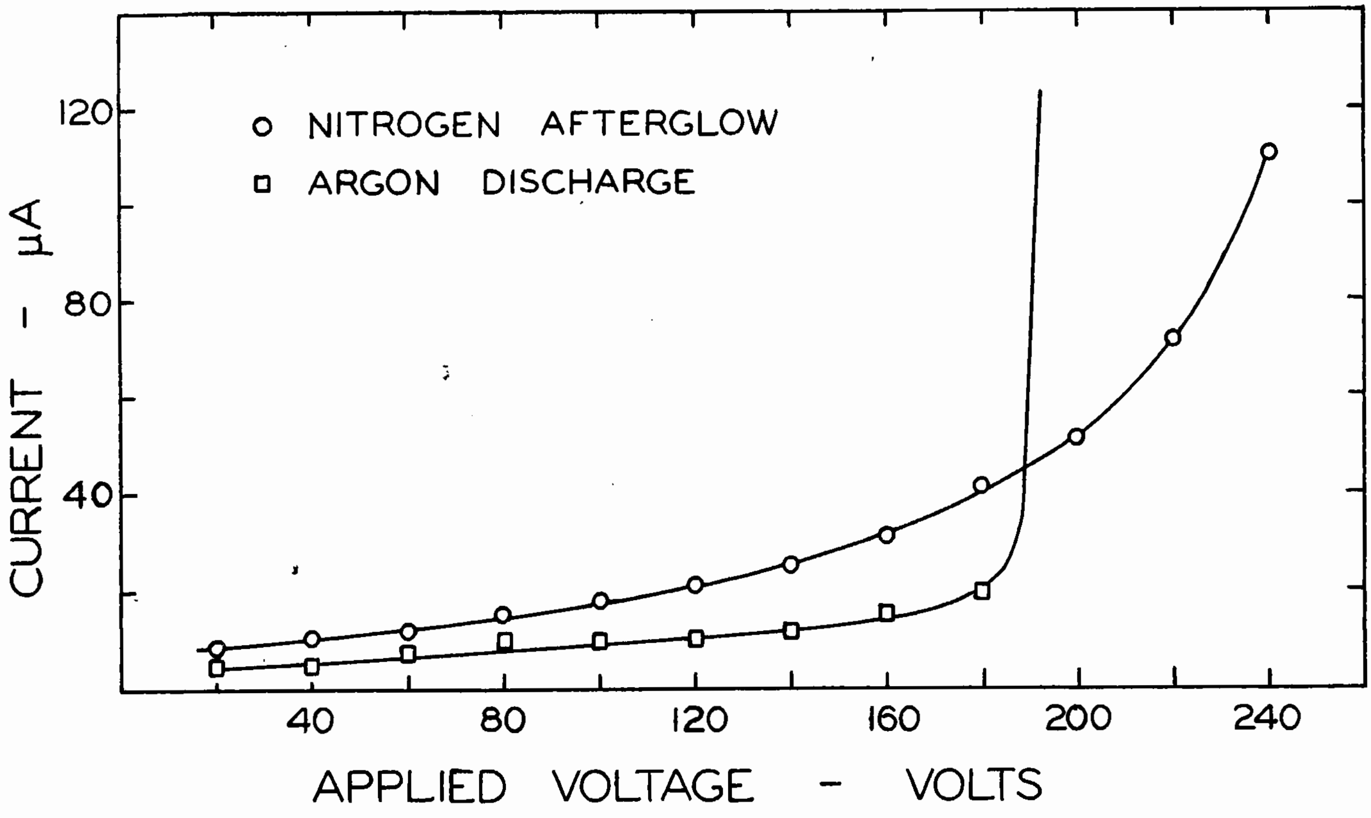
Current As A Function of Impressed Voltage In
Conductivity Cell

TABLE I

CURRENT FLOWING (MICROAMPERES)

APPLIED VOLTAGE (VOLTS)	NITROGEN			ARGON			
	NO DISCHARGE	DISCHARGE ON		NO DISCHARGE		DISCHARGE ON	
		VOLTS INCREASE	VOLTS DECREASE	VOLTS INCREASE	VOLTS DECREASE	VOLTS INCREASE	VOLTS DECREASE
20	0	9	9	0	0	5	5
40	0	11	10	0	0	5	
60	0	12	12	0	0	8	
80	0	15	14	0	0	10	8
100	0	18	16	0	0	10	
120	0	21	19	0	0	10	10
140	0	25	22	0	0	12	
160	0	31	28	0	0	15	
180	0	41	38	0	0	20	20
200	0	51	49	0	270	500	500
220	0	71	70	500	500		
240	0	110	110				

Figure V



until the applied voltage reaches a critical "sparking potential" whereupon it increases rapidly with the voltage. Once the discharge is excited a reduction of the applied potential does not result in zero current at the "sparking potential". Rather the current decreases gradually until the so called "extinction potential" is reached. This behavior was observed for argon (Columns 5 and 6 Table I) but not in nitrogen since the high sparking potential required for this gas was not attainable with our apparatus.

In the presence of charged particles current will flow at all values of the applied potential. This can be seen to occur with both argon and nitrogen which had been subjected to condensed discharge. The actual relationship between voltage and current shown in Fig.V is not exactly the same as those described by Emeleus (28) in which a "saturation" portion was obtained before reaching the rapid increase in the vicinity of the "sparking potential". However "saturation currents" are only reported for static systems while in our experiments the tendency of the charged particles to follow the flow stream might be expected to produce the gentle slope which was observed.

It can be shown on the basis of the ionization theory of conduction that under the conditions where a "saturation current" exists the current passing between the electrodes would be

Current = qe (volume of gas ionized)

where q = no. of charged particles/cc/second

e = charge on particles

If it is assumed that the value of the current at 100 volts corresponds to the "saturation current" obtained in a static system then q can be estimated to be approximately 10^{13} charged particles per cc per second of nitrogen afterglow. At the flow rate of 10^{-4} moles per second this corresponds to a value of about one charged particle per 10^{7} molecules in the gas stream. This value agrees reasonably well with the more accurate estimate made by Benson (5), using a microwave technique, of one particle in 2.5 x 10^{8} molecules. Thus it can be concluded that nitrogen and argon which have been subjected to condensed discharge do indeed contain charged particles, although to a lesser extent in the case of argon.

Several new types of discharge tube were constructed in an attempt to decrease the concentration of these charged particles. The first of these is shown as 'B' in Fig.I. The gas flowed from the centre of the tube to the electrodes where the 'active nitrogen' was withdrawn.

It was hoped that any charged particles formed in the discharge tube would either be destoryed by passing over the electrodes or be repelled by the electrical fields and thus be constrained to remain in the tube. This tube gave the least interference with the mass spectrometer of any design tried. However the electrodes were soon destroyed, presumably as the result of the high temperatures produced by charged particle bombardment.

The next design tried is shown in Fig.II. The gas was introduced above the electrodes and the 'active nitrogen' withdrawn beneath them. As before, it was hoped that charged particles would be destroyed by the electrodes before leaving the tube. The interference between this tube and the high voltage of the mass spectrometer was also quite low. Unfortunately however, this tube seemed to produce less 'active nitrogen' as determined by the mass spectrometer method which will be described later. It may be interesting to note at this point that the intensity of the afterglow was equally strong in the tubes leading from the anode and cathode. This is rather surprising since it might have been expected that the active nitrogen would most likely be formed in the vicinity of the cathode.

Further experiments were conducted to determine the nature of the charged particles and to see whether they could be removed completely by an auxillary electrode. The arrangement is indicated in Fig.IV labelled 'probe' experiment. The 'probe' electrodes were made of hollow aluminium cylinders two centimeters in length, one centimeter in diameter and having a wall thickness of two millimeters.

When voltages up to 2000 volts negative to ground were applied to the 'probe' electrodes no deflection in the microammeters (μa) was observed. This suggested the absence of positive ions. When positive voltages to ground were applied deflections were observed on the upper microammeter. Since negative ions of nitrogen are unknown this indicated that the charged particles responsible for the observed conductivity are electrons, a conclusion which is identical to that arrived at by Benson. At 2000 volts current pulses as high as 20 microamperes were detected. The lower meter however showed no deflection.

A similar 'probe' electrode raised to 2000 volts potential above ground was inserted between the discharge tube and the mass spectrometer leak in the hope that it would eliminate the interference with the mass spectrometer high potential. The arrangement, shown in Fig.II, proved to be quite successful.

THE EFFECT OF PRESSURE ON THE SENSITIVITY OF THE MASS SPECTROMETER

Preliminary experimentation indicated that the optimum pressure at which to operate the discharge tube was in the range 1-2 mm. of Hg. Since detection of the new species appearing in the afterglow was dependent on observations of differences in the ratio of mass 28 and mass 14 ion currents between normal nitrogen and active nitrogen, it was necessary to establish that both the sensitivity of the mass spectrometer to these ions and to their ratio was constant in the region 1-2 mm. of Hg.

Experiments to determine the pressure dependence of the sensitivity were performed using a static system. The nitrogen was introduced into the mass spectrometer from a two litre volume in order to minimize the pressure drop resulting from diffusion of the gas through the leak. The pressure was measured by a McLeod gauge and the ion currents recorded. The experiment was repeated for various pressures of nitrogen in the two litre vessel. Two separate series of experiments were performed with an electron accelerating voltage of 50 volts and a filament emission of 100μa. The ion current at mass 28 due to residual traces of N_2 and CO in the mass spectrometer itself were substracted from the total ion current at mass 28. The sensitivity of the instrument was taken as the deflection in centimeters of the recorder divided by the pressure in mms. of nitrogen producing that deflection. The results are given in Table II and Fig.VI.

The results indicate that both the ratio of the ion currents and the sensitivity of the instrument to the ion currents is constant in the region 1-2 mm. of Hg.

EXPERIMENTAL PROCEDURE FOR MASS SPECTRAL ANALYSIS OF ACTIVE NITROGEN

The basic procedure used in preparing and analyzing 'active nitrogen' will now be described with the aid of Fig.I.

Stopcocks S_6, S_4, S_3, S_2, S_{11}, and S_8 were opened and stopcocks S_5, S_{10}, S_9 and S_7 were closed. The three-way stopcock S_1 was turned so as to connect the atmosphere 'blow off' manostat M_1 to the pump and isolate the cylinder N. The pumping lines, flow meters and furnace were then evacuated through the pump. Stopcock S_2 was then closed and S_1 turned so as to connect the cylinder N to the system. A flow of nitrogen was started through the manostat M_1 and the copper furnace C turned on and allowed to reach operating temperature for

Table II

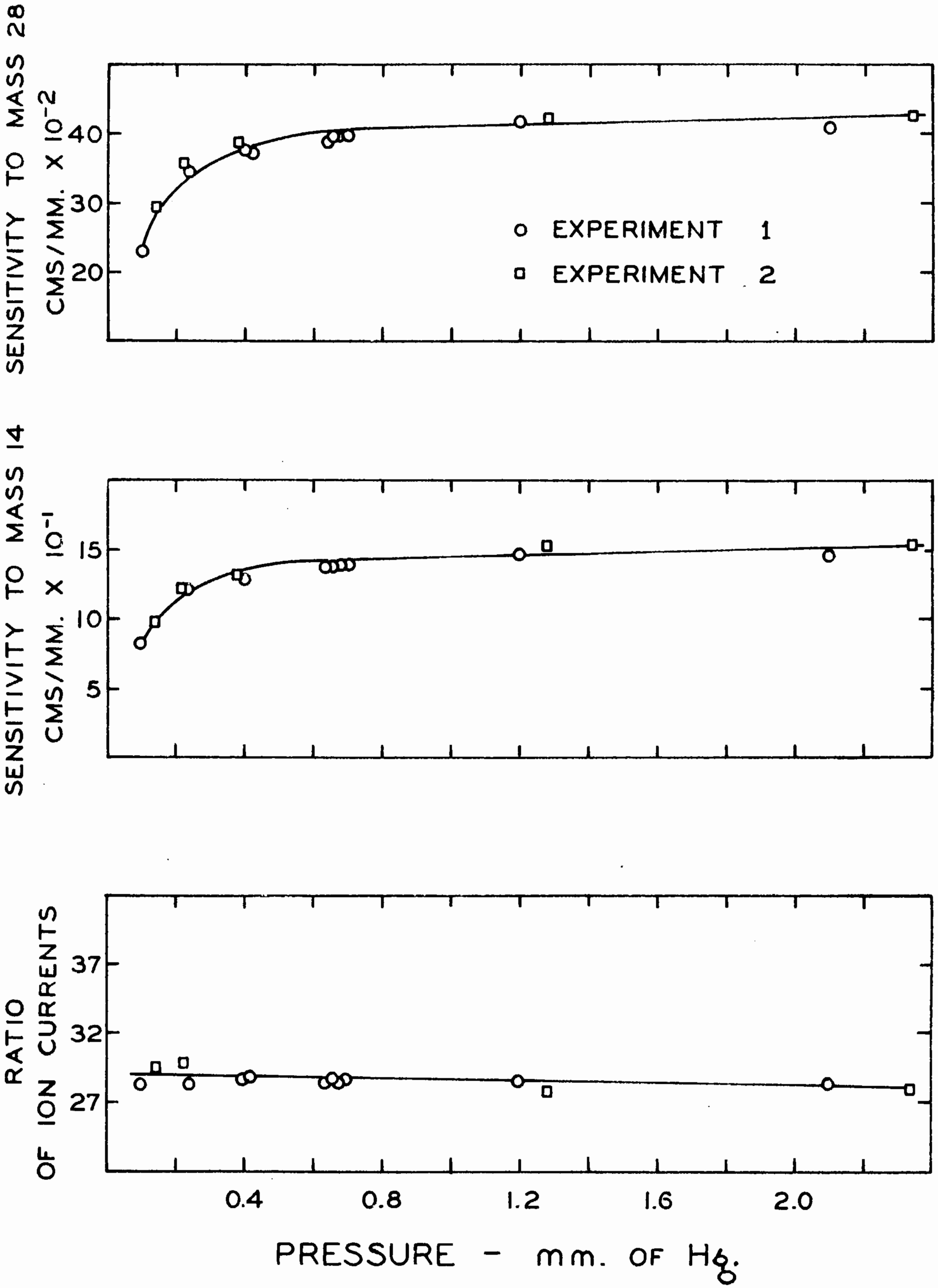
Effect Of Pressure On Sensitivity And Ratio Of Ion Currents

TABLE II

EXPERIMENT NO.	PRESSURE OF NITROGEN IN SYSTEM (MM)	MASS 28 ION CURRENT (CMS. x 10^2) (CORRECTED)	MASS 14 ION CURRENT (CMS. x 10)	SENSITIVITY (CMS/MM.)		RATIO OF ION CURRENTS $\frac{28}{14}$
				MASS 28 x 10^2	MASS 14 x 10	
I	2.10	85.9	30.4	40.9	14.5	28.2
	1.20	49.9	17.5	41.6	14.6	28.4
	0.70	27.9	9.78	39.9	13.9	28.6
	0.68	26.9	9.48	39.5	13.9	28.3
	0.66	26.1	9.06	39.5	13.7	28.8
	0.64	24.9	8.76	38.9	13.7	28.4
	0.42	15.5	5.41	37.0	12.9	28.7
	0.40	15.1	5.26	37.7	13.2	28.6
	0.24	8.22	2.92	34.3	13.2	28.2
	0.10	2.34	0.83	23.4	8.30	28.2
II	2.34	99.9	35.9	42.7	15.4	27.8
	1.28	54.2	19.6	42.3	15.3	27.7
	0.70	28.4	10.1	40.6	14.4	28.1
	0.38	14.8	5.22	38.8	13.7	28.3
	0.22	7.89	2.67	35.8	12.1	29.6
	0.14	4.09	1.39	29.3	9.92	29.4

Figure VI

Effect Of Pressure On Sensitivity And Ratio


SENSITIVITY TO MASS 28
CMS/MM. X 10^{-2}
40
30
20
EXPERIMENT 1
EXPERIMENT 2
SENSITIVITY TO MASS 14
CMS/MM. X 10^{-1}
15
10
5
RATIO
OF ION CURRENTS
37
32
27
0.4
0.8
1.2
1.6
2.0
PRESSURE - mm. OF Hg.

½ hr. Dry ice-acetone mixture was added to the dewar on trap T_1.

Meanwhile if argon was required a flow of gas was started through the manostat M_2 and liquid nitrogen applied to the trap T_2. Stopcock S_8 was closed and argon admitted to T_2 through stopcock S_7. Approximately ten cms^3 of liquid was condensed and then stopcock S_7 was closed. S_8 was opened and any more volatile gases were removed by pumping for several minutes. S_8 was then closed and the argon system was ready for operation.

As soon as the copper furnace had reached operating temperature S_3 was closed, S_2 opened and then S_4 closed. This served to connect the two capillaries in series.

Since it was essential that steady flow conditions be attained before making any measurements the two flow systems were connected through stopcocks S_6 and S_{11} directly to the pump for at least one hour. Nitrogen was admitted through stopcock S_5 to the discharge tube while argon could be admitted directly over the leak by means of S_9. Stopcock S_{10} is then opened while S_6 and S_{11} are closed.

The mass spectrometer was then turned on. The electron accelerating potential was set at 50 volts and the emission from the filament set so that the deflection produced on the recording millivoltmeter could be conveniently measured. When the ion currents were constant they were recorded at masses 14 and 28 for nitrogen and 40 for argon. The discharge tube was turned on and when again constant these ion currents were likewise recorded. The effect of discharge rate will be discussed later. Finally the discharge tube was turned off and the ion currents were again determined in order to safeguard against accidental changes in either the functioning of the mass spectrometer or the flow conditions.

Results

When the discharge tube was excited the normal ratio of the ion currents 14/28 was found to increase. This suggested that there was a new species present in the afterglow which was not present in normal nitrogen gas which contributes to the ion current of mass 14. Under low noise conditions it was found that the decrease in the mass 28 ion current was nearly equal to the increase in the mass 14 ion current. However because of the small remaining electrical interference and the impossibility of keeping flow conditions identical both in the presence and absence of discharge a comparison of the ratio of the 14 to 28 ion currents is more significant than a comparison of the ion intensities themselves. It will be shown in the discussion that the difference in this ratio between normal and 'active nitrogen' is a measure of the amount of new species present in 'active nitrogen'.

Results of experiments to determine the most favorable operating conditions will now be described using the differences in 14/28 ratio as the criterion of performance.

EFFECT OF DISCHARGE RATE ON THE PRODUCTION OF NEW SPECIES

The discharge tube and electrical circuit previously described constitute a relaxation oscillator whose characteristics are given by the equation

$$T = C\ R \log (E - Vb)/(E - Vc)$$

where (T) is the periodic time of the discharges produced in the tube, (Vc) is the sparking potential of the tube, (Vb) is the extinction voltage, (R) is the series resistance, (C) the parallel capacitance, and E is the peak voltage output of the rectifier. By varying C, E and R it is possible to obtain from a given tube a range of oscillations between several kilocycles per second and one discharge every half minute (28). It was found convenient to vary the flash rate by controlling the rectifier output voltage. This was done by using a 'variac' to control the primary voltage of the power transformer.

The discharge tube was of the type shown in Fig.II. A pressure of 1.10 mm. of mercury of nitrogen gas in the discharge tube was found to produce satisfactory operation. The results are shown in Table III in terms of voltage input to the power transformer. The flash rate corresponding to an input of 42 volts was twenty pulses per second.

It appears that flash rate does not exert a very marked influence on the change in ratio of the ion currents. In subsequent experiments the input voltage to the power transformer was set 6 volts above the voltage at which the tube was extinguished.

EFFECT OF PRESSURE ON THE PRODUCTION OF NEW SPECIES

The pressure of nitrogen gas flowing through the discharge tube was altered by changing capillary F_1 in Fig.I which also changed the flow rate through the discharge tube. Strictly speaking then, the results obtained are due to the combined effect of flow rate and pressure. Since the capillary had to be changed for each new pressure setting these experiments extended over a period of several days. Therefore the variations in ratios shown in Table IV also included changes inherent in the mass spectrometer over this period of time.

Table III

Effect Of Flash Rate On The Difference In The Ratio (14/28)

Table IV

Effect Of Pressure On The Difference in The Ratio (14/28)

TABLE III

VOLTS INPUT TO "VARIAC"	ELECTRON ENERGY (VOLTS)	RATIO 14/28 WITH DISCHARGE	RATIO 14/28 WITHOUT DISCHARGE	DIFFERENCE IN THE RATIO
42	50	0.0389	0.0248	0.0141
40	50	0.0388	0.0248	0.0140
38	50	0.0373	0.0248	0.0125
36	50	0.0360	0.0248	0.0112
34	50	TUBE EXTINGUISHED		

TABLE IV

PRESSURE IN THE DISCHARGE TUBE (MM.)	ELECTRON ENERGY (VOLTS)	RATIO 14/28 WITH DISCHARGE	RATIO 14/28 WITHOUT DISCHARGE	DIFFERENCE IN THE RATIO
1.81	50	0.0450	0.0219	0.0231
1.42	50	0.0446	0.0205	0.0241
1.22	50	0.0408	0.0202	0.0206
.90	50	0.0380	0.0267	0.0113
.88	50	0.0326	0.0249	0.0077
.40	50	0.0238	0.0238	0.0

In spite of this it seems possible to assert that the discharge tube should be operated in the region 1-2 mm. of Hg. It was interesting to note that at 0.40 mm. the character of the discharge changed markedly from a pulsed flash to a striated column type of discharge and simultaneously the ability of the discharge to produce a change in the ion current ratios was lost.

DETERMINATION OF THE APPEARANCE POTENTIAL OF THE NEW SPECIES

The increase in the 14/28 ratio suggested the presence of atomic nitrogen in the afterglow but it was necessary to substantiate this by measurement of the appearance potential of the new species.

Introduction

The appearance potential of an ion can be defined as the minimum energy that an electron must possess before it can produce that ion by collision. However a given ion may be produced by several processes each of which may require a different minimum energy. Thus for example the N ion could be formed by electron bombardment of ground state nitrogen atoms by the process

$$N + e \longrightarrow N^{+} + 2e \qquad \ldots\ldots(1$$

The appearance potential for this process could be represented by the expression

$$A(N^{+}) = 1(N) + Ee$$

where $1(N)$ is the ionization potential of atomic nitrogen, ie. the energy difference between the ground states of the normal atom and the ion, and Ee is the excitation energy of the ion, ie. the difference in energy between the ground state of the ion and the excited state in which the ion may actually be formed.

N^{+} ions could also be formed by electron bombardment of nitrogen molecules by the process

$$N_2 + e \longrightarrow N^{+} + N + 2e \qquad .....(2$$

The appearance potential for this process could be represented as

$$A(N^{+}) = I(N) + D(N_2) + Ee + K.E.$$

where $D(N_2)$ is the dissociation energy of molecular nitrogen, Ee is the excitation energy, in this case of both the ion and the neutral atom produced, and K.E. is the kinetic energy which these fragments possess. In many cases Ee and K.E. are small or even zero. The appearance potentials of N^{+} from processes (1) and (2) would then be expected to differ by an amount approximately equal to the dissociation energy of the nitrogen molecule, ie. by about 9.8 eV.

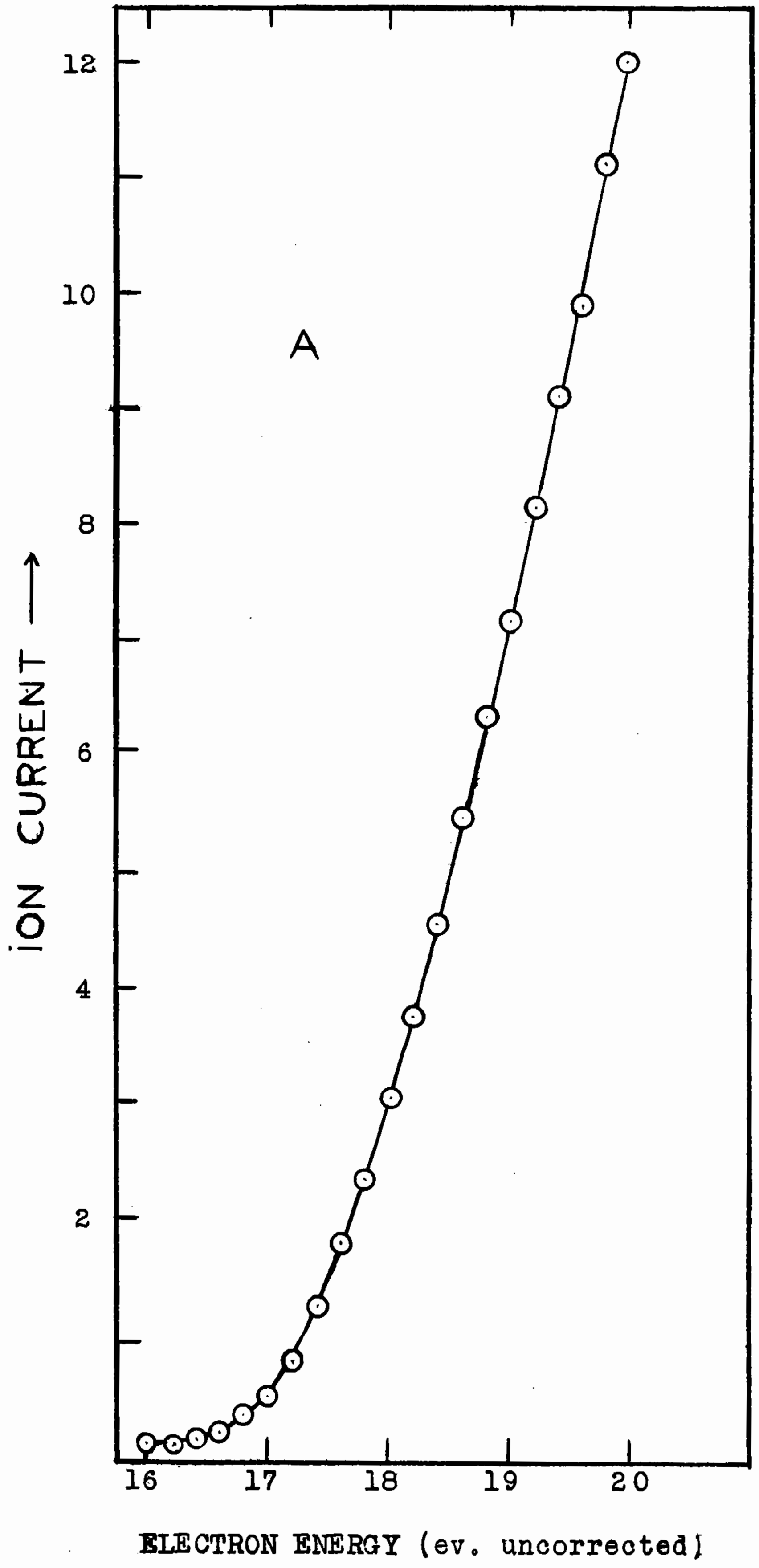
Appearance potentials may be determined from ionization efficiency curves. The ionization efficiency curve is a plot of the ion current due to a single ion species as a function of the potential difference through which the ionizing electrons are accelerated. The curve is obtained by focusing the mass spectrometer on the required ion and recording the ion current arriving at the collector as a function of the electron energy.

An ionization efficiency curve for argon is shown in Fig. VII. It is typical of the type of curve obtained with ions formed by a single process such as (1) or (2). At low electron energies the curve is asympotic to the voltage axis. The origin of this "tail" has been the subject of considerable controversy but is due in part, at least, to the energy spread of the ionizing electrons.

Experiments on the probability of ionization by Compton and Van Voorhis, using electron sources emitting electrons with a spread of energies, have shown that the probability increases with electron energy from a zero value at the ionization threshold (Ei) up to a maximum at about 5 Ei after which it falls off at higher energies. Studies of the way in which the probability of ionization

Figure VII

Ionization Efficiency Curve for Argon



A
ION CURRENT ⟶
12
10
8
6
4
2
16
17
18
19
20
ELECTRON ENERGY (ev. uncorrected)

varies using monoenergetic electrons has given a different picture. For this purpose special precautions were taken to ensure that the incident electron beam was homogeneous in energy. The first work of this kind was carried out by Lawrence (60) and later by Nottingham (78) who refined the apparatus. These workers found that in the case of mercury vapour, ionization set in at 10.4 volts, rose to a maximum at 10.8 volts followed by a minimum at 11.05 volts, while structural details were observed up to about 16 volts. There is at present some difference of opinion concerning the character of the rise of the probability at $E = Ei$. Lawrence and Haupt (60)(41) contend that the probability of ionization is a maximum at Ei and that the curves generally obtained eg. by Compton and Van Voorhis (see also argon Fig. VII) are summation curves of ionization and excitation levels at close lying intervals above Ei. The following is an example of the explanations which have recently been postulated. An electron with $E = Ei$ has a certain finite probability of ionizing. This is a maximum at $E = Ei$ and zero at $E < Ei$. As E increases above Ei the probability of ionization decreases in some sort of exponential fashion. Before the probability has fallen to zero the electron energy reaches a value $E_1 > Ei$ at which ionization by a new mechanism suddenly occurs, which now adds its maximum probability at E_1 to that of the declining probability of the E_1 mechanism. This in turn also falls off. Then another mechanism at a value $E_2 > E_1$ sets in and so on. The potentials corresponding to peaks above Ei ie. E_1, E_2 etc. are called ultraionization potentials. If the electron source has a spread of energies these separate jumps will not be resolved and the curve observed will rise monotonously.

There is a possibility that two distinct processes may give rise simultaneously to the same ion. If the energy requirements for these processes are different the ionization efficiency curve takes on a more complex character. Instead of being a smooth sigmoid, the curve shows a break in the region where the probability of the process requiring the higher energy electrons is decreasing rapidly while the lower energy process is occurring with high probability. McDowell and Warren (67) have observed this in the case of the formation of CH_2 from methane. When such composite curves are obtained they provide evidence of multiple processes.

Below 50 electron volts the ion current at mass 14 occurs exclusively by process (2). Thus the ionization efficiency curve is similar to that shown for argon.

However if 'active nitrogen' also contains nitrogen atoms then process (1) could also contribute to the ionization efficiency curve for mass 14. Since these two processes have been shown to differ in their minimum energy requirements by an amount roughly equivalent to the dissociation energy of molecular nitrogen, that is, 9.8 eV a composite curve similar to that obtained by McDowell and Warren would be expected. Such a composite curve would offer direct evidence for the existence of a new species, while the determination of the minimum energy for the two components of this curve might allow their identification.

There are two main problems involved in determining appearance potentials from ionization efficiency curves. Appreciation and adequate control of the various instrumental factors affecting reproducibility of such curves and the formulation of a satisfactory procedure in the region of onset of ionization are essential for the precise determination of the appearance potential.

Instrumental Factors

In conventional mass spectrometers designed for general analysis the total emission or the trap current is usually maintained constant by regulation of the filament current to compensate for line voltage fluctuations. But such regulation will attempt compensation for the change in emission which would otherwise be produced by a change of the electron accelerating voltage and result therefore in considerable filament temperature change. Filament temperature changes have been shown (Waldron and Wood (107)) to affect the length and shape of the tail of the ionization efficiency curve.

In addition to the energy spread of the electrons emitted from the type of source used in these experiments, the mean energy of the group of electrons effective in producing dissociation of the molecule and ionization of the fragments is significantly different from the energy arising from the known applied accelerating voltage. There are several reasons for this. There is a contact difference of potentials between the filament and ionization chamber. Additional disturbances arise from the fact that the ionization chamber itself is not an ideal field free space.

For these reasons the mass spectrometer is used as a comparator. The apparent appearance potential of an inert gas, such as argon, given by the uncorrected electron energy is compared with the known ionization potential accurately determined spectroscopically. The difference obtained gives the correction necessary at the time of the comparison and under the conditions then existing in the ion source. The calibration gas must be introduced simultaneously with the unknown since it has been found (Waldron and Wood loc. eit.) that an ionization efficiency curve obtained for an experimental gas alone is grossly different from that obtained in the presence of the calibration gas.

Methods of Comparing Ionization Efficiency Curves

Even when two curves have been obtained under the best experimental conditions there still remains the problem of deciding by what method the two curves should be compared. The difficulty of fixing any particular point of theoretical significance about the tail of the ionization efficiency curve where there is a gradual change of gradient, was fully recognized nearly thirty years ago in electron impact studies of the critical potentials of gases. However various methods have been suggested and applied.

Method I:- Critical Slope Method

If the usual ionization efficiency curve is redrawn on a semi logarithmic scale the exponential character of the tail becomes evident. Honig (48) has suggested that the distribution of energies is quasi-Maxwellian and on this basis has arrived at an expression for Ni, the ion current, as a function of electron energy.

If ln Ni is plotted as a function of voltage the curve approaches a straight line and it can be shown that the point where the slope is equal to

$$\frac{d(\ln Ni)}{dV} = \frac{2}{3kT}$$

where k = Boltzman's constant
T = filament temperature

corresponds to the critical voltage at which ionization begins. This method should correct for all but contact potential errors. However the assumptions involved in this method still makes the method essentially empirical. Nevertheless it yields accurate values in many cases.

Method II:- Method of Extrapolated Voltage Differences

This method was suggested by Warren (108). Ionization efficiency curves for the experimental gas and calibration gas are plotted so as to make parallel the approximately linear portions. This is done by multiplying one curve by a suitable constant factor. A curve relating the difference in voltage between the two curves for various values of ion current is then plotted and extrapolated to zero current. Lossing (65) has suggested a method involving comparison of the voltage at which the ion current falls to 1% of its value at 50 volts when the ionization efficiency curve is plotted on a semi-logarithmic scale. These two methods have been shown to be equivalent.

Method III:- Linear Extrapolation Method

This method has the advantage that it avoids comparisons in the region where measurements are less accurate due to small ion currents. It involves adjusting the ionization efficiency curves for the experimental and calibration gas so that the slopes of their linear portions are equal. The linear portion is then extrapolated to the voltage axis.

This method has been criticized by Vought and Mariner and Bleakney (106)(66) on the basis that it assumes first that there is a linear portion to be extrapolated and secondly that the tail length is invariable for all ionization efficiency curves. There is also some danger that fine changes in gradient will be missed using this procedure.

Methods I and II, although theoretically more sound, are limited to the measurement of ions of moderately high abundance. However method III does not suffer from this limitation and was chosen as the method of comparison in this work since only small ion currents were observed for the new species.

Experimental

Apparatus:-

Several features of the mass spectrometer may appropriately be considered here in the light of the difficulties outlined above in the determination of appearance potentials.

In an orthodox ion source, (see Fig. VIII) the electron gun consists simply of filament and anode. Entry of the electrons emitted by an incandescent ribbon filament to the ionization chamber is controlled by a single defining slit at one end of the chamber. The potential difference applied between the filament and the ionization chamber controls the average energy of the ionizing electrons. Electrons pass through a wider slit at the far end of the chamber to be caught in an electron trap which is usually maintained at a slightly higher potential than the ionization chamber itself. The electron beam is usually concentrated by means of a weak magnetic field.

Besides uncertainty due to the contact difference in potential between the filament and the ionization chamber potential disturbances have to be considered in assessing precisely the energy of the ionizing electrons.

Potential disturbances arise from the proximity of high potential fields in the ion gun. They can be minimized but never completely eliminated. In the orthodox Nier source positive ions formed as a result of electron bombardment are removed from the ionization chamber by means of a repeller plate which is kept at a positive potential with respect to the ionization chamber. This positive field exerts a marked effect on the electron beam. This aberration was largely eliminated in this work by withdrawing the ions by means of a small potential, impressed on an electrode located beneath the exit slit of the chamber.

Many mass spectrometers use electrostatic scanning. That is, ions are focused by changing the potential difference through which they are accelerated, before being deflected by a constant magnetic field. The use of this variable electrical field below the ionization chamber introduces electrical field penetration of the type just mentioned which varies with the mass of the ion being focused. This introduces large errors in comparisons of experimental gases with a single reference gas of different mass. Magnetic scanning was therefore used in these experiments. That is, ions were accelerated through a fixed potential and focused by varying the magnetic field. This arrangement introduces a constant error which can be eliminated along with contact potential errors by comparison with a single standard.

Measurement of the accelerating voltage applied to the electrons was made by connecting a Weston model 622, 0-20 ua microammeter in series with appropriate resistances between filament and case of the electron gun to provide full scale deflections of either 60 or 20 volts. The circuit is given in Fig. VIII. With this arrangement it was possible to read on the 0-60 volt range to within ± 0.3 volts and on the 0-20 volt range to within ± 0.1 volts.

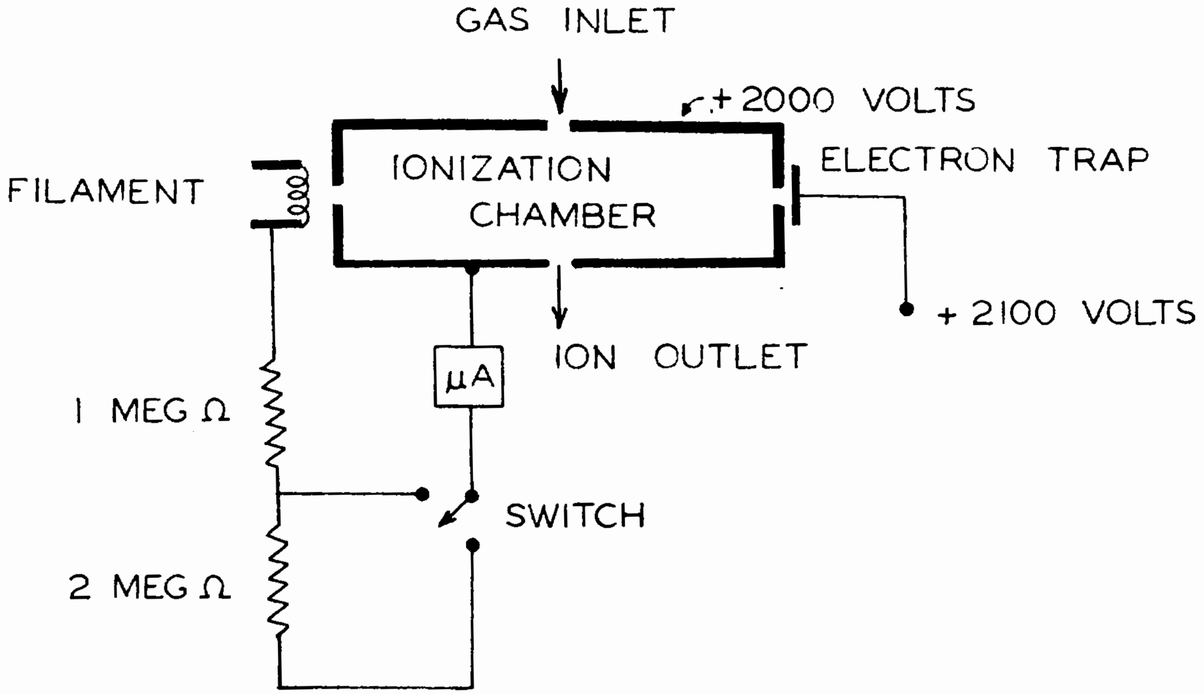
Method of Determining Ionization Efficiency Curve

The flow system shown in Fig.I was set in operation as previously described. The pressure of argon gas in the system was chosen to give an ion current corresponding in magnitude to the increase in the mass 14 ion current when the discharge tube was excited. The ion gun of the mass spectrometer was focused to give maximum ion current when the gas was being bombarded by 60 volt electrons. No difference in focusing was found for the ions of mass 14, 28 or 40. Filament emission was set at a level, usually 70µa, which gave a suitable reading on the recording millivoltmeter.

With the discharge tube off, ion currents at masses 14, 28 and 40 were recorded at a value of 60 volts for the

<u>Figure VIII</u>

Electron Gun And Circuit To Measure Energy Of
Ionizing Electrons


GAS INLET
+ 2000 VOLTS
IONIZATION CHAMBER
FILAMENT
ELECTRON TRAP
+ 2100 VOLTS
ION OUTLET
μA
1 MEG Ω
SWITCH
2 MEG Ω

for the electron accelerating potential. The accelerating voltage was then lowered in steps of a few volts at first and finally in 0.2 volt steps as the ion current became small. Ion currents were recorded till they dropped to 0.05% of their values at 60 volts. The accelerating voltage was readjusted to 60 volts and the ion currents were compared with the initial readings.

The discharge tube was then excited. Ion currents for the three m/e ratios were redetermined as the electron energy was lowered and finally the 60 volt value was again checked. A typical set of readings are shown in Table V.

Calibration Curve

Lossing (65) has pointed out that the differences between the observed and the spectroscopic appearance potentials are not necessarily the same over a range of appearance potentials. Therefore before the argon appearance potential can be used to correct the values obtained for the other ions it was necessary to know the relation between apparent and spectroscopic appearance potentials.

This was determined by preparing a mixture of argon, helium and nitrogen. The mixture was admitted at a pressure of 30-40 microns to the leak of the mass spectrometer which was connected to a two litre ballast volume. The ion currents at masses 40, 4, and 28 were

(follows page 60)

determined at an electron accelerating voltage of 60 eV. This applied voltage was decreased to within one or two volts of the potential at which the ion current had dropped to one percent of its value at 60 volts. Ion intensities were recorded as the accelerating voltage was decreased in steps of 0.2 volts until they had decreased to about 0.5% of their initial values. A similar experiment was performed for a mixture of argon and ethane using the ion intensities at mass 28 for the latter. The ion currents were normalized by assigning an arbitrary value of 100 to the ion currents at 60 eV. The data thus obtained is given in Table VI. The ionization efficiency curves from these results were quite parallel and the linear extrapolation method was used to determine the apparent appearance potential.

Table VII shows the comparison between the apparent appearance potentials and the spectroscopic ionization potentials. Figure IX shows a plot of these values against one another. It will be seen that a straight line was obtained having a slope of unity with a maximum deviation not greater than 0.2 eV. This indicates that a single correction based on the argon value as standard could be used without introducing an error greater than this. Periodic repetitions of this experiment

Table VI

Normalyzed Ion Currents As Functions Of Electron Energies For Calibration Gases

Table VII

Difference Between Spectroscopic And Apparent Appearance Potentials For Calibration Gases

TABLE VI

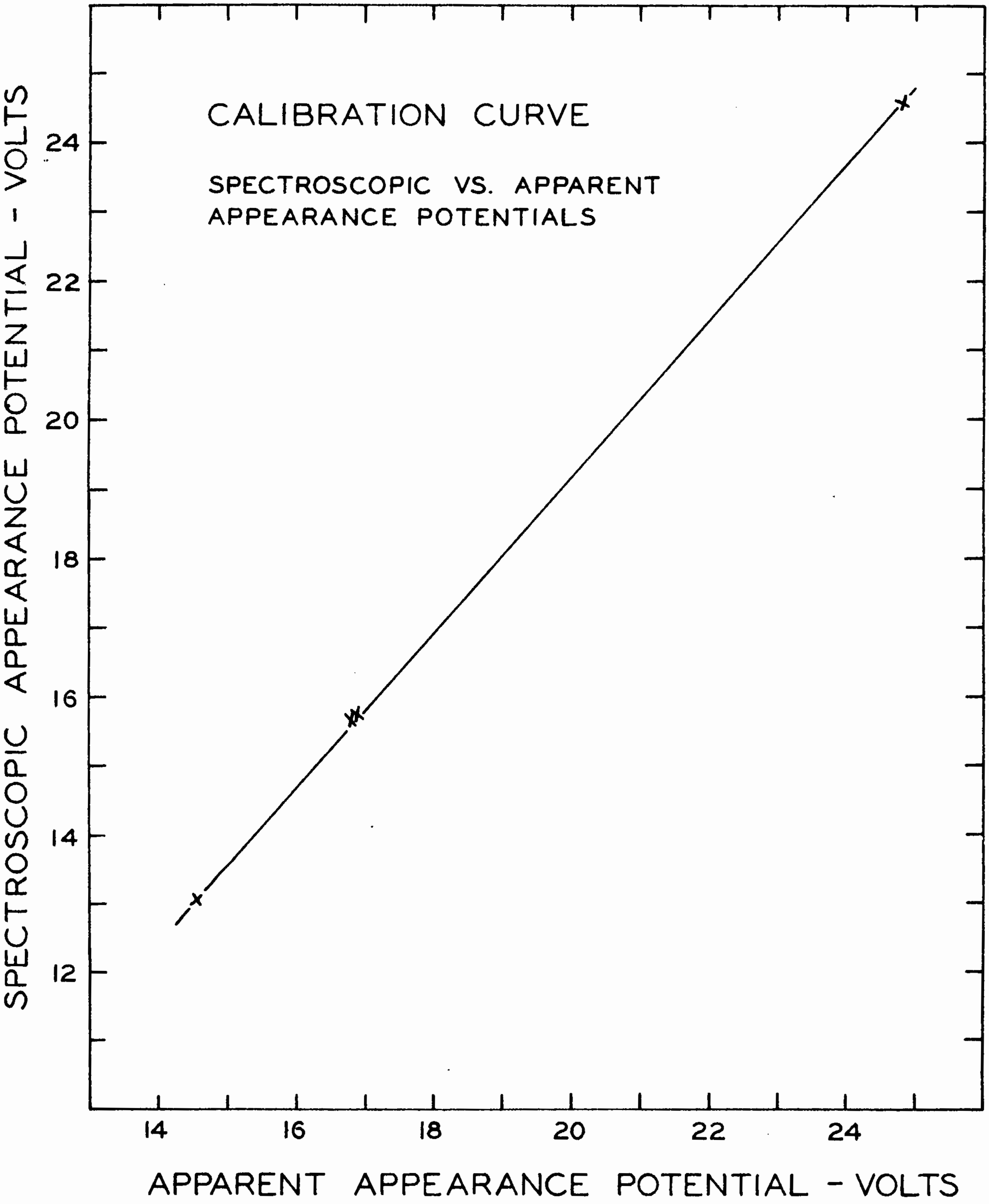
ELECTRON ENERGY VOLTS	Ion Currents (CMS.) NORMALIZED				
	MIXTURE I		MIXTURE II		
	ETHANE (MASS 28)	ARGON (MASS 40)	NITROGEN (MASS 28)	HELIUM (MASS 2)	ARGON (MASS 40)
60	100	100	100	100	100
25.8				3.91	
25.2				1.43	
24.9				0.59	
24.6				0.27	
17.4		3.13	2.15		2.16
17.2		2.32	1.50		1.26
17.0		1.42	.99		0.87
16.8		0.90	.73		0.62
16.6		0.52	.59		0.52
13.8	5.28				
13.6	4.02				
13.4	3.06				
13.2	2.15				
13.0	1.47				
12.8	0.92				
12.6	0.50				

TABLE VII

SUBSTANCE	APPARENT APPEARANCE POTENTIAL	SPECTROSCOPIC APPEARANCE POTENTIAL	DIFFERENCE (VOLTS)
ETHANE	12.82	11.76	1.06
ARGON	16.90	15.75	1.15
HELIUM	24.89	23.56	1.32
NITROGEN (28)	16.80	15.70	1.10

Figure IX

Apparent Appearance Potentials As A Function Of Spectroscopic Appearance Potentials


CALIBRATION CURVE
SPECTROSCOPIC VS. APPARENT
APPEARANCE POTENTIALS
SPECTROSCOPIC APPEARANCE POTENTIAL - VOLTS
24
22
20
18
16
14
12
14
16
18
20
22
24
APPARENT APPEARANCE POTENTIAL - VOLTS

produced essentially identical results.

Results of Ionization Efficiency Measurements on 'Active Nitrogen'

Table V shows the normalised ion efficiency measurements for masses 28 and 14 of nitrogen obtained with and without discharge, along with those for argon, measured simultaneously. Fig.X shows a curve for argon and mass 28 plotted on a semilogarithmic scale in order to include all the data. The circles represent values obtained in the absence of discharge while the crosses represent values obtained when the discharge was excited. No differences are seen as the result of discharge.

Figure XI again shows the argon curve along with the curves at mass 14. The mass 14 curve obtained when the discharge was excited is markedly different from that for normal nitrogen, thus providing concrete evidence for the existence of the new species.

The differences between the two mass 14 curves should be a measure of the contribution of this new species. These differences are shown in Table V as $\Delta 14$ and are plotted with normal coordinates on Fig.XII, along with argon data for comparison purposes. An inflection will be noted in the $\Delta 14$ curve which indicates that this curve is itself composite and therefore must no page 66

TABLE V

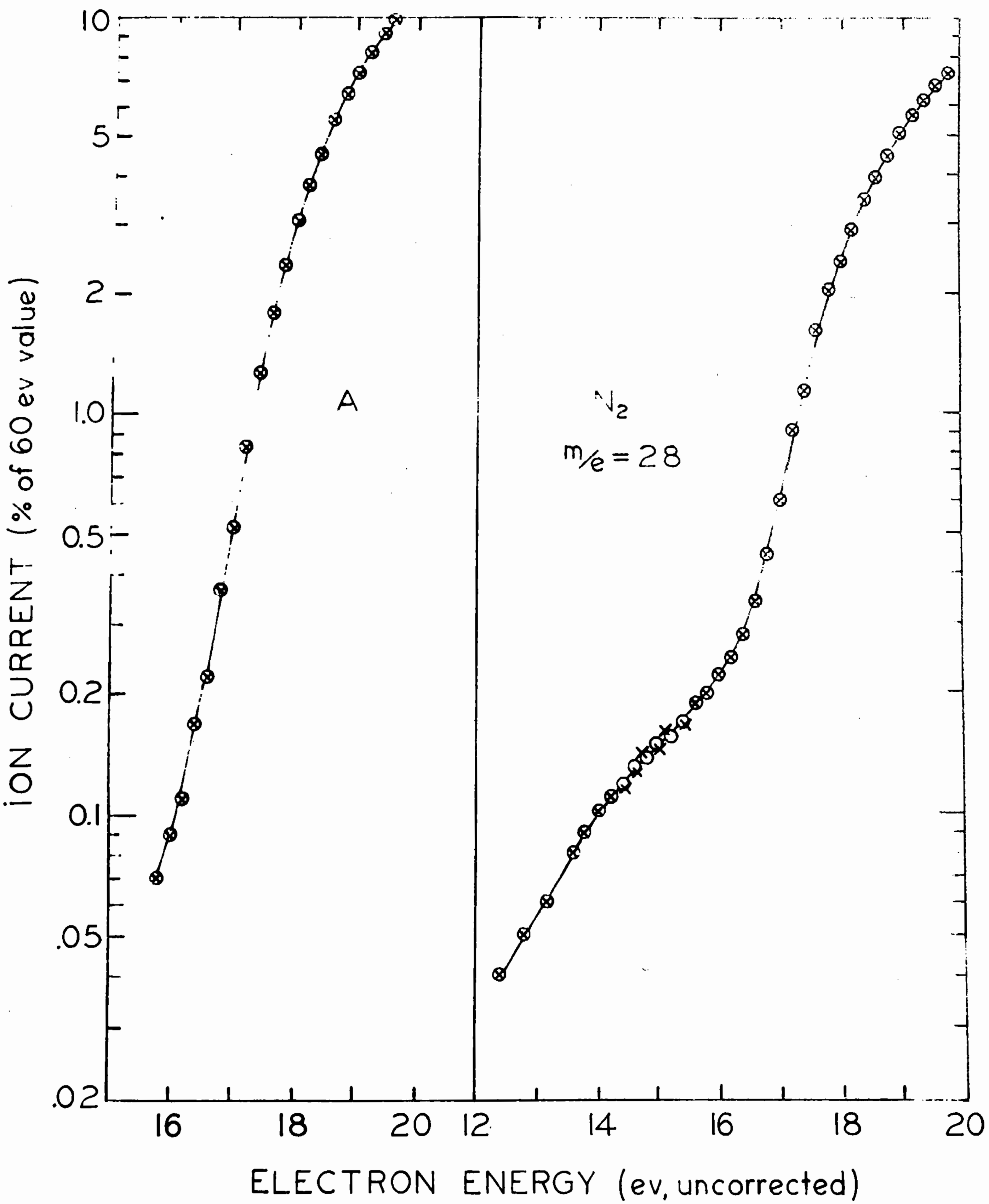
Data for the Ionization Efficiency Curves With and Without Discharge

TABLE V

ELECTRON ENERGY (VOLTS)	DISCHARGE ON				DISCHARGE OFF		
	NITROGEN				NITROGEN		
	MASS 14	MASS 28	Δ14	ARGON	MASS 14	MASS 28	ARGON
60	100	100	100	100	100	100	100
30	19.39				19.34		
29.4	16.24				16.11		
28.8	13.83				13.70		
28.2	10.99				10.90		
27.6	8.70				8.56		
27.0	7.16				6.42		
26.4	5.14				4.63		
25.8	3.62				2.79		
25.2	2.19				1.31		
24.6	1.44				0.46		
24.0	0.985				0.15		
23.4	0.834				0.070		
22.8	0.787				0.028		
22.2	0.684						
21.6	0.576						
21.0	0.506						
20.4	0.450						
19.8	0.383						
19.4			11.11				
19.2			9.38	8.50			8.50
19.0	0.184	5.11	8.33			5.11	
18.8	0.164	4.50	6.25	6.77		4.50	6.77
18.6	0.121	3.91	6.31			3.91	
18.4	0.122	3.48	5.90	4.94		3.48	4.94
18.2	0.116	2.89	5.56	3.68		2.89	3.68
18.0	0.109	2.40	4.86	2.98		2.40	2.98
17.8	0.096	2.12	4.18	2.31		2.12	2.31
17.6	0.082	1.62	3.47	1.55		1.62	1.55
17.4	0.069	1.14	2.78	1.14		1.14	1.14
17.2	0.056	0.90	2.08	0.76		0.90	0.76
17.0	0.043	0.60	1.39	0.53		0.60	0.53
16.8		0.45		0.38		0.45	0.38
16.6		0.34		0.25		0.34	0.25
16.4		0.28		0.12		0.28	0.12
16.2		0.22		0.10		0.22	0.10
15.8		0.20		0.029		0.20	0.029
15.4		0.17				0.17	
15.0		0.15				0.15	
14.2		0.11				0.11	

Figure X

Semilogarithmic Plot of Nitrogen m/e = 28 And Argon Ionization Efficiency Curves



ION CURRENT (% of 60 ev value)
10
5
2
1.0
0.5
0.2
0.1
.05
.02
A
N₂
m/e = 28
16
18
20
12
14
16
18
20
ELECTRON ENERGY (ev, uncorrected)

have arisen from two separate processes.

The linear portions of the Δ 14 curve were extrapolated to the electron energy axis and compared with a similar extrapolation of the linear portion of the argon curve. This method was considered to be applicable because of the similarity of the slopes of these curves. As mentioned before, the low abundance of this species precludes the use of the alternate methods.

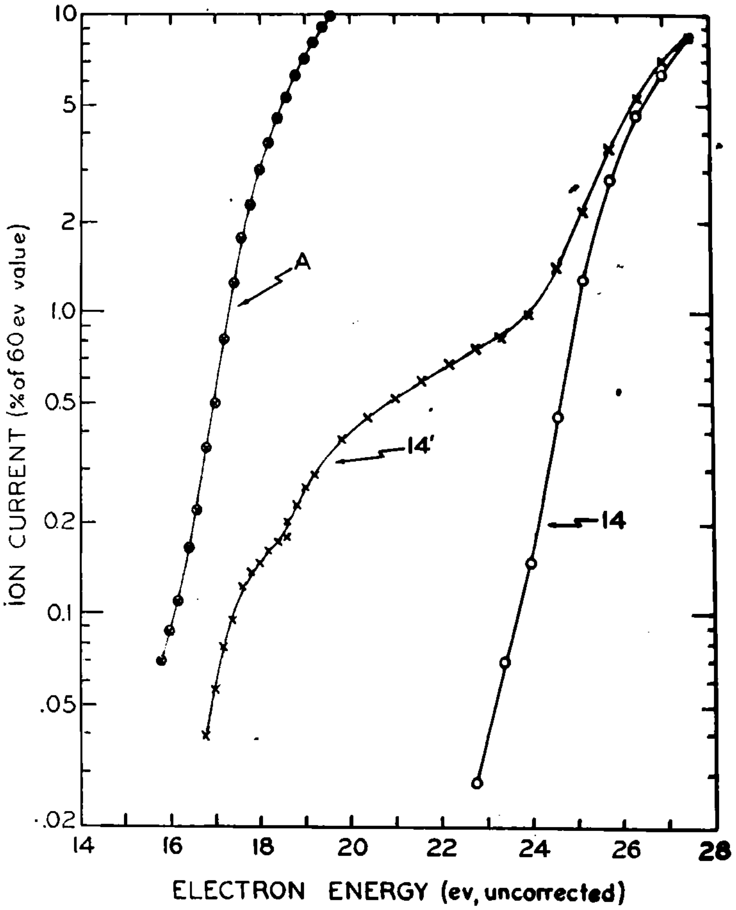
This experiment was repeated and Table VIII shows the result of six independent measurements. The average appearance potential obtained by extrapolation of the linear portion of the Δ 14 curve having the smaller slope was $14.72 \pm .28$ and that for the portion having the larger slope was $15.9 \pm .3$. In view of the uncertainties involved in the extrapolation and in the calibration curve an accuracy of not greater than 0.3 eV can be claimed for these values.

An examination of the spectrum of active nitrogen revealed no ion currents at any other mass number.

no page 68

Figure XI

Semilogarithmic Plot Of Argon Together With
Nitrogen m/e = **14** Ionization Efficiency Curves



10
5
2
1.0
0.5
0.2
0.1
.05
.02
14
16
18
20
22
24
26
28
ION CURRENT (% of 60 ev value)
ELECTRON ENERGY (ev, uncorrected)
A
14'
14

Figure XII

Normal Plot of Argon Together With New Species (Δ14)

Ionization Efficiency Curves

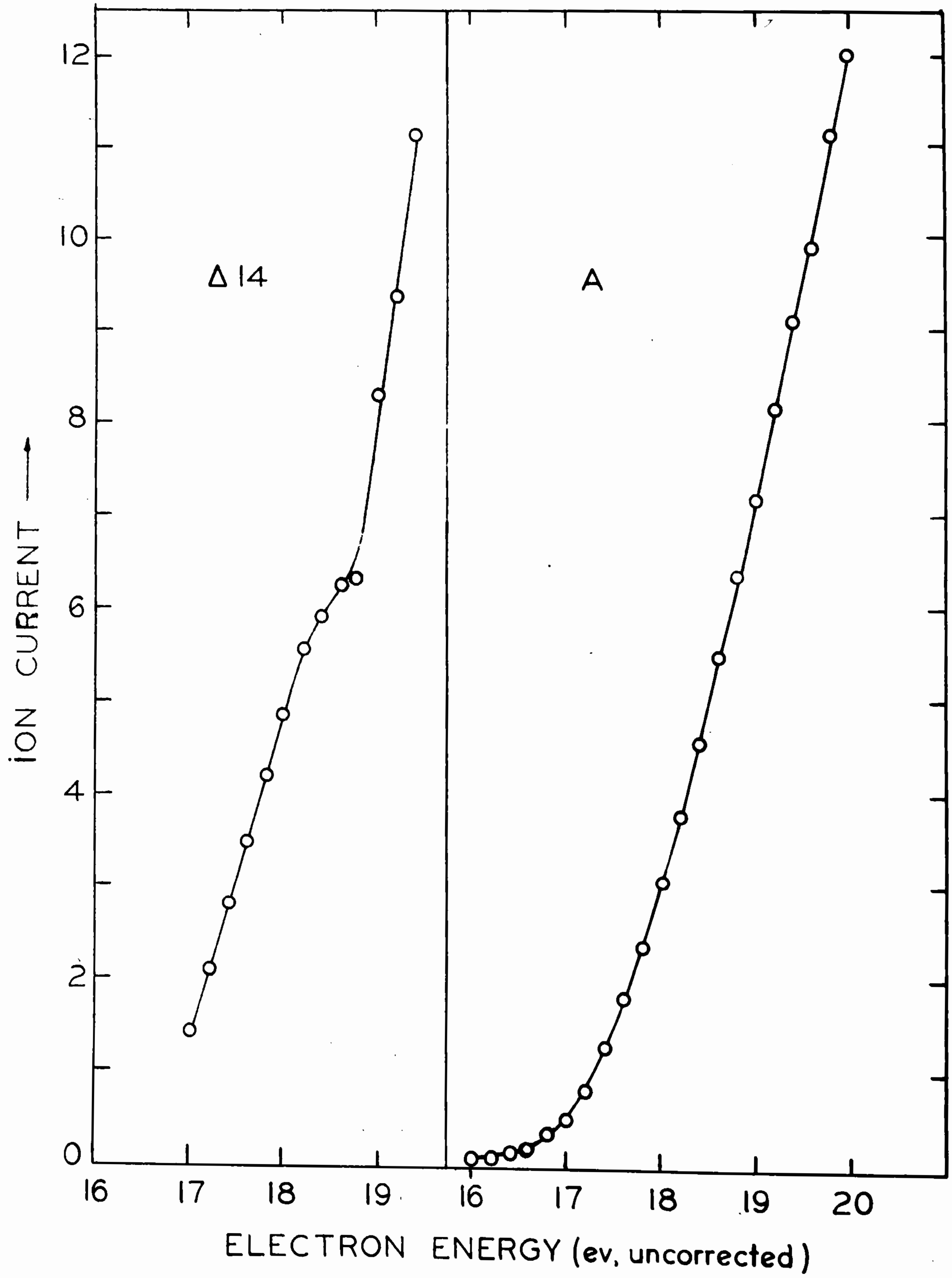

12
10
8
6
4
2
0
ION CURRENT ⟶
Δ 14
A
16
17
18
19
16
17
18
19
20
ELECTRON ENERGY (ev, uncorrected)

Table VIII

Appearance Potentials Of New Species Together With An Estimate Of The Maximum Concentration Present In The Afterglow

TABLE VIII

CALCULATED MAXIMUM CONCENTRATION OF NEW SPECIES $\left(\frac{14'}{28'}-\frac{14}{28}\right)100 =$	APPARENT APPEARANCE POTENTIAL (VOLTS)				SPECTROSCOPIC APPEARANCE POTENTIAL (VOLTS)			DIFFERENCE IN APPEARANCE POTENTIAL OF TWO SPECIES (VOLTS)
	WITHOUT DISCHARGE	WITH DISCHARGE						
			$\Delta 14$			$\Delta 14$		
PERCENT	ARGON	ARGON	SPECIES 1	SPECIES 2	ARGON	SPECIES 1	SPECIES 2	
.14	17.55	17.55	15.90	-	15.75	14.10	-	
.08	17.70	17.70	16.60	17.70	15.75	14.65	15.65	1.00
.20	17.78	17.78	16.90	17.80	15.75	14.87	15.77	.90
.30	17.81	17.81	16.60	17.75	15.75	14.54	15.50	.96
.10	17.05	17.05	16.40	17.90	15.75	15.10	16.60	1.50
.12	17.30	17.30	16.60	17.30	15.75	15.05	15.75	.70
Av. .16 ± .06						Av. 14.72 ± .28	Av. 15.85 ± .29	Av. 1.01 ± .19

(follows page 69)

DISCUSSION OF RESULTS

Atoms, molecules, and ions have all been suggested as possible components of the afterglow. These species will be considered from the point of view of the ionic products that might be obtained as the result of electron bombardment.

I. Atomic Nitrogen: The spectroscopic ionization potential of the nitrogen atom has been reported as 14.54 eV. This value is considered to correspond to the ionization of the ground state ^4S atoms. The value of 14.8 eV obtained in this investigation for the lower appearance potential of the new species is in agreement with 14.54 eV within experimental error. The existence of normal ^4S atoms in the nitrogen afterglow is therefore indicated.

If excited atoms were present their appearance potential would be lower than 14.54 eV to the extent of their separations from the ground state, unless of course excited states of the ions were produced. If it is assumed that this does not occur it follows that excited atoms were not present in the afterglow in concentration large enough to be detected by this method.

II. N_3 :- This species has been suggested by Uri and Herzberg (103). Possible ionization processes for N_3 are

(1) $N_3 + e \rightarrow N_3^+ + 2e$

However no ion current corresponding to m/e = 42 was detected which indicates that this process does not occur.

(2) $N_3 + e \rightarrow N_2^+ + N + 2e$

The appearance potential for m/e = 28 arising by this process would be:

$$A(N_2^+) = I(N_2) + D(N_2\text{-}N) + E + K\ E.$$
$$= 15.7 + D(N_2\text{-}N) + E + K\ E.$$

That is, it would be greater than that for the molecular ion produced from ordinary nitrogen by the amount of energy required to break the N_2-N bond, plus any excitational or kinetic energy of the fragments. However within the experimental error of 0.1% the ionization efficiency curves for mass 28 with and without discharge were superimposed. Therefore this process does not contribute to the formation of N_2^+ ions to greater than 0.1% of their formation from normal nitrogen.

(3) $N_3 + e \longrightarrow N^+ + N_2 + 2e$

The appearance potential for m/e = 14 would be:

$$A(N^+) = I(N) + D(N-N_2) + E + K.E.$$
$$= 14.54 + D(N-N_2) + E + K.E.$$

This process could account for the detection of an atomic ion (N^+) with a higher appearance potential than that of the normal atom. The atomic ion so produced would have an appearance potential higher than 14.54 eV by at least the amount of energy required to break the $N-N_2$ bond. This process might account for the presence of a N^+ ion appearing at 15.9 eV, the second appearance potential of the Δ14 curve, if the strength of the N_2-N bond were 1.1 eV.

III. N_2' Excited nitrogen molecules

(4) $N_2' + e \longrightarrow N_2^+ + 2e$

The probability of this process occurring might depend on the state of the excited nitrogen molecule. This process occurs with high probability for nitrogen molecules in the $X^1\Sigma^+_g$ ground state and presumably would be probable for molecules in other singlet states (eg. $a^1\Pi$).

This process might not be probable for molecules in triplet states due to the multiplicity change involved. The appearance potential of the N_2^+ ion would be 15.7 eV, less the excitation energy of the molecular state. Since no evidence was found for a new species from the shape of the ionization efficiency curve for mass 28 when the discharge was excited, it may be assumed that no molecular ions arising from this process were formed within the experimental error of 0.1%.

(5) $N_2' + e \rightarrow N^+ + N + 2e$

This process might have a low probability for molecules in singlet states. Since impact of 60 volt electrons with molecular nitrogen in the $X\,{}^1\Sigma_g^+$ state gives N^+ ions only in the proportion 1/30 to N_2^+ ions, it might be argued that molecules in singlet states would favor process (4). Thus if this process were responsible for the shape of the mass 14 ionization efficiency curve of 'active nitrogen' then a discontinuity should also have been observed in the mass 28 curve by process (4) in about the same proportion. This was not found and so if this process does occur it might be expected that the N_2' is not in a singlet but perhaps in a triplet state. The appearance potential for N^+ ions by this process would be 14.54 eV plus the energy required to break the N-N bond of the excited molecule. It therefore would not explain the first appearance potential of 14.8 eV unless the energy of dissociation of the (N-N) bond was very small. It could however explain the second appearance potential of 15.9 eV if the dissociation energy is 1.1 eV.

IV. N_2 Nitrogen Ions :- This species could not have been detected by the mass spectrometer since the top plate of the ionization chamber is 2000 volts above ground and thus N_2^+ ions would not be able to penetrate to the ion gun. While the afterglow as produced by condensed discharge was found to conduct electricity, the results could most easily be explained on the basis of free electrons. Moreover only positive potentials on the auxillary electrode (Fig. IV), previously mentioned, caused deflections of the microammeter, negative potentials producing no effect. Since N_2 does not form negative ions this leads to the conclusion that the conductivity of active nitrogen is due solely to electrons and that nitrogen ions are absent at appreciable distances from the discharge tube.

Summary

On the basis of the type of ions produced and the energy required it seems possible that ^4S nitrogen atoms, excited N_2 molecules or N_3 might exist in the afterglow.

If molecules in triplet states are contributing to process (5) then they must belong to those states which contribute to the first positive band system since it is from this system that the known radiation of the afterglow occurs. Only certain members of the $B^3\Pi g$ and $A^3\Sigma u$ states occur in the afterglow. These are the 11th, 12th and 6th vibrational levels of the $B^3\Pi g$ system and the 7th and 8th vibrational levels of the $A^3\Sigma u$ system. The 7th and 8th vibrational levels of the $A^3\Sigma u$ system lie between 2.14 and 2.31 eV below the 12th vibrational level which is known to predissociate into ^4S atoms. This would set the appearance potential of the highest $A^3\Sigma u$ molecules known to be present in the afterglow at 14.54 2.2 = 16.74 eV. On the other hand the 6th vibrational level of the $B^3\Pi g$ state lies only 1.32 eV below the $V = 12$ level and might form N^+ ions with an appearance potential of $14.54 + 1.32 = 15.86$ eV. This latter value is in agreement with the second experimentally determined appearance potential of 15.9 eV.

It is not easy to see however why an appreciable concentration of these molecules should exist in the afterglow. This state is not known to be metastable and therefore has a lifetime with respect to radiation of about 10^{-8} second. On this basis the species contributing to the N ion current with the appearance potential of 15.9 eV is not likely to be $B^3\Pi g$ (v = 6) molecules but some other species with the same energy characteristics. Moreover if it is accepted that the occurrence of process (5) is unlikely for singlet state molecules then one can only conclude that metastable molecules cannot account for the ionic species which we observed.

Our attention is therefore directed to those theories of 'active nitrogen' that utilize ^4S atoms to explain the properties of the afterglow in order to see if any of these mechanisms is able to explain the formation of N^+ ions with an appearance potential of 15.9 eV. Most theories utilizing nitrogen atoms are open to criticism on the grounds that they either postulate the presence of metastable atoms (42)(44)(55)(80) which were not detected, metastable molecules (14)(13)(55) or utilize three body recombination (42)(44) to account for the selective formation of the energy levels observed in the afterglow. Even the theory of reverse predissociation proposed by

Reinecke (87) which seems to surmount successfully other objections is not able to explain the formation of N^+ ions with two different appearance potentials. His "quasi molecule" formed by the union of a ^4S atom with a ground state molecule under the influence of weak binding forces

$$N_2(X^1\Sigma^+_g) + N(^4S) \longrightarrow \text{(Quasi Molecule)}$$

would probably give only the atomic ion N^+ when bombarded with electrons

$$\text{(Quasi Molecule)} + e \longrightarrow N^+ + N_2(X^1\Sigma^+_g) + 2e$$

with an appearance potential of 14.54 eV plus the amount of energy in the weak bond (presumably of the order of 0.01 eV). This theory must therefore be judged inadequate to explain the results obtained in this research.

Since the weakest point in the argument against the presence of a metastable molecular state is the supposition that singlet molecules would tend to give molecular rather than atomic ions, one would be inclined to judge that this is incorrect.

Either an activated molecule or the presence of the species N_3 must be invoked to explain the presence of N^+ ions with an appearance potential of 15.9 eV. Nothing is known about the species N_3 and so it is impossible to form an opinion as to the probability of its presence. However Nicholls (76) has suggested that the ground state of the $a^1\Pi$ system might be metastable. This level coincides with the 6th vibrational level of the $B^3\Pi g$ state and it is possible that electron bombardment of this state could lead to an atomic ion with the correct appearance potential providing the transitions involved are probable.

One concludes therefore that while one of the species found to be present is most easily explained on the basis of ^4S atoms, the other, is in some doubt. An explanation may be possible when further research has elucidated more clearly the singlet systems of nitrogen and their characteristics.

Concentration of Active Species in the Afterglow

In order to compare the results of this investigation with those of other workers it would be of considerable interest to estimate the concentration of the active species in the afterglow. In view of the uncertainty in their identification which has just been discussed an unequivocal calculation cannot be made. However an upper limit can be estimated on the assumption that only ^4S atoms are responsible for the change in the mass 14 ionization efficiency curve. On this basis the ratio of nitrogen atoms to normal nitrogen molecules in the afterglow would be given by an expression

$$\frac{N}{N_2} = \frac{\Delta 14}{28'} \quad \frac{S_N}{S_{N_2}}$$

where $\Delta 14$ is the increase in ion current of mass 14

$28'$ is the mass 28 ion current with discharge excited

S_N is the sensitivity of the mass spectrometer to nitrogen atoms

S_{N_2} is the sensitivity of the mass spectrometer to ordinary molecular nitrogen

Expanding we get

$$\frac{N}{N_2} = \frac{1}{28'} \left[14' - 14 \times \frac{28'}{28} \right] \frac{S_N}{S_{N_2}}$$

where $14'$ is the mass 14 ion current with discharge excited

14 is the mass 14 ion current with discharge off

$$\frac{N}{N_2} = \left[\frac{14'}{28'} - \frac{14}{28} \right] \frac{S_N}{S_{N_2}}$$

Nothing is known about the sensitivity of the mass spectrometer to nitrogen atoms. However the sensitivities for non-dissociative ionizations do not differ markedly for most gases. When S_N was put equal to S_{N_2} this expression yielded concentrations of atomic nitrogen between 0.1% and 1.5% depending on the type and condition of the discharge tube used. This assumption for S would not be expected to be in error by greater than a factor of three. Since this calculation provides an upper limit it can be safely stated that atomic nitrogen is not detected in concentrations greater than five percent.

As previously mentioned Benson (5) investigated 'active nitrogen' calorimetrically. He reported the active species to be present to the extent of about 0.3% which is in substantial agreement with the above estimate. E. Inn (private communication) has recently obtained evidence for the presence of atomic nitrogen by absorption in the vacuum ultraviolet. A value for the concentration could not be given due to the absence of data on the absorption coefficient. However, a reasonable guess was made and led to a concentration of less than two percent.

(follows page 82)

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

(1) The nitrogen afterglow has been investigated by means of a free radical mass spectrometer.

(2) A difference in the ratio between normal and 'active nitrogen' indicated the presence of new species.

(3) Ionization efficiency curves were determined. The curves at mass 28 were identical while the curve at mass 14 for 'active nitrogen' was markedly different compared to that for normal nitrogen. The discontinuities observed in the mass 14 curve indicated the existence of two new species.

(4) Appearance potentials for these new species were determined by extrapolation of the ionization efficiency curves.

(5) The theories of nitrogen afterglow were reviewed on the basis of the results obtained. It was concluded that atomic nitrogen is a likely constituent. The other component may be either N_3 an excited N_2 molecule. having a dissociation energy of about 1.1 eV. The possible excited states consistent with these results and with the observed spectroscopic characteristics of the afterglow have been critically discussed.

BIBLIOGRAPHY

1. Angerer, E. V., Physikal Z., 22, 497 (1921)
2. Baker, H. B. and Strutt, R. J., Ber. 47, 801 (1914)
3. Baker, H. B., Strutt, R. J., Tiede, E. and Domcke, E. Ber. 47, 2283 (1914)
4. Bay, F. and Steiner, W., Z. Physik. Chem. B3, 149 (1929)
5. Benson, J. M., J. Applied Phys. 23, #7, 757 (1952)
6. Biondi, M. A., and Brown, S. C., Phys. Rev. 76, 1697 (1949)
7. Birge, R. T., Phys. Rev., 23, 294 (1924)
8. Birge, R. T., Nature, 114, 642 (1925)
9. Birge, R. T., Nature, 117, 81 (1926)
10. Blades, H. and Winkler, C. A., Can. J. Chem. 29, 1022 (1951)
11. Bonhoeffer, K. F., Z. Physik. Chem., 113, 199 (1924)
12. Burke, J. B. B., Phil. Mag., 1, 342 (1901)
13. Cario, G., Z. Physik, 89, 523 (1934)
14. Cario, G. and Kaplan, J., Zeits. für Physik, 58, 769 (1929)
15. Cario, G. and Reinecke, L. H., Abh. Braunchiv Wiss. Gesell 1, 8 (1949)
16. Chao, K. T. and Chang, H. P., Phys. Rev., 76, 970 (1949)
17. Classen, J., Jahib. d. Hamburg Wiss. Anst. Berheft (1907)
18. Classen, J., Phys. Z., 9, 762 (1908)
19. Compte, P., Physik Z., 14, 74 (1913)
20. Constantinides, P. A., Nature 119, 163 (1929)
21. Cygan, G., Acta. Phys. Polon., 11, 189 (1951)
22. Dempster, A. J., Phys. Rev., 11, 316 (1918)

23. Douglas, A. E., and Herzberg, G., Canad. J. Phys. 29, 294 (1951)

24. Easson, B., and Armour, F., Proc. Roy. Soc. (Edinburgh) 48 (1928)

25. Eltenton, G. C., J. Chem. Phys., 15, 455 (1947)

26. Eltenton, G. C., Rev. Inst. Franc. Petrole, 4, 468 (1949)

27. Eltenton, G. C., J. Phys. Coll. Chem., 52, 463 (1948)

28. Emeleus, K. G., The Conduction of Electricity Through Gases, Methuen and Co. Ltd., London 1951

29. Foote, P. D., Ruark, A. E. and Chenault, R. L., Phys. Rev. 25, 241 (1925)

30. Foote, P. D., Ruark, A. E., Chenault, R. L. and Rudnik, C., J.O.S.A., 14 17 (1927)

31. Fowler, A. and Strutt, R. J., Proc. Roy. Soc. (London) A85, 377 (1911)

32. Frost, A. A. and Oldenberg, O., Phys. Rev., 48, 66 (1935)

33. Gaydon, A. G., Nature, 153, 407 (1944)

34. Gaydon, A. G., Proc. Roy. Soc. (London) A182, 286 (1944)

35. Gaydon, A. G. and Penny, C., Proc. Roy. Soc. (London) A183, 374 (1945)

36. Glockler, G. C., J. Chem. Phys., 16, 602 (1948)

37. Graham, R. L., Harkness, A. L. and Thode, H. G., J. Sci. Instr. 24, 119 (1947)

38. Greenblat, J. H. and Winkler, C.A., Can. J. Res. 27B, 721 (1949)

39. Greenblat, J. H. and Winkler, C. A., Can. J. Res., 27B, 732 (1949)

40. Hagstrum, H. P., J. Chem. Phys., 16, 848 (1948)

41. Haupt, C. R., Phys. Rev., 38, 282 (1931)

42. Helb, M. H. and Sponer, H., Phys. Rev., 59, 925 (1941)

43. Herbert, W. S., Herzberg, G. and Mills, Can. J. Research, 15A, 35 (1937)

44. Herman, R. L., Compt. Rend., 211, 773 (1940)

45. Herzberg, G., Z. Physik, 26, 885 (1928)

46. Herzberg, G., Nature, 161, 283 (1948)

47. Hipple, J. A., and Stevenson, D. P., Phys. Rev., 63, 121 (1943)

48. Honig, R. E., J. Chem. Phys., 16, 105 (1948)

49. Ingold, K. V. and Lossing, F. P., J. Chem. Phys. 21, #2, 368 (1953)

50. Ingold, K. V. and Lossing, F. P., J. Chem. Phys. 21, #7, 1135 (1953)

51. Ingold, K. V., Henderson, I. H. S. and Lossing, F. P., J. Chem. Phys. 21, #12, 2239 (1953)

52. Jackson, L. C. and Broadway, L. F., Proc. Roy. Soc. (London) A127, 678 (1938)

53. Johnson, R. C., Nature, 119, 9 (1927)

54. Kaplan, J., Nature, 134, 289 (1934)

55. Kaplan, J., Phys. Rev., 73, 494 (1948)

56. Kneser, H. O., Ann. Physik. 87, 717 (1928)

57. Kubo, J. O. and Hamada, H., Phys. Rev., 42, 795 (1932)

58. Kubo, J. O. and Hamada, H., Phil. Mag., 15, 103 (1933)

59. Kubo, J. O. and Hamada, H., Science Rept. Tohokee Imp. Univ., First Ser., 23, 289 (1934)

60. Lawrence, E. O., Phys. Rev., 28, 947 (1926)

61. Lewis, B., J. Am. Chem. Soc., 50, 27 (1928)

62. Lewis, E. P., Astrophys. J., 12, 8 (1900)

63. Lossing, F. P., Ingold, K. V., Henderson, I. H. S., J. Chem. Phys., 22, #4, 621 (1954)

64. Lossing, F. P. and Tickner, A. W., J. Chem. Phys., 20, #5, 907 (1952)

65. Lossing, F. P., Tickner, A. W., and Bryce, L. J. Chem. Phys. 19, 1254 (1951)

66. Mariner, T. and Bleakney, W., Phys. Rev., 72, 807 (1947)

67. McDowell, C. A. and Warren, J. W., Discussions of the Faraday Soc., Hydrocarbons #10, p.53 (1951)

68. Mitra, S. K., Science and Culture, 9, 49 (1943)

69. Mitra, S. K., Nature, 154, 212 (1944)

70. Mitra, S. K., Nature, 154, 576 (1944)

71. Mitra, S. K., Nature, 154, 831 (1944)

72. Mitra, S. K., Science and Culture, 16, 488 (1951)

73. Mitra, S. K., Phys. Rev., #4, 516 (1953)

74. Mullikan, R. S., Nature, 114, 349 (1924)

75. Muschlitz, E. E. and Goodman, L., J. Chem. Phys. 21, 2213 (1953)

76. Nicholls, R. W., Nature, 162, 231 (1948)

77. Nier, A. O. C., Rev. Sci. Instr. 18, 398 (1947)

78. Nottingham, W. B., Phys. Rev., 55, 203 (1939)

79. Oldenberg, O., Phys. Rev., 87, #5, 786 (1952)

80. Oldenberg, O., Phys. Rev., 90, 727 (1953)

81. Pirani, M. and Lax, E., Chem. Zentr. io 17, (1923)

82. Rayleigh, Lord, Proc. Roy. Soc. (London) A151, 567 (1935)

83. Rayleigh, Lord, Proc. Roy. Soc. (London) A176, 1 (1940)

84. Rayleigh, Lord, Proc. Roy. Soc. (London) A176, 16 (1940)

85. Rayleigh, Lord, Proc. Roy. Soc. (London) A180, 140 (1942)

86. Rayleigh, Lord, Proc. Roy. Soc. (London) A189, 296 (1947)

87. Reinecke, L. H., Zeit für Physik. 135, 361 (1953)

88. Robertson, A.J.B., Proc. Roy. Soc. (London) A199, 394 (1949)

89. Robertson, A.J.B., Mass. Spec. Conf. 1950, p.47 (London Institute of Petroleum (1952)).

90. Rudy, R., J. Franklin Inst. 201, 247 (1926)

91. Saha, M. N. and Sur, N.K., Phil. Mag., 118, 425 (1924)

92. Sponer, H., Zeit für Physik., 34, 622 (1925)

93. Strutt, R. J., Proc. Roy. Soc. (London), A85, 219 (1911)

94. Strutt, R. J., Proc. Roy. Soc. (London), A86, 105 (1912)

95. Strutt, R. J., Proc. Roy. Soc. (London), A86, 56 (1912)

96. Strutt, R. J., Proc. Roy. Soc. (London), A86, 262 (1912)

97. Strutt, R. J., Proc. Roy. Soc. (London), A86, 302 (1912)

98. Strutt, R. J., Proc. Roy. Soc. (London), A87, 539 (1913)

99. Strutt, R. J., Proc. Roy. Soc. (London), A93, 254 (1917)

100. Strutt, R. J., Proc. Roy. Soc. (London), A102, 453 (1922)

101. Tiede, E., Ber. d. D. Phys. Ges., 46, 4065 (1913)

102. Trick, G. S. and Winkler, C. A., Can. J. Chem., 30, 915 (1952)

103. Uri, N. and Herzberg, G., Discussions of the Faraday Soc., #14, P.127 (1953)

104. Van de Ziel, A., Physica. 4, 373 (1937)

105. Versteeg, J. and Winkler, C. A., Can. J. Chem., 31, 1 (1953)

106. Vought, R. H., Phys. Rev., 71, 93 (1947)

107. Waldron, and Wood Mass Spectrometry Conference 1950 p.16 (London Instit. of Petroleum 1952)

108. Warren, J. W., Nature, <u>165</u>, 810 (1950)

109. Willey, E.J.B., J. Soc. Chem. Ind., <u>43</u>, 263 (1924)

110. Willey, E.J.B., and Rideal, E. K., J. Chem. Soc. 1804 (1926)

111. Willey, E.J.B., Nature, <u>119</u> (1927)

112. Willey, E.J.B., J. Chem. Soc., 2188 (1927)

113. Willey, E.J.B., J. Chem. Soc., 1620 (1928)

114. Willey, E.J.B., J. Chem. Soc., 228 (1929)

115. Willey, E.J.B., J. Chem. Soc., 336 (1930)

116. Willey, E.J.B., and Stringfellow, W.A., Nature, <u>126</u>, 349 (1930)

117. Willey, E.J.B., and Stringfellow, W.A. J. Chem. Soc., 142 (1932)

118. Willey, E.J.B., Nature, <u>138</u>, 1054 (1936)

119. Worley, R. E., J. Chem. Phys., <u>16</u>, 533 (1948)

120. Wrede, E., Z. Physik., <u>54</u>, 53 (1929)

PUBLICATIONS

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 21, No. 12, 2233–2234, December, 1953
Printed in U. S. A.

Mass Spectral Investigation of "Active" Nitrogen

D. S. JACKSON AND H. I. SCHIFF
Department of Chemistry, McGill University, Montreal, Canada

(Received October 12, 1953)

ALTHOUGH much speculation has been made regarding the composition of "active" nitrogen, no experimental determination has yet been reported. A study of the nitrogen afterglow was therefore undertaken with the aid of a mass spectrometer. Purified nitrogen was passed through a discharge tube at a pressure of approximately 1 mm Hg and at a flow rate of 1.03×10^{-5} moles/sec. The walls of the discharge tube and the glass tubing leading to the mass spectrometer were "poisoned" with metaphosphoric acid. The nitrogen was subjected to a condensed discharge by means of an electrical circuit similar to that described by Greenblatt and Winkler.[1] From the discharge tube the gas was pumped through a conventional diffusion and rotary pump assembly. At a distance of 50 cm from the discharge tube a small central portion of the gas stream was continuously sampled into the mass spectrometer through a leak, 30 microns in diameter and 10 microns in length, made in a quartz thimble. The leak and sampling system were similar to those used by Tickner and Lossing in the detection of free radicals.[2] An electron energy of 50 electron volts was used in the ion source of the mass spectrometer.

When the discharge tube was excited the ion intensity corresponding to mass 28 was found to decrease while the intensity for mass 14 increased, suggesting the presence of atomic nitrogen. Values of the ratios of the ion intensities for mass 28 and 14 are shown in Table I for various values of nitrogen pressure and electron energy. No additional peaks were found when the discharge tube was excited (such as 42 corresponding to N_3).

Preliminary measurements were made of the ion intensities as a function of electron energy both with and without the discharge. The normalized curves for mass 28 were superimposed thus giving no indication of the presence of excited nitrogen molecules. The curve obtained for mass 14 when the discharge tube was excited was displaced toward lower electron energies relative to the curve obtained without discharge. This again suggests the presence of atomic nitrogen although the actual value of the appearance potential for the mass 14 peak must first be made before positive identification can be made. Work along this line is now in progress and a full report will be published shortly.

TABLE I.

Pressure mm Hg	Electron energy ev	Mass 28/14 ratio no discharge	Mass 28/14 ratio discharge on
1.03	70	24.5	18.5
1.03	50	26.0	23.8
1.03	40	38.9	26.8
1.03	30	44.5	31.1
1.03	20	168.8	81.0
0.64	50	27.5	24.6
1.09	50	25.9	23.6
1.45	50	24.2	22.2
1.70	50	23.3	22.0
2.24	50	21.4	19.8

The authors would like to thank the Canadian Industries Limited for the granting of an award to one of us (D. S. J.).

[1] J. Greenblatt and C. A. Winkler, Can. J. Research **B27**, 721 (1949).
[2] A. W. Tickner and F. P. Lossing, J. Chem. Phys. **20**, 907 (1952).

Subsequent publications arising from this thesis will be inserted here when available.