

can be interpreted, although they are not as clear as in the case of HgH.

My best thanks are due to Professor C. Bialobrzanski for his continued interest in the progress of this work. This paper was submitted in August of last year for publication in the *Acta*

Physica Polonica. Subsequent events have made it impossible to proceed with the printing of this journal, and the paper has therefore been rewritten and is presented here. I am very much indebted to Professor F. A. Jenkins for the kind help he has given me in the writing of this paper.

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The Ionization and Dissociation of Water Vapor and Ammonia by Electron Impact

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The results of a mass-spectrometric study of the products of ionization and dissociation of water vapor and ammonia by electron impact are given. The ionizing potential of the H₂O molecule is found to be 13.0 ± 0.2 volts, and of the NH₃ molecule 10.5 ± 0.1 volts. The possible processes responsible for the formation of the various ions observed, both positive and negative, are discussed. Ions observed in H₂O vapor are H₂O⁺, OH⁺, O⁺, H⁺, H₂⁺, H₃O⁺, O⁻, and H⁻. Ions observed in NH₃ are NH₃⁺, NH₂⁺, NH⁺, N⁺, H⁺, NH₃⁺⁺, NH₂⁻, and H⁻.

INTRODUCTION

THE use of the mass spectrometer for the study of products of ionization and dissociation has come to be recognized as a valuable method of attack on the problem of molecular structure.¹⁻⁴ In view of the excellent and thorough exposition of the method in previous papers, particularly that of Smith,³ it will be sufficient to state here that the procedure is, briefly, as follows: (1) ions formed by collision between the bombarding electrons and the vapor or gas are observed and identified; (2) their intensities and appearance potentials, which are really upper limits, are measured; (3) these data are combined with all available thermochemical and band spectroscopic data in an effort to ascertain the processes occurring and to estimate various bond energies.

While both the H₂O and NH₃ molecules have

been investigated previously,⁵⁻⁷ lack of high resolving power, on the one hand, and relatively low sensitivity of the instruments on the other, have left the data on these molecules in a somewhat uncertain state. Further, more recent but incomplete data^{8, 9} obtained at various times have not been in agreement with the earlier work. It appeared justifiable to presume, therefore, that a thorough investigation of the two molecules with the present apparatus might yield consistent and more complete information.

APPARATUS

The mass spectrometer which was used in the present investigation was employed previously in a study of the dissociation products of C₆H₆, C₂H₄, and HCN.^{4, 10} The differential pumping system has been improved in order to make more certain that products of thermal dissociation do

¹ H. D. Smyth, *Rev. Mod. Phys.* **3**, 347 (1931). This article contains a summary of, and references to, earlier work.

² de Groot and Penning, *Handbuch der Physik*, Vol. 23 (Springer, Berlin, 1933). Also a resumé.

³ L. G. Smith, *Phys. Rev.* **51**, 263 (1937).

⁴ A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.* **54**, 1037 (1938).

⁵ H. A. Barton and J. H. Bartlett, *Phys. Rev.* **31**, 822 (1928), on water vapor.

⁶ J. H. Bartlett, *Phys. Rev.* **33**, 169 (1929), on ammonia.

⁷ H. D. Smyth and D. W. Mueller, *Phys. Rev.* **43**, 116 (1933), on water vapor.

⁸ P. Kusch, unpublished, on water vapor.

⁹ R. F. Baker, unpublished, on ammonia.

¹⁰ P. Kusch, A. Hustrulid and J. T. Tate, *Phys. Rev.* **52**, 843 (1937).

not diffuse back into the ionizing region. The filament has been moved farther from the collision chamber and the cross section of the pumping lead increased. A diagram of apparatus is given in Fig. 1. That products of thermal dissociation may readily occur is indicated by the fact that the relative abundances of the different ions are affected in a marked way by the hot filament of an ionization gauge. Since the results obtained with a tungsten filament operated very "hot" and an oxide-coated filament operated "cold" were the same, it is evident that the differential pumping was successful.

WATER VAPOR

Water which was distilled several times in a vacuum, and from which the middle fraction was taken, was admitted to the mass spectrometer through a long capillary. The pressure of the water vapor in the ionization chamber could be readily adjusted by varying the temperature of the bulb containing the water.

A typical mass spectrum of the heavier positive ions is given in Fig. 2. Argon was used to calibrate the mass and voltage scales. All the ions found, their relative abundance at electron energy of 100 volts, and their appearance potentials are given in Table I. On the basis of $H_2O^+ = 100$, the relative abundances of the impurities present were as follows: CO_2 less than 0.07; CO less than 0.05; O_2 none; and H_2 none.

Bichowsky and Rossini¹¹ give 2.51 volts as the

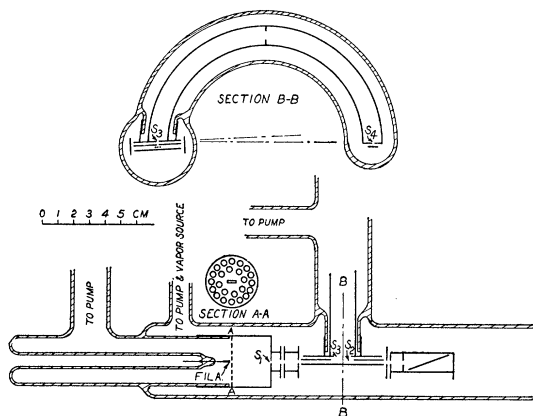


FIG. 1. Mass spectrometer with differential pumping on both analyzer and filament.

¹¹ Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).

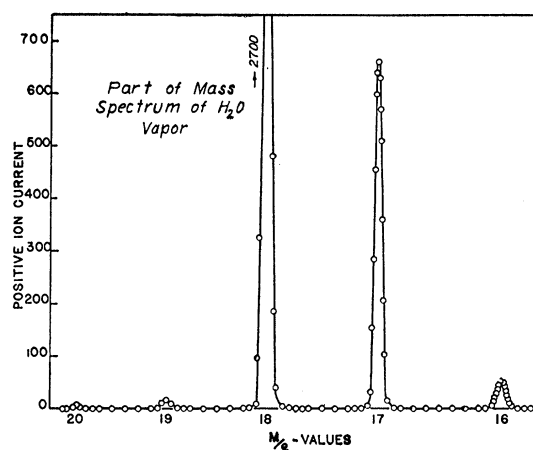


FIG. 2. Mass spectrum of heavy ion group observed in water vapor.

energy required to dissociate one molecule of water into its components in the state in which they exist under ordinary conditions. By use of the dissociation energies of oxygen, hydrogen, and (OH) , $D(O_2) = 5.09$ volts, $D(H_2) = 4.46$ volts, and $D(OH) = 4.4$ volts given by Spomer,¹² the energies required for the dissociation of water into various components may be calculated. The values are given in Table II.

POSITIVE IONS

H_2O^+

The observed ionization potential of water was 13.0 ± 0.2 volts. Barton and Bartlett⁵ and Mackay¹³ have observed the values 13.0 and 13.2 volts, respectively. Kusch⁸ and Baker⁹ obtained 12.8 and 13.0 volts, respectively. Smith and Bleakney¹⁴ reported a value of 12.59 volts. Smyth and Mueller⁷ have determined an ionization potential at 12.7 volts. Another ionization potential at 16.0 volts reported by them was not observed in the present investigation. As shown by Fig. 3, no irregularity occurred in the ionization efficiency curve from which the ionization potentials are determined. The marked change in slope observed by Smyth and Mueller certainly does not occur.

Smyth and Stueckelberg¹⁵ have suggested that

¹² H. Spomer, *Molekülspektren* (J. Springer, 1935).

¹³ C. A. Mackay, *Phys. Rev.* **24**, 319 (1924).

¹⁴ L. G. Smith and W. Bleakney, *Phys. Rev.* **49**, 883A (1936).

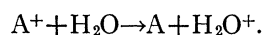
¹⁵ H. D. Smyth and E. C. G. Stueckelberg, *Phys. Rev.* **32**, 779 (1928).

TABLE I. Ions observed in water vapor. Electron affinity of oxygen taken as 2.2; of hydrogen as 0.7 volt.

ION	INTENSITY AT 100 VOLTS	APPEARANCE POTENTIAL (VOLTS)	PROBABLE PROCESS	CALCULATED MINIMUM ENERGY	EXCESS ENERGY OR DEDUCED I.P.
H ₂ O ⁺	100	13.0±0.2	H ₂ O→H ₂ O ⁺		I(H ₂ O) = 13.0 ev
OH ⁺	23.2	18.7±0.2	H ₂ O→H+OH ⁺	I(OH)+ 4.91 ev	I(OH) ≲ 13.8
O ⁺	2.0	18.8±0.5	H ₂ O→H ₂ +O ⁺	18.6	
		28.1±1.0	H ₂ O→2H+O ⁺	23.1	W(O ⁺) ≲ 5.0
H ₃ O ⁺		13.8±0.5			
H ⁺	5.0	19.5±0.2	H ₂ O→OH+H ⁺	18.4	W(H ⁺) ≲ 1.1
H ₂ ⁺	0.07	23.0±2.0	H ₂ O→O+H ₂ ⁺	20.6	
H ₁ ⁻	0.6*	5.6±0.5	H ₂ O→OH+H ⁻	4.7	
			H ₂ O→O+H+H ⁻	8.8	
O ⁻	0.15	7.5±0.3	H ₂ O→2H+O ⁻	7.3	
		23.7±0.5	H ₂ O→H+H ⁺ +O ⁻	20.8	
		36.0±3	H ₂ O→H ⁺ +H ⁺ +O ⁻	34.3	

* At maximum.

there is an ionization potential of water just below that of argon. They deduce this from the apparently high probability of the reaction:



An alternative explanation suggested by them, and more likely in view of the present results, is that ionization by a collision of the second kind is accompanied by excitation to a higher vibrational state than results from ionization by electron impact. Mulliken¹⁶ predicts that water may have ionization potentials at 16 and 17 volts, but no evidence has been found in the present work to substantiate this prediction.

OH⁺

The value $A(OH^+) = 18.7 \pm 0.2$ volts obtained here is in agreement with the values obtained by Smyth and Mueller, Kusch, and Baker. Since OH can arise only from the state *b*, Table II,

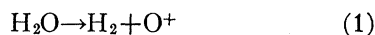
$$A(OH^+) = 5.1 + I(OH) + (\text{kinetic and excitational energy}),$$

which yields

$$I(OH) \leq 13.6 \text{ volts.}$$

O⁺

This ion appears first at 18.8 ± 0.5 volts. The process



is evidently responsible, for the minimum energy required is 18.6 volts.

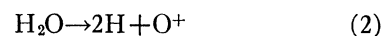
A break in the efficiency curve occurs at 28.1 ± 1.0 volts, as is shown by Fig. 4. If the

¹⁶ R. S. Mulliken, Phys. Rev. **40**, 56 (1932).

TABLE II. Energies of possible states of combination in which an oxygen and two hydrogen atoms may exist.

STATE	CONFIGURATION	ENERGY (VOLTS)
<i>a</i>	H+H+O	9.5
<i>b</i>	H+OH	5.1
<i>c</i>	H ₂ +O	5.0
<i>d</i>	H ₂ O	0

process



is assumed to take place, the minimum energy required is 23.1 volts. This leaves 5.0 volts excess energy. While it is quite likely that the neutral hydrogen atoms may take up a considerable portion of the excess as kinetic energy, there do exist excited states in O II of energies 3.3 and 5.0 volts. These are ²D⁰ and ²P⁰, respectively.¹⁷ It is to be noted that the probability of formation of O⁺ by process (2) is much greater than for process (1). The failure of earlier workers⁷⁻⁹ to observe the break at 28 volts may be due to the fact that a small amount of CO₂ impurity smooths out the curve to such an extent that the break is not apparent. In order to ascertain whether or not both processes (1) and (2) occur, it was, therefore, necessary to determine how much the CO₂ impurity contributed to the O⁺ efficiency curve. A short and separate study of the O⁺ from CO₂ revealed that the contribution from an amount of CO₂ comparable with that found to be present in the H₂O sample is negligible and, therefore, the above processes do occur.

¹⁷ R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

H^+

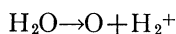
This ion appears at 19.5 ± 0.2 volts and evidently arises from the process



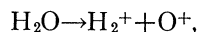
for which the minimum energy required is 18.4 volts. A large portion of the excess is probably taken up as kinetic energy by the products of the collision.

 H_2^+

The probability of formation of this ion is small, and the appearance potential is 23.0 ± 2.0 volts. The process



is the only one possible and requires 20.6 volts. If H_2^+ were the result of a secondary process or if it were present as an impurity, it would be expected to appear not far from $I(\text{H}_2) = 15.3$ volts. The above process evidently does occur. Smyth and Mueller observed $A(\text{H}_2^+)$ as 33.4 volts though there was evidence of H_2^+ at lower energies. If the process



requiring 34.1 volts, occurs, it would be very difficult to observe the break in the curve because of the low intensity of the H_2^+ peak.

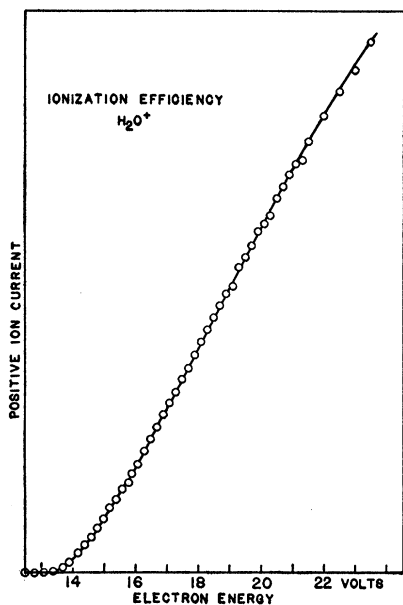


FIG. 3. Portion of the ionization efficiency curve of H_2O^+ .

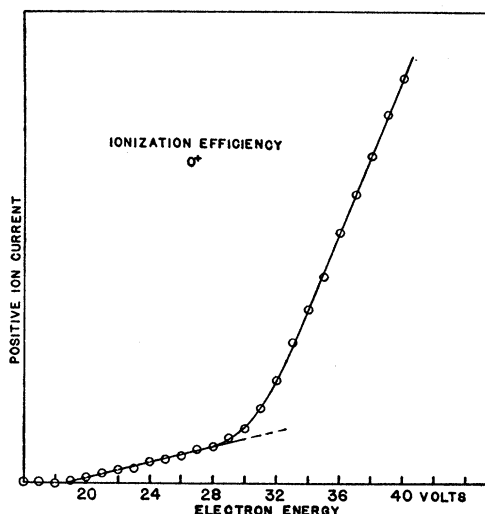


FIG. 4. Portion of the ionization efficiency curve of O^+ from H_2O .

 H_3O^+

This ion appears at 13.8 ± 0.5 volts. Its intensity relative to H_2O^+ varies as the square of the pressure. It is either the result of a secondary process or the H_3O molecule is unstable and is present in H_2O in an amount which is a function of the pressure. At about 10^{-4} mm Hg, the intensity relative to H_2O^+ is approximately 0.5.

NEGATIVE IONS

 H^-

The ionization efficiency curve for H^- is shown in Fig. 5. In contrast to the curves for positive ions which rise steadily with increasing energy of the impinging electron this curve indicates that H^- is formed only when the energy is confined to a relatively narrow region. This is the well-known phenomenon of resonance capture of the electron.

H^- appears at 5.6 ± 0.5 volts and rises to a maximum at about 7.1 volts. There is another maximum, much weaker, at about 8.9 volts which is not completely resolved from the first. Lozier,¹⁸ and Smyth and Mueller have observed this ion and Lozier found by the method of retarding potentials that those ions forming the first maximum possess kinetic energy of 1.5 volts; those forming the second maximum possess 3.2 volts kinetic energy. The maxima which Lozier

¹⁸ W. W. Lozier, Phys. Rev. **36**, 1417 (1930).

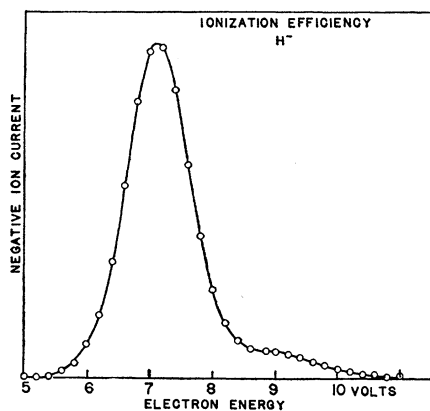
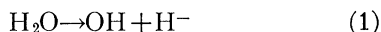


FIG. 5. Ionization efficiency curve for H^- from H_2O .

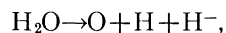
observed were centered at 6.6 and 8.8 volts, in good agreement with the present work.

The energy required to form H^- by the process



is 4.2 volts, and if we add Lozier's value of 1.5 volts kinetic energy to this, H^- should appear at 5.7 volts and this agrees well with the observed value. If it is presumed that the second group arise from process (1), but from a different excited state of the H_2O after capture of the electron, it should appear at 7.4 volts, and while this appearance is masked completely by the first group, the presence of the maximum at 8.9 volts would indicate agreement fully as good as in the preceding case.

From the present data, it would appear improbable that the process



requiring 8.8 volts, occurs.

O^-

When the magnetic field of the mass spectrometer is reversed or changed for the purpose of studying ions of widely different masses, the mass scale must be recalibrated. As only one negative ion in the range M/e 18 to 16 was observed, it became necessary to introduce some gas which is known to yield a negative ion, or ions, in this range which have been identified. CO is known to yield O^- , and was therefore admitted to the apparatus, and the negative ion from H_2O , in this range, was identified as O^- .

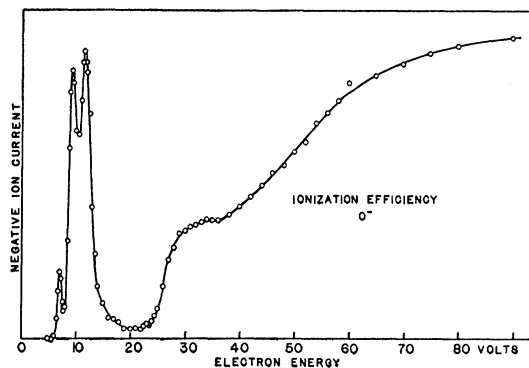


FIG. 6. Ionization efficiency curve for O^- from H_2O .

In Fig. 6 is the ionization efficiency curve of O^- . It is different from that of H^- in that three resonance peaks appear, and it is formed at all energies above the initial appearance at 7.5 ± 0.3 volts.

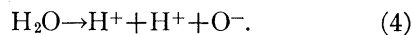
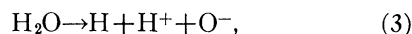
The process



requires 7.3 volts, and this accounts satisfactorily for the first resonance peak. Since this peak and the second in the H^- efficiency curve occur at approximately the same energy of the bombarding electrons, it is possible that the same excited state of the H_2O^- following capture and preceding dissociation may be responsible for both. If this be so, it would appear from the relative intensities that dissociation by process (2) is more probable than by (1) from which the H^- emerges with about 3 volts kinetic energy. The second and third peaks are presumed to arise from dissociation of the H_2O from excited and unstable states following capture of the electron.

Subsequent breaks in the efficiency curve occur at 23.7 ± 0.5 volts and at 36 ± 3.0 volts. Smyth and Mueller⁷ have reported these appearances as 22 ± 3 volts and 36 ± 4 volts, respectively.

They apparently result from the processes



(3) requires 20.8 volts and (4) 34.3 volts.

A thorough search failed to reveal the presence of other negative ions. In this we have been unable to confirm the previously reported detection of OH^- in water vapor.

AMMONIA

The ammonia used in this experiment was taken from a tank of liquid synthetic ammonia and fractionally distilled under vacuum. A sample of one liter at 20 cm pressure was taken from the middle portion and tests in the mass spectrometer showed that it contained less than 0.5 percent water vapor and hydrogen impurity.

Table III summarizes the results obtained. All the ions which have been observed as products of dissociation and their relative intensities at 100 volts electron energy are listed. It can be said that each ion observed is the result of single impact between an ammonia molecule and the bombarding electron for the relative intensity of each ion remained constant with variation in pressure.

In Table IV we have the energies of the several states of combination of one nitrogen and three hydrogen atoms. For the computation of these energy states, the following values of heats of dissociation and formation have been used:

$$D(\text{H}_2) = 4.46 \text{ volts}, \quad D(\text{N}_2) = 7.35 \text{ volts}, \\ Qf(\text{NH}_3) = 0.47 \text{ volt},^{11} \text{ and } D(\text{NH}) = 3.4 \text{ volts.}^{19}$$

POSITIVE IONS

 NH_3^+

The first ionizing potential of ammonia is observed to be 10.5 ± 0.1 volts. Mackay¹³ and Bartlett⁶ have previously reported values of 11.1 and 11.2 volts, respectively, while Baker obtained 10.4 volts.

¹⁹ G. Herzberg, *Molecular Spectra and Molecular Structure*.
1. *Diatomic Molecules* (Prentice Hall, 1939).

TABLE III. Ions observed in ammonia.

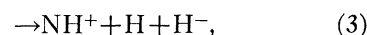
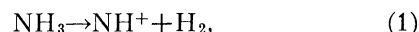
ION	INTENSITY AT 100 VOLTS	APPEARANCE POTENTIAL (VOLTS)	PROBABLE PROCESS	CALCULATED MINIMUM ENERGY	EXCESS ENERGY OR DEDUCED I.P.
NH_3^+	100	10.5 ± 0.1	$\text{NH}_3 \rightarrow \text{NH}_3^+$		$I(\text{NH}_3) = 10.5 \text{ ev}$
NH_2^+	78	15.7 ± 0.1	$\text{NH}_3 \rightarrow \text{NH}_2^+ + \text{H}$	$I(\text{NH}_2) + 3.8 \text{ ev} (?)$	$I(\text{NH}_2) = 11.9 (?)$
NH^+	4.5	19.4 ± 0.5	$\text{NH}_3 \rightarrow \text{NH}^+ + \text{H}_2$	$I(\text{NH}) + 3.0$	$I(\text{NH}) \leq 16.4$
		23.7 ± 0.5	$\text{NH}_3 \rightarrow \text{NH}^+ + 2\text{H}$	$I(\text{NH}) + 7.5$	
N^+	1.7	24.9 ± 0.5	$\text{NH}_3 \rightarrow \text{N}^+ + 3\text{H}$	25.4	
		$28.0 \pm 0.5 (?)$	$\text{NH}_3 \rightarrow \text{N}^{*+} + 3\text{H}$	27.3	$W \leq 0.7$
H^+	0.5	23.3 ± 0.5	$\text{NH}_3 \rightarrow \text{NH} + \text{H} + \text{H}^+$	21.0	
		26.9 ± 0.5	$\text{NH}_3 \rightarrow \text{N}^* + 2\text{H} + \text{H}^+ (?)$	26.7	
H_2^+	0.02	15.5 ± 0.5	$\text{H}_2 \rightarrow \text{H}_2^+$	15.3	
			$\text{NH}_3 \rightarrow \text{NH} + \text{H}_2^+ (?)$	18.3	
NH_3^{*+}	0.02	42 ± 3	$\text{NH}_3 \rightarrow \text{NH}_3^{*+}$		$I(\text{NH}_3^+) \leq 31.5$
H^-	0.15	5.8 ± 0.3	$\text{NH}_3 \rightarrow \text{N} + \text{H}_2 + \text{H}^-$	5.7	
		23.0 ± 1.0	$\text{NH}_3 \rightarrow \text{NH}^+ + \text{H} + \text{H}^-$	23.2	
NH_2^-	0.3	6.0 ± 0.5	$\text{NH}_3 \rightarrow \text{H} + \text{NH}_2^-$		

 NH_2^+

This ion can be formed by one process only, and $I(\text{NH}_2)$ is, therefore, estimated as $A(\text{NH}_2^+) - E_{\text{state } d} = 11.9$ volts. The energy of the state d will be discussed under the treatment of negative ions.

 NH^+

There are three processes from which this ion may originate and that at least two do occur is indicated by the shape of the ionization efficiency curve (Fig. 7). The first appearance is at 19.4 ± 0.5 volts and a sharp break in the curve is noted at 23.7 ± 0.5 volts. The difference in energy between these is 4.3 volts, a value so close to that of $D(\text{H}_2)$, that of the processes



(1) and either (2) or (3) may be assigned with some confidence. $I(\text{NH})$ is found to be ≤ 16.4 volts. Kusch, Hustrulid and Tate in their work on HCN find for an upper limit $I(\text{NH}) = 19.2$. They took for $D(\text{NH})$ 4.2 volts. If the value, 3.4 volts, is used, their $I(\text{NH})$ becomes 18.4 volts,

TABLE IV. Energies of the several states of combination of one nitrogen and three hydrogen atoms.

STATE	CONFIGURATION	ENERGY (VOLTS)
<i>a</i>	$\text{N} + 3\text{H}$	10.9
<i>b</i>	$\text{NH} + 2\text{H}$	7.5
<i>c</i>	$\text{N} + \text{H} + \text{H}_2$	6.4
<i>d</i>	$\text{NH}_2 + \text{H}$	3.8
<i>e</i>	$\text{NH} + \text{H}_2$	3.0
<i>f</i>	NH_3	0

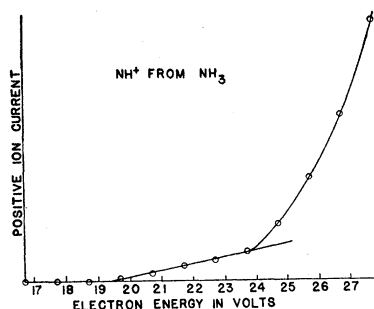


FIG. 7. Portion of the ionization efficiency curve for NH^+ from NH_3 .

leaving the discrepancy at 2.0 volts. Conversely if $D(\text{NH})=4.2$ is used in the present work $I(\text{NH})\cong 17.2$ volts. While it cannot be assumed flatly that in the present case the products of dissociation are all unexcited, it would appear that in the case of HCN excess energy of the order 1 volt or more does exist. The process (3) will be discussed under H^- .

N^+

This ion first appears at 24.9 ± 0.5 volts and from the table, using the energy value of state a and $I(\text{N})=14.5$, we find that N^+ should occur at 25.4 volts. While these values agree within the limits of error, normally it would be expected that the experimental value lie above that calculated. That it does not is believed to be due to the fact that a small amount of N_2 impurity was found in the ammonia sample, and N^+ from N_2 is known to occur at 24.3 volts. This, then, combined with the fact that the N^+ from ammonia is of low intensity would lead to the expectation that N^+ should appear at an electron energy somewhere between the two possible values, the contribution from the impurity having the effect of masking the appearance of N^+ from ammonia very slightly.

The second appearance of N^+ , at 28.0 ± 0.5 volts, while not as pronounced as the break in the NH^+ curve, does seem to exist, and it is suggested that the process



may be responsible where the excitation energy is of the order 2.5 volts. The 1D state of N II is approximately 1.9 volts above the ground state so that this process is entirely possible.

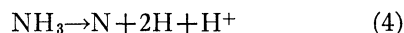
H^+

This ion first appears at 23.3 ± 0.5 volts and from the table the energy required for the process



is found to be 21 volts. This leaves 2.3 volts excess energy to be distributed among the NH and the two hydrogens and the electrons.

Energy required for the process



is 24.4 volts so it is not likely that this process can account for the initial appearance of H^+ . As for the break in the efficiency curve at 26.9 ± 0.5 volts, this is some 2.5 volts higher than required for the process (4), and while the nitrogen may emerge from the dissociation in an excited state, it would not be unreasonable to suppose that the hydrogens possess considerable kinetic energy. At any rate, the excess energy in both appearances of the hydrogen ion is approximately the same.

NH_3^{++}

This ion appears at 42 ± 3.0 volts, from which it is deduced that

$$I(\text{NH}^+) \cong A(\text{NH}_3^{++}) - I(\text{NH}_3) \cong 31.5 \text{ volts.}$$

NEGATIVE IONS

NH_2^-

This ion appears at 6.0 ± 0.5 volts. The ionization efficiency curve, as shown in Fig. 8, exhibits a maximum at 7.3 ± 0.5 volts and some evidence

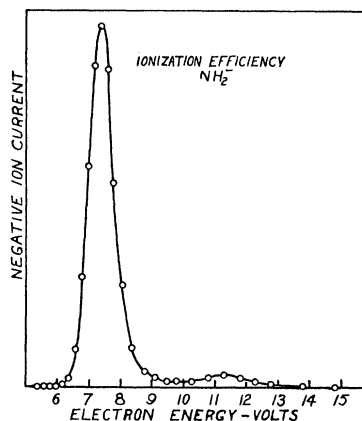


FIG. 8. Ionization efficiency curve for NH_2^- from NH_3 .

of another at about 11.3 volts. At energies above 15 electron volts, this ion is not formed. The process is evidently that of resonance capture of the impinging electron.

Since this negative ion is the only one observed in the M/e range 17 to 14, it was not possible to identify it as NH_2^- until CO was admitted to the apparatus. When this was done, the peak increased in intensity, indicating the ion to be of $M/e=16$, since, as was pointed out in the discussion of water vapor, the negative ion from CO is O^- .

Of all the states in Table IV the energy of d is the most uncertain. The value, 3.8 volts, has been set more or less arbitrarily for there exists very little experimental or theoretical work from which a value of the energy necessary to remove *one* hydrogen atom from the ammonia molecule may be obtained.²⁰

Since about 7.5 volts are required to remove two hydrogen atoms, it is believed that a value in the neighborhood of approximately one-half the above cannot be far wrong.

If this be so, then excess energy of the order two volts plus the electron affinity is observed in the process

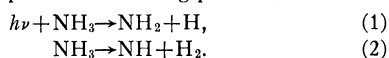


From a study of the electron configuration of the NH_2 molecule, it would be expected that it possesses characteristics somewhat similar to those of fluorine. In particular it would be expected to show a rather large electron affinity of the order 2 or 3 volts. It is, therefore, suggested that the energy of the state d is approximately correct and that NH_2^- is formed in an excited state and that the hydrogen takes up the excess energy.

H^-

This ion is also formed by resonance capture of the electron. It first appears at about 5.8 volts

²⁰ N. E. Bradbury, J. Chem. Phys. 2, 827 (1934), in discussing data obtained by other writers on the photochemical decomposition of ammonia and his own data on the formation of negative ions in ammonia, at relatively high pressures, proposes the following processes:



The process (1) is said to occur at approximately 4.7 volts energy and (2) to require 3.0. The latter is in agreement with the energy of the state c in the table. It is not revealed how this value for (2) was arrived at.

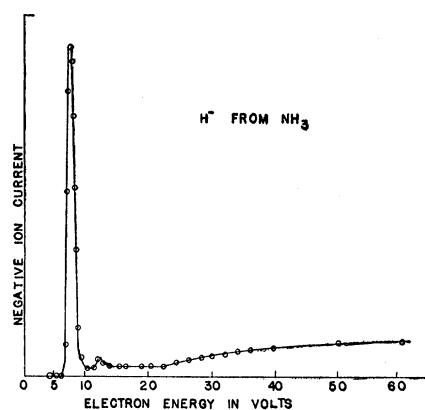
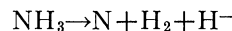


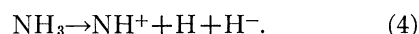
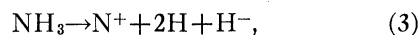
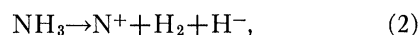
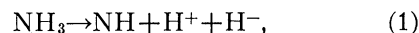
FIG. 9. Ionization efficiency curve for H^- from NH_3 .

with a maximum at about 7.2 volts and another break in the current-voltage curve, indicating formation by another process, occurs at 23 volts (Fig. 9). For the initial appearance the process



is evidently responsible, 5.7 volts being necessary, that is, state c less 0.7 volt (electron affinity of hydrogen).

There are four possible processes which may account for the second break in the H^- curve. These are



(1) requires 20.3 volts which leaves about 2.7 volts excess energy; (2) requires 20.2 volts; and (3) requires 24.7 volts. If the value of $I(\text{NH})$ deduced above is utilized, the energy necessary for (4) is 23.2 volts. While, of course, (1) and (3) are not ruled out, (4) would appear to be the more reasonable choice even though $I(\text{NH})$ is somewhat uncertain.

Although other negative ions such as NH^- and N^- are said to have been observed in ammonia in previous investigations, a very thorough search at electron energies from 4 volts up to 100 volts has failed to reveal any trace of these ions, and as both the resolving power and sensitivity of the present apparatus are superior with respect to the previous investigations, it can be stated with some confidence that these ions, if they do exist, are certainly of abundance <0.005 .