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Effect of Electric Fields on the Decomposition of Ammonia by Alpha-Rays

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The following values have been obtained for the ion yields in the alpha-ray decomposition of gaseous ammonia in the absence and presence of electric fields at 30°C and 100°C:

30°C	no field	1.37
	half-saturation	1.17
	full saturation	1.08
100°C	no field	2.42
	half-saturation	2.06
	full saturation	2.01

The results are interpreted upon the hypothesis that in a field sufficiently strong to produce half-saturation, the ions are neutralized upon the plates without decomposition. If this hypothesis is correct, of the ion yield 1.37 at 30°C, 0.40 is the ion yield due to recombination of ions and 0.97 the ion yield due to other mechanisms. Similarly of the ion yield 2.42 at 100°C, 0.72 is the ion yield due to recombination of ions and 1.70 the ion yield due to other mechanisms. Possible mechanisms of that part of the reaction consequent on ion recombination and of that part of the reaction independent of ion recombination are discussed.

IN the passage of alpha-particles through a gas both primary and secondary ionization result. The primary ionization is due to collisions of alpha-particles with molecules and the liberated electrons may have velocities between 0 and $2V$, where V is the velocity of the alpha-particle. If the speed of the ejected electrons is sufficiently high, they may in turn produce a number of ions before they come to rest. The number of ions produced by secondary ionization is approximately four-fifths of the total ionization.^{1,2} However, the total energy of the alpha-rays is frequently more than twice the energy used in ionization and it is known that some of this energy produces excited or metastable molecules. The collision of an alpha-particle with a molecule may also directly split the molecule into radicals or atoms.

Some photochemical reactions are known to be initiated by excited molecules which decompose either directly or on collision with a neutral molecule. This type of mechanism is represented by the photochemical decomposition of ammonia.³ Other reactions produced by light occur due to the immediate splitting of the irradiated molecule, as with chlorine in the synthesis of hydrogen chloride from the elements.⁴

These mechanisms which have been used to explain photochemical reactions also seem plausible in alpha-ray decomposition. Or metastable molecules may decompose on collision with other molecules. Sufficient energy is liberated on the neutralization of ions to initiate chemical reaction. Reaction may occur on the neutralization of ions (clustered or not) or on ions before neutralization. One or the other of these mechanisms, or a combination of two or more, has been used by different investigators to explain reactions initiated by alpha-rays.

If some of the ions could be removed from the gas before neutralization, the value of the ion yield determined under such conditions might give some indication as to the mechanism of the reaction. Essex and FitzGerald⁵ successfully determined the ion yield in the decomposition of ammonia by alpha-rays using the saturation current method to determine the number of ions produced. Their work suggested the possibility of determining the yield in electric fields sufficient to produce saturation, that is, under conditions under which recombination of ions in the gaseous phase does not occur. This paper is a report of ion yield measurements in the decomposition of ammonia by alpha-rays in the presence and absence of strong electric fields. The ion yields are compared and possible mechanisms discussed.

¹ Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, p. 145.

² H. Bethe, *Ann. d. Physik* **5**, 400 (1930).

³ E. O. Wiig and G. B. Kistiakowsky, *J. Am. Chem. Soc.* **54**, 1806 (1932).

⁴ M. Bodenstein and Taylor, *Zeits. f. Elektrochem.* **22**, 53 (1916).

⁵ H. Essex and D. FitzGerald, *J. Am. Chem. Soc.* **56**, 65 (1934).

EXPERIMENTAL DETAILS

The apparatus is represented diagrammatically in Fig. 1. It was constructed of Pyrex glass, except for the reaction vessel through which the heavy platinum leads to the platinum electrodes were sealed. The electrodes were 4 cm in diameter. The cylindrical vessel, 11 cm long and 6.5 cm in diameter, was blown of soft glass and was connected to the rest of the system by a graded seal. To prevent electrical discharge between the electrodes and the glass walls and also to prevent current conducted through and over the glass from inclusion in the ion current, thin copper disks were cemented to both ends of the reaction vessel. The cement used was a mixture of "Liquasol" and finely powdered silver. The disk at the high potential end was 5 cm in diameter and electrically connected to the high potential lead. The disk at the low potential end, 3 cm in diameter was provided with a hole 5 mm in diameter through which passed the lead to the low potential electrode. This disk was grounded. The radioactive material, an isotopic mixture of radium and mesothorium was placed in the depression of the reaction vessel and the vessel was surrounded by an air bath maintained at constant temperature.

The ammonia was obtained from a solution of ammonia in ammonium thiocyanate and was dried as it passed over crushed potassium hydroxide and barium oxide. Previous to introducing an ammonia sample, the entire system was evacuated by means of a mercury vapor pump to a pressure of less than 10^{-5} mm as measured by the McLeod gauge. While the system was being evacuated, trap T' was surrounded with liquid air⁶ and dry ammonia was admitted. When sufficient ammonia was condensed to fill the apparatus at more than the desired pressure, the stopcock to the generator was closed and evacuation continued until the pressure with the pump in operation, was again less than 10^{-5} mm. The liquid air was then removed and the ammonia allowed to evaporate, the first portion to vaporize being withdrawn through the pump. Then the stopcock to the

⁶ The liquid air used in this investigation was provided by the General Electric Company of Schenectady, New York, through the courtesy of Dr. L. M. Willey, to whom the authors wish to express their gratitude.

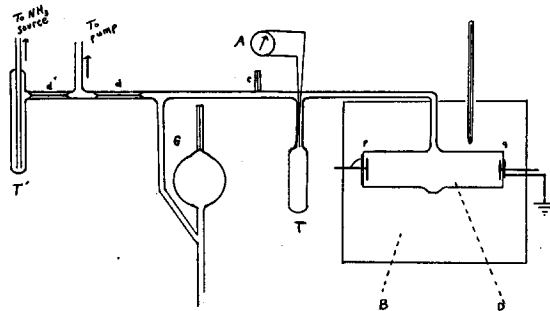


FIG. 1. T' and T , Traps for condensing out ammonia; d' and d , Pyrex barometer tubing; G , McLeod gauge, volume of bulb = 108.7 cc, radius of capillary = 0.443 mm; A , thermocouple and millivoltmeter; c , capillary, used to open system; B , constant temperature air bath; D , reaction vessel, length = 11.0 cm, diam. = 6.5 cm, vol. = 339 cc, electrode distance = 10.2 cm; p , high potential end of vessel; g , grounded end of vessel.

pump was closed and the remaining ammonia allowed to vaporize. After vaporization was complete the ammonia was again condensed, the stopcock to the pump was opened when the condensation was nearly complete and the last fraction not yet condensed was removed through the pump. This procedure of successive vaporization, condensation and evacuation was repeated three or four times until the pressure at equilibrium after freezing out the ammonia was less than 5×10^{-5} mm. The liquid air was then placed around trap T , enough ammonia condensed there to fill the apparatus at more than the desired pressure and the connection to the ammonia reservoir sealed at d' . This sample was then vaporized and enough ammonia withdrawn to give the desired pressure (calculated from the volumes of the system before and after sealing). The remaining ammonia was again condensed and the system evacuated to a pressure of 10^{-6} mm and the pump sealed off at d .

The electrical connections are shown in Fig. 2.

With the system filled at the desired pressure, the transformer was run up to 20,000 volts, the switch tripped and readings taken on the galvanometer and the electrostatic voltmeter as the potential dropped. Characteristic curves obtained on plotting galvanometer deflections versus voltage are shown in Fig. 3. That the great majority of the positive ions arrived at the plate is indicated first by the fact that the current reached a constant value at high potentials. Second, separate experiments were carried out

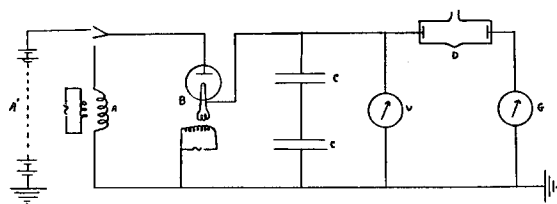


FIG. 2. *A'*, storage battery, 1071–1118 volts; *A*, transformer, G.E. type K, form E, capacity 3kva; *B*, rectifying tube, G.E. Kenetron, type KP-2, voltage on primary of filament transformer (11 to 1 ratio) 70; *C*, condensers, G.E., capacity=0.25 mf, 18,000 volts; *V*, electrostatic voltmeter, G.E. type EL-2, 30,000 volts; *D*, glass vessel, platinum electrodes; *G*, galvanometer, L+N type R, internal resistance=516 ohms, sensitivity= 1×10^{-10} amp./mm at 1 meter.

for evidence of arrival of ions at the glass. With the galvanometer inserted between the low potential shield and the ground, the current to this shield both in the absence and presence of radioactive material was measured. No difference was observed. Third, the ion yields obtained in the absence of fields agree with those obtained by other investigators.

After thirteen or more hours the ammonia was frozen out and the residual pressure measured after ten minutes. The liquid air was kept around the trap for about an hour during which time the residual pressure was frequently measured. In none of the runs was any change in pressure observed during this time. The time at which the

ammonia was again vaporized was considered as the starting time of the reaction, pressure changes thereafter being assumed to be due only to ammonia decomposition. The nitrogen and hydrogen were considered to be present in stoichiometric proportions.^{7–9} Current-potential curves were taken at regular intervals during the run. Subsequent to each set of current measurements the galvanometer was calibrated. This was accomplished by determining with a potentiometer the potential necessary to give the same swings through a known resistance. In the runs at 100°C the pressure was such that the gas density was the same as in the runs at 30°C.

In calculating the rate of decomposition from the pressure changes, the different temperatures of the various portions of the system were taken into account. Pressure correction for these effects was determined in the following manner. A drying tube filled with soda-lime was sealed on to the capillary *c* through a stopcock. After the system had been thoroughly evacuated and sealed at *d*, dry air was admitted to a low pressure, where the simple gas laws hold with considerable accuracy, and the stopcock was closed. The pressure of the air in the system was read on

⁷ E. Wourtsel, *Le Radium* **11**, 332 (1919).

⁸ A. Koenig and Th. Brings, *Zeits. f. physik. Chemie, Bodenstein Festband*, 541 (1931).

⁹ A. Luyckx, *Bull. soc. chim. Belg.* **43**, 160 (1934).

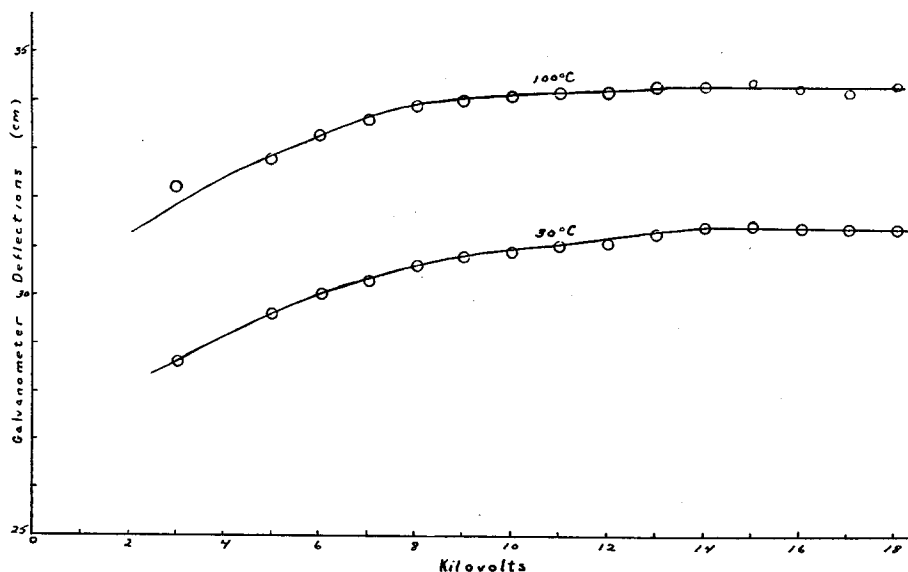


FIG. 3.

the manometer formed by the tube leading to the McLeod gauge and by the leveling bulb. Then liquid air was placed around trap *T* and its level adjusted to contact with the attached thermocouple. After ten minutes the pressure of the air was again read. It follows from the gas laws that the relation between *P*, the pressure without the liquid air around the trap and *P_L*, that with the liquid air is

$$P = P_L \frac{V_t T_r + V_s T_L - V_t T_L}{V_s T_L},$$

where *V_t* is the volume of the trap at liquid-air temperature, *V_s* is the total volume of the system, *T_r* is room temperature and *T_L* is the temperature of the trap partly immersed in liquid air. *V_s*, *V_t*, *T_r* and *T_L* are constants. Hence the above relation reduces to

$$P = K P_L.$$

The value of *K* determined in the above manner was found to be 1.23 when the bath was at 100°C and 1.16 when it was at 30°C. Because of the low pressure (approximately 10 cm) these values determined for air hold accurately for nitrogen-hydrogen mixtures. This correction was applied to all the residual pressure readings with ammonia. At this pressure *P*, 349 cc of the nitrogen-hydrogen mixture were at the temperature of the bath and 222 cc at room temperature.

The greatest known uncertainty in the experimental measurements from which the ion yields were calculated was in the pressure measurements. Assuming an uncertainty in reading the McLeod gauge of 0.5 mm, the probable error in yields does not exceed 3 percent.

The experimental data and the calculated ion yields are presented in Table I. A sample

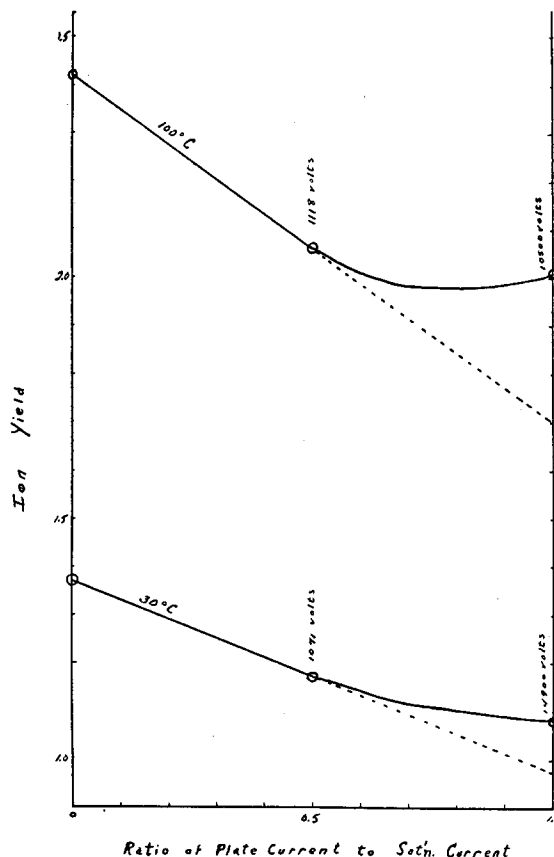


FIG. 4. Since the potential for half-saturation is but 0.1 of that for saturation, the curve to half-saturation is drawn as a straight line.

calculation follows. The results are shown graphically in Fig. 4.

Sample calculation (For run at 100°C and no field)

M—Number of gram mole of ammonia decomposed.

Number g mole of $N_2 + H_2$ in 348 cc

$$\frac{0.0435 \times 348}{760 \times 82.1 \times 373} = 6.50 \times 10^{-7},$$

TABLE I.

TEMP. °C	PRESS. OF NH ₃ (CM)	POTENTIAL (VOLTS)	*DURATION (HOURS)	RESIDUAL PRESSURE CHANGE (MM)	ROOM TEMP.	CURRENT AMP. $\times 10^{-8}$		ION YIELD
						SATN.	TO PLATE	
30	62	0	173.7	0.0345	23°C	5.92	0	1.37
30	62	1071	118.5	0.0196	22	5.79	2.88	1.17
30	62	14900	124.2	0.0201	23	6.10	6.10	1.08
100	76	0	125.0	0.0435	22	5.21	0	2.42
100	77	1118	126.1	0.0352	24	4.89	2.49	2.06
100	76	10500	70.1	0.0186	27	4.71	4.76	2.01

* The duration of the run was obtained by subtracting from the total time the time during which the ammonia was condensed.

Number g mole of $N_2 + H_2$ in 222 cc

$$= \frac{0.0435 \times 222}{760 \times 82.1 \times 295} = 5.25 \times 10^{-7},$$

$$M = \frac{(6.50 + 5.25) \times 10^{-7}}{2} = 5.88 \times 10^{-7}.$$

N —Number of gram ions present.

$$\text{Number amp.} = 5.21 \times 10^{-8},$$

$$\text{Number coulombs} = 5.21 \times 10^{-8} \times 125.0 \times 3600,$$

$$N = \frac{5.21 \times 10^{-8} \times 125.0 \times 3600}{96500} = 2.43 \times 10^{-7}.$$

$$M/N \text{—Ion yield} = \frac{5.88 \times 10^{-7}}{2.43 \times 10^{-7}} = 2.42.$$

Preliminary experiments were carried out in which the residual pressure was measured as a function of time in the absence of radioactive material both in the absence and presence of electric fields. The observed residual pressure changes were small and equal to zero within the experimental error of these measurements. It may be assumed, therefore, that decomposition due to catalysis and electric discharge plays a negligible part in the measured reaction.

Ion yields were initially determined by the described procedure using a vessel in which about one-third of the volume was behind the plates and without exterior shields. The results shown in Table II were obtained.

In these preliminary experiments the ion yield in no field at 100°C was very much higher than that obtained by others and it was found that the saturation current at 100°C was only about 68 percent of that at room temperature, even when precautions were taken not to unnecessarily disturb the distribution of the radioactive material. Temperature¹⁰ should affect but slightly the number of ions produced by the alpha-particles at constant density. However, temperature does affect the velocity of diffusion of the emanation and it seems likely that at 100°C a

large fraction of the ions from the emanation and its decomposition products were being produced behind the plates where the field strength was low and insufficient to bring all of them to the plates, before recombination. Hence the calculated value of the number of ions formed by the radioactive material was low. The conductivity from plate to plate in the absence of ionizing radiations was negligible with this vessel. Apparently the specific resistance of the glass used was a great deal higher than that from which the final reaction vessel was constructed.

To avoid errors from the indicated source the reaction vessel used in the final measurements was constructed with the electrodes as close to the ends as practical without contact. Preliminary experiments with such a vessel, however, showed the presence of slight discharges between the electrodes and the glass. Errors of this sort were eliminated by the copper shields.

Even with the final vessel the saturation current at the higher temperature was only about 90 percent of that at 30°C . The space behind the electrodes was too small to account for this discrepancy. It is believed that the major portion of this difference is due to removal by convection currents of a larger quantity of the emanation and, therefore, of its decomposition products from the reaction vessel to the connecting tube at the higher temperature. The connecting tube projected vertically upward from the reaction vessel through the cover of the constant temperature air bath. Considerable convection might result from the large temperature gradient within a few centimeters of the reaction vessel. Some error may result but it should not be large as the paths of the alpha-particles produced in the connecting tube are greatly shortened and hence the number of ions not brought to the plates is small.

TABLE II.

	ROOM TEMP.		100°C	
	VOLTAGE	ION YIELD	VOLTAGE	ION YIELD
No field	0	1.25	0	3.10
50% sat'n.	765	1.16	383	2.65
98% "	—	—	4600	2.51
100% "	17000	1.09	10300	2.76

¹⁰ A. Becker and Ilsemarie Schaper, *Zeits. f. Physik* **79**, 186 (1932); **91**, 422 (1934).

DISCUSSION OF RESULTS

Ion yields in absence of electric fields

The ion yields here reported of 1.37 at 30°C and 2.42 at 100°C give a temperature coefficient of 0.015 units per degree. They were obtained at extremely low intensities of ionization. Ion yields to be found in the literature, with the exception of the earlier and more qualitative values obtained by Essex and FitzGerald⁵ in this laboratory, are at much higher intensities of irradiation, in most cases several hundred times as great, and cannot, therefore, be directly compared.

Luyckx¹¹ has, however, in a recent careful and accurate work determined the effect of intensity of ionization in the ammonia decomposition at 19°C and has extrapolated his data to zero intensity. As the lowest intensity at which he measured the ion yield in the neighborhood of atmospheric pressure is approximately thirteen times as great as in these experiments, the Luyckx value to be used for comparison is the extrapolated value at zero intensity. It is 1.27 at 19°C or $1.27 (1 + 0.015 \times 11)$ at 30°C which equals 1.44. This value compares favorably with 1.37 obtained in the present study. Luyckx made no measurements at higher temperatures. If, however, the effect of intensity can be assumed the same at 100°C as at 19°C, the limiting value of the ion yield may be approximated at 100°C by the following relation

$$0.87 : 1.27 = 1.63 : (M/N_{\infty})_{100^{\circ}\text{C}},$$

where 0.87 and 1.63 are the interpolated values at 19°C and 100°C, respectively, based on the values Jungers¹² obtained on the recalculation of Wourtsel's⁷ results. The ion yield at 100°C and at limiting intensity is thus found to be 2.38 as compared with the present value of 2.42. The effect of intensity at temperatures other than room temperature has not been studied. Jungers¹³ in a study of the effect of temperature on the ion yields for the decomposition of ammonia and deuterio-ammonia, reports that the yield for ammonia at 100°C and 52.5 mm is 1.87 times that at 20°C.

¹¹ A. Luyckx, *Bull. soc. chim. Belg.* **43**, 117 (1934).

¹² J. C. Jungers, *Bull. soc. chim. Belg.* **41**, 377 (1932).

¹³ J. C. Jungers, *J. Phys. Chem.* **40**, 155 (1936).

The direct method of ion yield determination used in this laboratory eliminates many uncertainties which enter into other methods involving, in the method of homogeneous irradiation, the assumption of the validity of Geiger's law, and depending on the accuracy of the hypotheses used regarding the distribution of the Ra A and Ra C' between the walls and the gas, on the values assigned to the ranges and resulting ionization of the various alpha-particles and on calculations regarding the effect of recoil atoms. Where the effect has been taken into account at all, the methods of correcting for the unequal distribution of the ionization along the trajectory of an alpha-particle appear particularly doubtful. Most of these sources of error are also present in the method of central irradiation, together with the errors involved in the determination of the decrease in range of an alpha-particle due to the thickness of the central glass bulb containing the radon.

The effect of electric fields

The data, here presented, are the first regarding the effect of electric fields on the ion yield. In a field less recombination of ions occurs in the gaseous phase and in a saturation field no recombination of ions can take place in the gas. The results show that as the field is increased, the first effect is to decrease the ion yield. The decrease in the yield, however, is not proportional to the current (Fig. 4), an effect particularly marked at the higher temperature, indicating at high potentials the initiation of a new mechanism of decomposition or the increase in efficiency for decomposition of a reaction already taking place.

Due to the presence of other molecules and atoms to take up the energy, the neutralization of ions at a plate might be expected to result in less decomposition than in the gaseous phase. If it is assumed that the low fields result in neutralization at the plate without decomposition, the ion yield due to recombination of ions in the gas phase can be calculated from the results. Considering the values at 30°C, at which the ion yield in no field is 1.37 and that at half-saturation is 1.17 (a difference of 0.20), the ion yield due to the recombination of ions is 0.40. An analogous calculation at 100°C leads to an ion yield due to

recombination of ions of 0.72. Decomposition per ion pair due to other mechanisms than ion recombination is calculated on this assumption to be at 30°C, $1.37 - 0.40 = 0.97$ and at 100°C, $2.42 - 0.72 = 1.70$. It is to be noted that the voltage for half-saturation is only about one-tenth that for full saturation.

MECHANISM

Decomposition of ammonia in the presence of alpha-rays would certainly be expected to take place by other mechanisms than ion recombination. As only a relatively small fraction of the energy of alpha-rays is used in ion production, a considerable portion of this energy must go into producing excited molecules. Studies of the photochemical decomposition and of the absorption spectrum of ammonia show fairly definitely that excited molecules of ammonia decompose spontaneously to NH_2 and H. All recent work on the photochemical decomposition of ammonia postulates this as the first step.^{3, 14-16}

Duncan^{17, 18} in studying the absorption spectrum of ammonia, has shown the presence of four band systems, the first of which is due to the displacement of electrons to the first excitation level. This system shows no line structure in the bands and is of the type known as "predissociation," which have been interpreted as indicating that spontaneous dissociation immediately follows excitation to this stage. The other three band systems show line structure, which indicates that spontaneous dissociation does not occur from higher excited states. Dissociation might, however, occur on collision of ammonia molecules in these higher excited states with neutral molecules. In the far ultraviolet the absorption spectrum is continuous which indicates that ammonia molecules are decomposed directly by high energy quanta probably, according to Duncan, into N and 3H. Molecules of ammonia excited to the first level should then decompose spontaneously, those excited to

higher levels might decompose on collisions or spontaneously after the fall of the displaced electron to the first level. If this occurs, fluorescence should be observed. Duncan is studying the visible and near ultraviolet region for evidence of fluorescence. Electrons of energies equivalent to the quanta which are responsible for continuous absorption might be expected to produce direct dissociation in the manner indicated.

Still other mechanisms of ammonia decomposition are possible. Mund,¹⁹ for instance, considers that decomposition may occur in the molecules clustered about an ion before neutralization. Such a mechanism seems to explain most satisfactorily the synthesis of hydrogen chloride from hydrogen and either positive or negative chlorine ions produced by a point discharge.²⁰ In this case Gunther and Holm believe that a chlorine ion attaches chlorine molecules to itself and that the chlorine molecules dissociate on the surface of the cluster. The atoms thus formed start chain reactions with the hydrogen. However, a mechanism of this kind appears less probable for reactions requiring considerable energy of activation.

According to modern theory, by far the larger part of the energy lost by the passage of charged particles through gases is lost in inelastic collisions. In the case of alpha-ray ionization for air approximately four-fifths^{1, 2} of the ionization is secondary, that is, due to inelastic collisions of electrons with molecules. Lunt and Meek²¹ have calculated, for the passage of electrons through hydrogen, the distribution of the energy loss among ionization, excitation, vibration and elastic collisions. If the distribution of the energy loss of electrons in collisions is assumed the same in passing through ammonia as is passing through hydrogen, approximately 8 percent of the energy of an alpha-particle is used up primarily in elastic collisions and 92 percent is distributed among ionization, excitation and direct decomposition. Since 11.3 eV¹⁷ is the ionization potential

¹⁴ H. W. Melville, *Trans. Faraday Soc.* **28**, 885 (1932).

¹⁵ R. A. Ogg, P. A. Leighton and F. W. Bergstrom, *J. Am. Chem. Soc.* **56**, 318 (1934).

¹⁶ L. Farkas and P. Harteck, *Zeits. f. physik. Chemie* **B25**, 257 (1934).

¹⁷ A. B. F. Duncan, *Phys. Rev.* **47**, 822 (1935).

¹⁸ A. B. F. Duncan and G. R. Harrison, *Phys. Rev.* **49**, 211 (1936).

¹⁹ W. Mund, *L'Action Chimique des Alpha Rayons en Phase Gazeuse* (Hermann et Cie, Paris, 1935).

²⁰ P. Gunther and K. Holm, *Zeits. f. physik. Chemie* **B33**, 407 (1936).

²¹ R. W. Lunt and C. A. Meek, *Proc. Roy. Soc.* **A157**, 146 (1936).

of ammonia and approximately 37 eV²² is expended in the formation of an ion pair in ammonia, 11.3/37 or 31 percent of the energy goes into ionization. Hence the remaining 61 percent or 0.61×37 which equals 23 eV goes into excitation. Assuming that the balance of the energy goes entirely into excitation at the first excitation level, $23/6.2^{23}$ or 3.7 excited molecules are produced per ion, which on the basis of our data at 30°C would mean an excited molecule yield of $0.97/3.7$ or 0.26. This is considerably greater than the quantum yield of 0.18²⁴ obtained in the photochemical decomposition of ammonia at ordinary temperatures and atmospheric pressure. This discrepancy can be accounted for upon the assumption that the energy of the alpha-particle which goes neither directly into ionization nor into kinetic energy is distributed between excitation and direct decomposition. The latter energy should be of high efficiency, if the decomposition is that postulated by Duncan, namely to N and 3H. It is of interest to note that a quantum yield of 0.69 was found by Kassel and Noyes²⁵ in the photochemical decomposition of ammonia at wave-lengths of 1600 to 1900 Å. Gedye and Rideal²⁶ suggest that this higher yield may be accounted for by the decomposition of the more highly excited molecules to NH and 2H, a reaction for which the quantum energy is sufficient at these wave-lengths. On the basis of Duncan's recent work this seems improbable, but the greater efficiency may be accounted for by collisions between molecules in the higher excited state and neutral molecules. However, in a recent paper Groth²⁷ working in the Schumann region of the ultraviolet reports an ion yield in the ammonia decomposition of 0.17 at 1470 Å and 1295 Å in complete agreement with the result of Wiig²⁴ at 2000 Å. This appears more probable. 1295 Å is still above the region of continuous spectrum and the corresponding quantum energy is insufficient for the decomposition to N and 3H.

If the spectrum of ammonia and its photo-

chemical decomposition have been correctly interpreted, it would appear probable that the mechanism of the reaction involved in the recombination of ions should be similar to that proposed for excited molecules. The recombination may take place, at least to some extent, in the falling of an electron to the first excited level followed by spontaneous decomposition or the electron may fall in directly with resulting decomposition to N and 3H, for which apparently, as the absorption spectrum becomes continuous at frequencies below that corresponding to the ionization potential, sufficient energy is available. A combination of these two methods of neutralization would be expected to result in an ion yield above the quantum yield of 0.18. The value calculated from the results of this work and on the basis of the stated assumptions is 0.40. If, before neutralization occurs, the positive ion has surrounded itself with neutral molecules to form a cluster, or if, as should happen after a longer interval due to the small electron affinity of ammonia, the neutralization is that of a positive cluster by a negative ammonia ion, the mechanism of the resulting reaction might be different, or the same. There seems to be no evidence available bearing on this point.

Bartlett²⁸ has carried out experiments in which electrons were accelerated into ammonia at low pressures and the resulting ions after acceleration by an electric field were analyzed by a magnetic field using the Dempster method. No negative ions were found. The positive ions produced were NH_3^+ , NH_2^+ and NH^+ . The variation in the intensity of the NH^+ and NH_3^+ lines with pressure showed definitely that the NH^+ ions were the result of collisions of NH_3^+ ions with neutral molecules. The NH_3^+ and NH_2^+ ions were both primary products produced by electrons of about the same energy, 11.2 and 12.0 eV, respectively, and in about equal numbers.

This work of Bartlett's indicates that in the passage of alpha-rays through ammonia, particularly as most of the ionization is by electrons, the primary ions are NH_3^+ and NH_2^+ in about equal numbers.

Taylor²⁹ in a study, by means of a modified

²² Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, pp. 81 and 82.

²³ R. S. Mulliken, *J. Chem. Phys.* **1**, 492 (1933).

²⁴ E. O. Wiig, *J. Am. Chem. Soc.* **57**, 1559 (1935).

²⁵ L. S. Kassel and W. A. Noyes, *J. Am. Chem. Soc.* **49**, 2495 (1927).

²⁶ G. R. Gedye and E. K. Rideal, *J. Chem. Soc.* 1160 (1932).

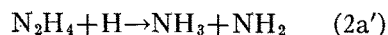
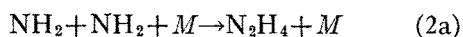
²⁷ W. Groth, *Zeits. f. physik. Chemie* **37**, 307 (1937).

²⁸ J. H. Bartlett, *Phys. Rev.* **33**, 169 (1928).

²⁹ D. D. Taylor, *Phys. Rev.* **47**, 666 (1935).

Aston type mass spectrometer, of the ions produced in ammonia by controlled electron collisions also found no NH^+ at low electron energies and low pressures. Since in fields of the strength used in the present work, the kinetic energies of the ions are not appreciably greater than the thermal energies of the surrounding molecules,³⁰ it is doubtful that NH^+ ions are produced by collisions.

If the simple interpretation which has been given to the results in electric fields is to hold, the ions neutralized on the plates must regenerate ammonia. Neutralization of the positive ions NH_3^+ and NH_2^+ in the presence of other atoms or molecules to remove the excess energy may result in the following reactions with the direct or indirect regeneration of ammonia.



These reactions are plausible on the basis of photochemical results. The quantum yield falls off very rapidly at low pressures. Wiig³¹ proposes the occurrence of reactions (2) and (2a) followed by (2a') to account for the decrease in quantum yield at pressures of ammonia below 100 mm, assuming that at these low pressures the reaction becomes heterogeneous and regeneration of ammonia occurs on the walls.

When the negative ammonia ions are neutralized, energy is required to remove the electron from the molecule and no chemical action can occur.

³⁰ See for instance, Darrow, *Electrical Phenomena in Gases* (1932), p. 195.

³¹ E. O. Wiig, *J. Am. Chem. Soc.* **59**, 627 (1937).

The reaction apparently initiated or greatly accelerated by high voltage must be due either to increased efficiency for decomposition of collisions of the ions on the plates or of collisions of the ions with gaseous ammonia molecules. The present work yields no information favoring either one or the other of these mechanisms. By increasing the life of the ions at the same potential gradient, information might be obtained bearing on this question. This might be accomplished by using a reaction vessel of the same general design but with a greater distance between the electrodes. The ions being removed to the plates would undergo more collisions due to the greater distance traveled. If the change in yield is due to increased efficiency of collisions of the ions with the plate, the yield in a vessel of this design should be the same as in the present work but if it is due to increased efficiency of collisions of ions with molecules, it should be greater.

An increase in temperature in both the photochemical^{15, 32} and radiochemical decomposition of ammonia results in a large increase in yield. In the present work the true ion yield is found to increase from 0.40 at 30°C to 0.72 at 100°C, and the ion yield due to other mechanisms, assumed to be mostly initiated by excited molecules, from 0.97 at 30°C to 1.70 at 100°C. In both cases the yield at 100°C is 1.8 times that at 30°C which is in conformity with the hypothesis that the primary and, therefore, also secondary mechanisms resulting from ion recombination and excited molecules are similar.

The results of this work show that by the study of radiochemical reactions in electric fields, the part of the reaction due to recombination of ions may be separated, at least to some extent, from that part due to other mechanisms. With some reactions the separation may be complete.

³² W. Kuhn, *Comptes rendus* **177**, 956 (1923); **178**, 708 (1924).