The Ion Yield in the Decomposition of Ammonia by Alpha Rays[1,2]

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Obviously, for a calculation of the ion yield for a chemical reaction, it is necessary that both the number of molecules reacting and the number of ions present in the reacting system, during a given time interval, be accurately known. For the reactions caused by alpha radiation that have been studied up to the present time, the numbers of molecules reacting chemically have generally been easily determined by analyses or by measurements of pressure changes: the determination of the numbers of ions present, however, has presented some difficulties. As Lind[3] has pointed out, it has rarely been possible to measure by the saturation current method intensities of ionization sufficiently great to produce appreciable amounts of chemical reaction, because the requisite ion concentrations exceed the limiting value for the attainment of saturation. For this reason, the numbers of ions present have, in the past, been calculated rather than directly measured. The methods of calculation that have been developed[4] all require accurate information concerning the nature of the radioactive substance and necessitate time-consuming measurements of its activity under particular experimental conditions.

Developments and improvements within the last few years in high tension transforming and rectifying equipment have provided a source of much higher voltages than were formerly available, and so have made possible the attainment of saturation currents corresponding to greater ion concentrations. The purpose of the investigation here reported was to demonstrate the practicability of measuring by the saturation current method, with the aid of some of this newer equipment, intensities of alpha ray ionization corresponding to measurable amounts of chemical reaction.

(1) From the thesis submitted by Dorothea FitzGerald to the Faculty of the Graduate School of Syracuse University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933.

(2) Presented at the Washington meeting of the American Chemical Society, March, 1933.

(3) Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Company, Inc., New York, 1928, pp. 46-47.

(4) Lind, ibid., Chap. 7; Mund, J. Phys. Chem., 30, 890-894 (1926), and others.

Experimental Details

A sketch of the apparatus used is shown in Fig. 1.

The radioactive material, a sample of mesothorium containing about 20% of radium, was placed in the depression in the vessel R. A grounded coil of copper wire, wrapped tightly around the vessel, prevented the flow of current across the outside walls and through the galvanometer. In order to eliminate galvanometer disturbances due to induction currents, the galvanometer and the lead from R to G were enclosed with grounded metal shields. Erratic deflections of the electrostatic voltmeter (probably caused by fluctuations in the 110-volt line) made it impossible to measure accurately the voltage while the transformer was in operation; current and voltage readings were therefore made only after the transformer had been shut off, while the charge on the condensers was slowly decreasing.
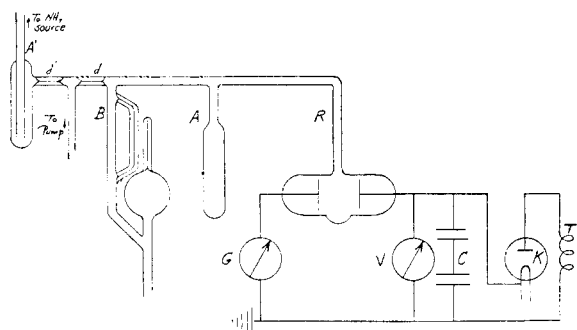

Fig. 1.—Apparatus. A and A', traps for condensing NH_3; volume of A, 35 cc.; B, McLeod gage; bulb 113.8 cc.; capillary 0.00283 cc./cm.; C, condensers, capacity 25 m. f., 18,000 volts; G, galvanometer, sensitivity 2.18 $\times 10^{-8}$ amp./cm.; K, kenotron rectifying tube, operated at max. current 2 m. a.; R, reaction vessel, volume 197.5 cc. electrode distance 5.7 cm.; T, transformer secondary, capacity 3 k. v. a.

The ion yield was obtained for the decomposition of ammonia at room temperature and atmospheric pressure. Results of preliminary experiments to be described below led to the adoption of the following procedure.

The entire system was evacuated by means of a Hyvac mercury vapor pump until the pressure, measured with the McLeod gage, was less than 10^{-5} mm. Trap A' was then surrounded with liquid air, and ammonia gas, obtained from a solution of ammonia in ammonium thiocyanate, and dried by passage over crushed potassium hydroxide and barium oxide, was admitted, more being condensed in A' than sufficient to fill the apparatus at a pressure of one atmosphere. The liquid air was removed, and the ammonia allowed to evaporate; the first portion to vaporize was withdrawn through the pump and discarded. The remainder, still at a pressure greater than atmospheric, was again frozen; after this condensation the pressure of the uncondensed gases was generally greater

than 10^{-4} millimeters. To remove these gases as completely as possible the process of successive evacuation, vaporization and condensation was repeated until the pressure, after freezing out the ammonia, was less than 5×10^{-5} millimeters: this generally required three or four repetitions of the cycle. A sample of ammonia thus prepared, sufficient to fill the apparatus at one atmosphere pressure, was condensed in A, the connection to the ammonia reservoir sealed at d', the system pumped out to a pressure of about 10^{-6} millimeters, and the pump sealed off at d.

The sample was then vaporized. After fifteen or more hours, the ammonia was condensed, the residual pressure measured and the ammonia again vaporized, the time of this latter vaporization being regarded as the starting time of the reaction. Changes in the residual pressure thereafter (assumed to be due to the production of a 1:3 nitrogen hydrogen mixture) were determined at intervals of a few hours until the pressure had increased to a value too high to be measured with the McLeod gage.

The number of molecules of ammonia decomposed was calculated from the pressure change (corrected for gas liberated from walls while ammonia was frozen out) by means of the gas laws. In determining the volume of the system to be used in this calculation account was taken of the cooling effect of the liquid air around the trap during pressure measurements. The number of ions present was calculated from occasional measurements of the saturation current.

Results

The results of preliminary experiments carried out before the decomposition measurements were begun are given in the following paragraphs.

(1) In the absence of radioactive material no current flowed through the galvanometer when the vessel was filled with dry ammonia at atmospheric pressure and connected as shown in Fig. 1. It was found, however, that if the system were not completely free of water vapor, conduction across the inner surface of the vessel began at about 10,000 volts, increased rapidly with increasing voltage and in some cases completely obscured the saturation current. In the final ion yield experiments it was, therefore, necessary that the apparatus and the ammonia be rigorously dried.

(2) When the ammonia contained only minute quantities of non-condensable gases, the rate of its freezing out was very rapid, and condensation was complete in less than ten minutes. In the presence of considerable quantities of non-condensable gases, condensation of ammonia was very slow; in one experiment at atmospheric pressure, in which the partial pressure of the foreign gas was less than seven centimeters, the ammonia was not completely frozen out even

after twenty-six hours. In the final measurements the ammonia was freed of impurities as far as was practicable, and ten minutes were allowed for condensation of the ammonia before pressure measurements were made.

(3) The residual pressure in the system, in the absence of radioactive material, was found to increase, over a period of from twelve to fifteen hours after sealing, to about 0.0017 mm. and thereafter to remain constant. The attainment of this constant pressure indicates that catalytic effects (of mercury vapor, platinum electrodes, etc.) on the decomposition of ammonia are negligible at this temperature.

(4) After the attainment of the above-mentioned constant pressure, non-condensable gas added to the system from a small bulb to a pressure of 0.0095 mm., remained in the gas phase (i. e., was not adsorbed), indicating that the total quantity of nitrogen and hydrogen formed by the decomposition of ammonia should be given by the pressure measurements.

(5) After the radioactive material was placed in the depression in the vessel R, and a sample of ammonia sealed into the system, it was found that while the ammonia was frozen out, the pressure in the system increased continuously at a rate of about 0.00009 mm. per hour. This pressure change is believed to be due to gases expelled from the walls by alpha-ray bombardment. Although no direct data were obtained relative to the quantity of gas liberated in this way in the presence of ammonia at atmospheric pressure, it was assumed to be very small because of stoppage of the alpha rays by the gas. Experiments are now in progress in this Laboratory to determine the validity of this assumption; some justification for it is indicated by the fact that calculations of ion yields, made on the assumption that gas is being liberated at all times at a rate of 0.00009 mm. per hour, led to results which vary greatly among themselves and which do not check those of other investigators.

A saturation curve typical of those obtained in all the final ion yield experiments is shown in Fig. 2; the greatest currents measured were 6.98×10^{-8} ampere.

The ion yields and the data from which they were calculated are given in Table I.

The extent of agreement of the average value, 1.09, with those of other investigators is shown in Table II.

TABLE I

DATA AND ION YIELDS FOR THE DECOMPOSITION OF AMMONIA AT ATMOSPHERIC PRESSURE

Time, hrs.	Press. change, mm.	Vol., cc.	Room temp., °K.	Galv. defl. cm.	Ion yield $-M_{NH_3}/N_{NH_3}^+$
22.75	0.004888	445	295	3.2	0.998
22.17	.004514	445	292	3.0	1.02
46.17	.01044	445	295	2.7	1.24
46.08	.01107	438	296	3.2	1.09

TABLE II

ION YIELDS FOR AMMONIA DECOMPOSITION

Investigator	Temp.,°C.	Ion yield
Wourtzel[5]	18	0.80
Wourtzel, recalcd. by Mund and Koch[6]	25	1.03
Wourtzel, recalcd. by Jungers[7]	25	0.93
Lind and Bardwell[3]	..	1.0
Mund and Koch[6]	5	0.88
Mund and Koch, recalcd. by Jungers[7]	25	1.145
Jungers[7]	25	0.97–1.027

It is believed that a much higher degree of accuracy is attainable by this method than is indicated by the ion yield values in Table I. The error in the pressure measurements probably does not exceed 1%: in the current measurements, 3%. Undoubtedly, the error in the current measurements can be reduced greatly by use of a more sensitive current measuring instrument. Since no special care was taken during the pressure measurements to keep the volume of liquid air around the trap constant, the magnitudes of the corrections to the volume of the gas because of cooling cannot be exactly stated, and may introduce an error of several per cent.

(5) Wourtzel, Radium. Le, 11, 289–297, 332–347 (1919).
(6) Mund and Koch, Ann. soc. sci. Bruxelles, 46, 279–284 (1926).
(7) Jungers, Bull. soc. chim. Belg., 41, 377–398 (1932).
(8) Lind and Bardwell, THIS JOURNAL, 50, 745–748 (1928).

in the M/N values; this error can easily be eliminated in future measurements.
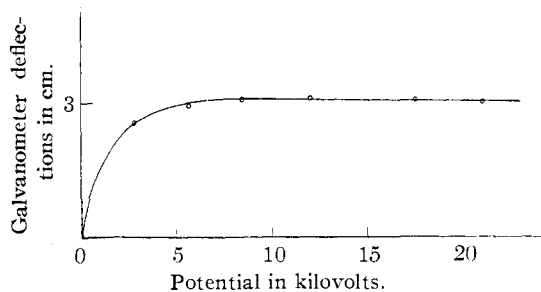

Fig. 2.—Saturation curve.

The method is to be recommended for its simplicity, promise of high accuracy and general applicability to reactions accompanied by pressure changes. It should prove especially useful in determining ion yields at higher temperatures and pressures, under which conditions calculation of the extent of ionization is rather uncertain.

Summary

1. A direct method for determining ion yields for reactions induced by alpha radiation has been described.

2. The ion yield for the ammonia decomposition has been determined by this method, and found to equal 1.09 at 22° and one atmosphere pressure.