THE SYNTHESIS OF AMMONIA BY ALPHA RAYS[1]

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Owing to the general interest in active nitrogen and the various efforts to learn something of its nature by means of its reactivity towards hydrogen and other reagents, the writers decided to reëxamine the behavior of a mixture of hydrogen and nitrogen under α radiation of radon.

Earlier experiments were made in a stagnant system by Cameron and Ramsay[2] who mixed hydrogen, nitrogen and radon in a volume of 2.3 cc. and judged the rate of ammonia synthesis from the resulting fall in pressure. From their results Lind[3] calculated the ion yield to be $+M_{NH_3}/N_{(N_2+H_2)} = 0.12$ or about 8 ion pairs for 1 molecule of ammonia formed. Later, Usher[4] repeated the experiments of Cameron and Ramsay with refinements. While he confirmed a reduction in pressure, he could find no very certain amounts of ammonia (less than 1% of that required by the pressure change) and attributed the decrease of pressure largely to a loss of hydrogen in the glass wall, which he in fact recovered by heating, together with a much smaller amount of nitrogen.

In the present experiments the writers employ the method of streaming a mixture of hydrogen and nitrogen past a thin α-ray bulb containing radon and later titrate the ammonia after direct absorption in water or in acid. Thus we avoid the disadvantages of a system of small volume.

Fortunately the stoichiometric mixture of highly purified hydrogen and nitrogen used in the Fixed Nitrogen Research Laboratory for catalytic synthesis of ammonia was at our disposal. This was passed at the rate of 50 cc. per minute under ordinary pressure through a glass sphere (625 cc. volume; 10.6 cm. diameter) at the center of which was mounted a thin α-ray bulb (1.4 mm. diameter; about 5μ wall thickness). The system is essentially that originally used for ozone synthesis[5] with some modification, as in later work,[6] of the method of sealing in the α-ray bulb and of retaining the radon in it.

Preliminary qualitative tests with Nessler reagent proved the production of ammonia. The quantitative titrating agents were 0.01 *N* sulfuric acid and 0.01 *N* potassium hydroxide solutions. Sodium alizarin sulfate

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[1] This work, which was carried out in the Fixed Nitrogen Research Laboratory at Washington, was the subject of a preliminary report at a Regional Meeting of the Society in Chicago, May, 1927.

[2] Cameron and Ramsay, *J. Chem. Soc.*, **93**, 988 (1908).

[3] Lind, *J. Phys. Chem.*, **16**, 581 (1912).

[4] Usher, *J. Chem. Soc.*, **97**, 389–405 (1910).

[5] Lind, *Am. Chem. J.*, **47**, 397 (1911); *Sitzb. Akad. Wiss. Wien*, **120**, 1709 (1911).

[6] Lind and Bardwell, This Journal, **45**, 2586 (1923).

was used as indicator,[7] the end-point always being reached from the alkaline side.

The *ionization* during an interval of reaction was calculated as follows. N ion pairs = millicuries of radon (measured in place by the γ-ray method) $\times$ total number of α-rays from 1 millicurie of Rn + RaA + RaC ($= 3 \times 1.772 \times 10^{13}$) $\times$ intensity of ionization per cm. of path per 1 α-ray for air N. T. P. in the system used, estimated as (3×10^4), $\times$ spec. ionization of $3H_2 + N_2$ mixture (= 0.41 when air = 1) $\times$ actual path in cm. ($= (10.6 - 0.14)/2$) $\times 273/(273 + t) \times P/760$ (when P = mean of initial and final pressures of any interval).

The data are shown in Table I.

TABLE I

YIELD OF AMMONIA PER ION PAIR

Reaction: $3H_2 + N_2 = 2NH_3$ in a flow system with α-ray bulb. Flow = 50 cc. per minute. E_0 = 96.2 m.c. Rn. Temp. = 25°.

April, 1926 init. time	Interval. hours	Radon decayed	Bar., mm.	Cc. of 0.01 N H_2SO_4	Moles $NH_3 \times 10^{18}$	Ion pairs $\times 10^{18}$	$\frac{M_{NH_3}}{N_{ions}}$	Absorbent
2 P.M., 4/23	4	2.84	742	0.40	2.4	8.7.1	0.276	Water[a]
6 P.M., 4/23	4	2.76	742	.37	2.2	8.4	.262	Water
10 P.M., 4/23	10.5	6.86	742	.65	3.9	21.0	.186	Water
9 A.M., 4/24	13.3	7.90	750	.73	4.4	24.0	.183	Water
10:20 P.M., 4/24	17.7	9.35	754	.80	4.8	29.0	.165	Water
4:10 P.M., 4/25	16.2	7.53	749	.63	3.8	23.3	.167	Water
8:30 A.M., 4/26	24.0	9.66	754	.78	4.7	30.2	.155	Water
8:30 A.M., 4/27	25.5	8.50	747	.90	5.4	26.4	.204	Acid[b]
10:15 A.M., 4/28	46.2	11.8	748	1.25	7.5	36.7	.205	Acid[c]

[a] About 75 cc. in a multi-bubble absorption flask.
[b] 0.5 cc. of 0.01 N H_2SO_4 in about 75 cc. of water.
[c] 1.0 cc. of 0.01 N H_2SO_4 in about 75 cc. of water.

Discussion of Results

From Table I (next to last column) one sees that there is a distinct synthesis of ammonia in an α-ray flow system. The yield is much higher than found by Usher[4] and nearly twice as high as reported by Cameron and Ramsay[2]—both in small volumes of stagnant gas.

As long as water was used as absorbent liquid, the yield recovered per ion pair fell steadily as the concentration of ammonia in the total gas diminished due to the decay of the radon. This suggests incomplete absorption. Although absorption in water is the standard method used in testing ammonia catalysts, our concentration is of much lower order, one part in 10^5 to 10^6 as against parts per 10^2 in catalysis. In the last two experiments some initial acid (not a final excess) was added to the water to obtain better retention of ammonia. The recovered yield was

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[7] Cohn, "Indicators and Test Papers," John Wiley and Sons, Inc., New York, 1902, p. 25.

increased and remained constant at 0.205, which is, however, considerably below the initial 0.276 in water, so that some doubt must remain as to the exact yield, which could only be settled by more elaborate experiments on absorption at low concentration. The yield appears to lie between 0.2 and 0.3 molecule of ammonia per ion pair.

From such a low ionic efficiency, relative to most other reactions that have been examined under α-radiation,[8] it is difficult to judge whether the *ions* of either reactant are directly responsible for the reaction. In a mixture of $3H_2:1N_2$ about 60% of the ionization produced by α-rays falls on the N_2 and 40% on the H_2, so that referring all the reaction to either set of ions would not raise the yield to a value that would aid in the decision. Furthermore, such reasoning loses its point if we accept the recent evidence of Harnwell[9] and others that positive ions capture electrons from molecules of lower ionization potential so that all of the ionization is transferred to one species of molecules. If it means that both components must be ionized (or activated) it is an interesting analogy with the recent result of Lewis[10] that it is necessary to activate both nitrogen (Strutt's method) and hydrogen (Wood's method) in order to synthesize ammonia by such means.

Equilibrium under α-Radiation

Although it is not the purpose of this paper to discuss the equilibrium of the reaction, one or two simple deductions will be made.

According to Wourtzel[11] the rate of decomposition of NH_3 by α-rays at 25° is approximately $-M_{NH_3}/N_{NH_3} = 1$, which has been confirmed by Lind and Bardwell.[12] If we take the rate of synthesis as $+M_{NH_3}/N_{(H_2 + N_2)} = 0.2$, then equilibrium as predicted on simplest assumptions from the two opposed rates should be realized in a mixture when 5 times as much ionization falls on the $3H_2 + N_2$ molecules as on the NH_3 molecules. Taking the specific molecular ionization of $3H_2 + N_2$ as 0.41 and that of NH_3 as 0.82, equilibrium should occur when 83.3% of initial NH_3 has been decomposed, that is, in 10 volumes of stoichiometric mixture to 1 volume of ammonia, or a mixture containing 9.09% of NH_3 by volume. No direct test of this prediction has been made. Since Usher found very little synthesis in a static system he concluded that equilibrium would lie almost entirely on the decomposition side. This conclusion is not supported by the present results on synthesis and is also at variance with the indications of the kinetic course of the decomposition. Application

[8] Lind, "Chemical Effects of α Particles," 2nd ed., Chemical Catalog Co., New York, **1928**, pp. 100–103.

[9] Harnwell, *Phys. Rev.*, **29**, 683 (1927); **29**, 830 (1927).

[10] Bernard Lewis, THIS JOURNAL, **50**, 27 (1928).

[11] Wourtzel, *Le Radium*, **11**, 342 (1919).

[12] Unpublished results.

of the general equation to Usher's data for decomposition[13] to 57%, showed that the velocity constant falls steadily as the reaction proceeds, as if due to reverse reaction. The results of Lind and Bardwell,[12] in which decomposition proceeded to 73%, show a similar and more far-reaching drop with some indication that the yield in synthesis is somewhat nearer 0.3 than 0.2 molecule per ion pair.

Summary

Using a method of flowing a stoichiometric mixture of hydrogen and nitrogen past an α-ray bulb, the rate of ammonia synthesis found by chemical titration is estimated to be 0.2 to 0.3 molecule per ion pair produced in the mixture, a yield higher than previously found in stagnant gases for this reaction but low in comparison with the majority of gas reactions under α-radiation. This yield in synthesis is in general accord with the observed fall of velocity constant in decomposition of ammonia by α-rays as a function of the ammonia concentration.

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AN INVESTIGATION OF THE REACTION OF SODIUM ALIZARIN MONO-SULFONATE WITH ALUMINUM UNDER DIFFERENT EXPERIMENTAL CONDITIONS WITH REFERENCE TO ITS USE IN COLORIMETRY

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A method for the colorimetric determination of aluminum has been reported by Atack,[1] in which the principal reagent is sodium alizarin mono-sulfonate (Alizarin Red S). With aluminum in alkaline solution this dye forms a red lake which is fairly stable in the presence of a considerable excess of acetic acid.

> "The original solution (5 to 20 cc.) is acidified with hydrochloric acid or sulfuric acid, as acetic acid would form the highly dissociated aluminum acetate, and this has been found to give a somewhat more intense coloration than the inorganic salts; nitric acid in considerable amounts leads to the partial destruction of the coloration. Ten cc. of glycerine and 5 cc. of a 1% solution of Alizarin S are added, the solution made up to about 40 cc. with water, and then rendered slightly ammoniacal. After standing for five minutes it is acidified with dilute acetic acid, the Alizarin S acting as an indicator, acetic acid being added until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard."

Commenting upon this procedure, Atack states in substance:

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[13] Lind, *J. Phys. Chem.*, **16**, 595 (1912).

[1] Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).