

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE SYNTHESIS OF AMMONIA IN THE LOW VOLTAGE ARC

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A detailed study of the synthesis of ammonia in the glow discharge^{1,2} has shown that the rate of formation is proportional to the current passing through the discharge, and is independent of the pressure between wide limits. The maximum rate of reaction was obtained for a 2H₂-N₂ mixture.

From these considerations an electrochemical equivalence law was proposed for the glow discharge which is comparable to Faraday's laws for electrolytes. This law is expressed as $dP/dt = \alpha I$, where P is the equivalent ammonia pressure, I the current and α a constant. This law has more recently been shown to have a universal application to the glow discharge.

The technique employed was such that a fair estimation of relative reactivities of atoms, excited molecules and positive ions could be made. The results showed that no reactivity could be assigned to active states other than positive nitrogen ions under the conditions of these experiments.

The present research was undertaken to test the following points: (1) Can the electrochemical equivalence law be applied to the low voltage type of arc? (2) Can any significance be given to the fact that a maximum rate was obtained for a 2H₂-N₂ mixture? (3) What is the relative reactivity of the 16.8 volt nitrogen ion as compared to the 24.5 volt ion? (4) Can the presence of various active states other than N₂⁺ ions be detected under conditions where the voltage of the exciting electron can be controlled?

The activation of nitrogen and hydrogen by controlled electron impacts has been studied by several investigators. Kunsman³ obtained no reactivity for electron speeds under 17 volts. Storch and Olsen⁴ report synthesis to start at about 15 volts. Their voltage-rate curves showed a sudden break near 23 volts and breaks for every four volts' increase thereafter. Caress and Rideal⁵ detected a synthesis beginning at 13 volts with breaks at 17, 23, 30 and 34 volts. From this they assigned the reactive states to be H', N₂⁺ and N⁺, successively, the breaks at 30 and 34 volts being due to combinations of the lower voltages. Recently

¹ Brewer and Westhaver, *J. Phys. Chem.*, **33**, 883 (1929).

² Brewer and Westhaver, *ibid.*, **34**, 153 (1930).

³ C. H. Kunsman, *Phys. Rev.*, **31**, 301 (1928).

⁴ Storch and Olsen, *THIS JOURNAL*, **45**, 1605 (1923).

⁵ Caress and Rideal, *Proc. Roy. Soc. (London)*, **115**, 684 (1927).

Brett⁶ has obtained voltage rate curves which he interprets as indicating breaks at 17, 18.5, 20.5, 24.5 and 27 volts, that correspond to the production of N_2^+ , $H + H^+$, N_2^+ , $N + N^+$ and $N' + N^+$, respectively. He observed reactivity in the absence of an applied field. From these observations he assumes the mechanism of synthesis to be the interaction of atomic hydrogen with one or the other of the active states cited.

Apparatus and Method of Procedure

The tube and electrical hook-up used are illustrated in Fig. 1. The capacity of the tube was 300 cc., while that of the McLeod gage and leads was 175 cc. Both two- and three-electrode tubes were tried. The presence of a grid may be a help in the case of simple electron excitation; however, it only introduced complications in the presence of an arc. The results presented in this paper were taken with the two-electrode arc.

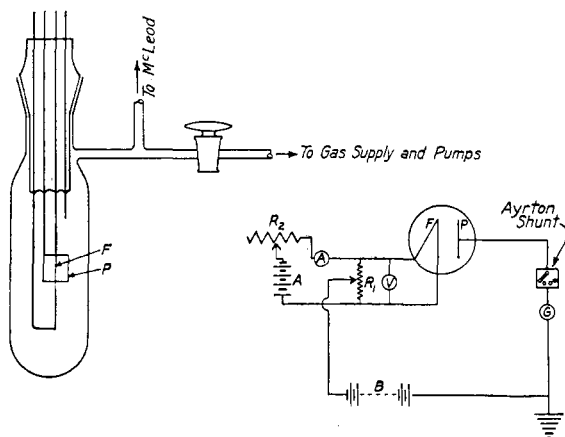


Fig. 1.—Tube with electrical connections.

Several types of filaments were tried, including tungsten, thoriated tungsten and barium and strontium coated platinum. The latter type obtained from the Bell Telephone Laboratories proved the most satisfactory. Most of the filaments were from 1 to 2 cm. in length, although longer filaments were used on occasions. The drop of potential along the filament was usually less than 0.5 volt. All filaments were thoroughly reduced in hydrogen before the experiments were started. The life of a filament was often as long as seventy-five runs with an average length of forty minutes each.

The $3H_2-N_2$ mixture was purified by passing over heated copper and glowing tungsten and through liquid air. Helium was purified by charcoal at liquid-air temperature. Spectroscopically pure neon was used directly. The argon was purified by standing in contact with heated calcium for hours.

The method of procedure was essentially the same as that described for the glow discharge. The system was filled to the desired pressure with the gas mixture to be studied. The tube was then immersed in liquid air and an arc was struck between F and P. The pressure was thereafter read at regular intervals, usually five minutes; the decrease in pressure with respect to time was taken as the rate of ammonia synthesis. During each run both the current and liquid air level were maintained constant.

⁶ Brett, *Proc. Roy. Soc. (London)*, **129**, 319 (1930).

Results

The Effect of Pressure.—The influence of pressure on the rate of synthesis for a $3\text{H}_2\text{-N}_2$ mixture is illustrated by line 1 of Fig. 2. The

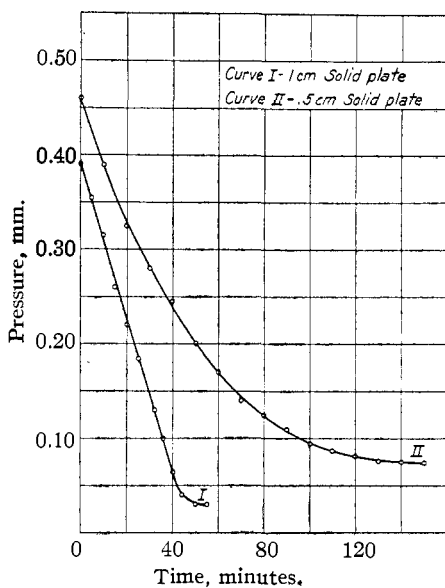


Fig. 2.

line is identical to similar time-pressure curves obtained in the glow discharge in that the rate is independent of the pressure over a wide range. The rapid dropping of the rate to zero at some minimum pressure characteristic of the discharge tube is common also to both types of arcs. It will be noted that the rate remains constant to 0.04 mm. pressure while no synthesis could ever be detected under 0.02 mm. with a plate diameter of 1 cm. or less.

The Effect of Current.—The relationship between current and rate is illustrated in Fig. 3. The low voltage arc is again similar to the glow discharge in that the rate of synthesis is proportional to the

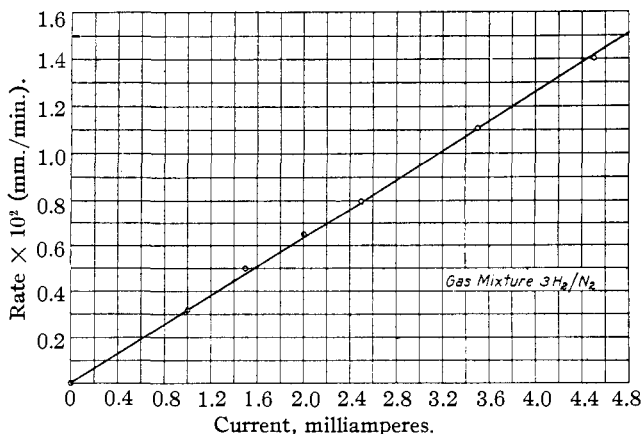


Fig. 3.

The Effect of Voltage.—The effect of varying the applied voltage between the filament and plate on the rate of clean-up is shown in Fig. 4.

The voltages given are not corrected for contact p. d. A direct measurement of the contact p. d. by voltage just necessary to stop electron emission showed the filament to be between 1.5 and 2.0 volts electronegative to the plate depending upon the conditions of the experiment. To obtain the correct voltages, therefore, the values given should be shifted about 1.5 volts to the right or raised by this amount.

These results were obtained with a filament which had been thoroughly reduced and on which over twenty runs had been made before any of the points given were taken. The general contour of curves obtained with new filaments is similar to that illustrated except that the total emissivity changes from time-to-time, tending to give breaks in the curve which in reality are due entirely to variations in the emissivity of the filament. These changes in emissivity are absent in a well worked-in filament.

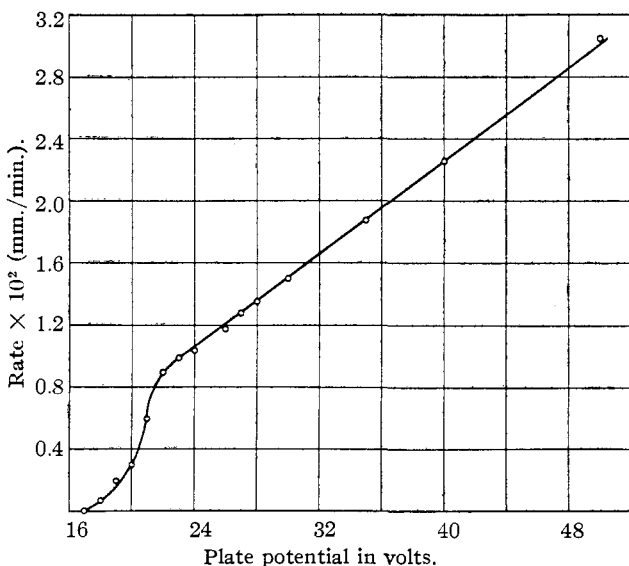


Fig. 4.

It will be seen from the curve that the reactivity at 17 volts is very small, no synthesis being detected at appreciably lower voltages. The rate increases rapidly with potentials between 17 and 23 volts, but thereafter the rate of change is linear over the range investigated.

In some instances a clean-up was detected under 17 volts, but the product frozen out on the walls invariably showed the vapor pressure of water. The clean-up could always be traced to an improperly reduced filament or to oxygen in the $3\text{H}_2\text{-N}_2$ mixture.

The Effect of the Filament.—The reactivity of a given filament appears to be affected both by its age and its length. Filaments 1 cm. in

length gave a faster rate than did those 2 cm. in length, while 8-cm. filaments were even slower. The length of the region over which the arc played was not materially changed by lengthening the filament. It seems possible that the slower rates observed with the longer filaments are due to decomposition of the positive ion clusters on the heated filament. The enhanced rates obtained with old filaments are probably due to the changes in the potential gradient around the filament since it becomes smooth and thin with use; all visible oxide drops off after about fifteen runs and the base metal appears thin and bright.

The Effect of the Plate.—Various types and dimensions of plates were tried. Curve I of Fig. 2 was taken with a solid cylindrical nickel plate 1 cm. in length and 1 cm. in diameter, while curve II was taken with a similar plate except the diameter was 0.5 cm. Tests with several diameters showed that at high pressures the rate was approximately the same irrespective of the diameter. At low pressures, however, the rate decreased with the diameter, while the minimum pressure to which the synthesis could be carried was raised.

An increase in the length of the plate beyond the length of the filament had no appreciable effect on the rate, *i. e.*, Curve I of Fig. 2 would be the same whether the plate was 1 or 2 cm. in length. An increase in length of both the filament and plate apparently decreased the rate, for the reasons stated under the effect of the filament.

Both solid, screen and spiral wire plates were tried. The results were the same at the higher pressures irrespective of the type of plate. At the lower pressures, however, the rate was much more constant for the open plate, *i. e.*, an open spiral plate of the dimensions used for Curve II of Fig. 2 gave a line quite similar to curve I. At the high pressures the arc for the spiral wire plates was entirely between the plate and the filament, while at the lower pressure it spread for an appreciable distance through and beyond the plate.

The Ratio of Hydrogen to Nitrogen.—The effect of varying the gas mixture on the rate of synthesis is illustrated in Fig. 5. These results were taken with comparatively new filaments to which the coating still adhered. For this reason the rates are somewhat lower than those given for the old filament in Fig. 4.

It will be seen that the maximum rate occurs in a mixture containing 83% nitrogen and 17% hydrogen for both the 19 and 30 volt arcs. In the case of the glow discharge the maximum rate was obtained with a mixture containing 33% nitrogen. The two arcs are similar, in that the rate in both cases is speeded up by excess nitrogen, although the acceleration is much more pronounced in the case of the low voltage arc.

Effect of Inert Gases.—The results obtained when helium, neon and argon are added to a $3\text{H}_2\text{-N}_2$ mixture are illustrated in Fig. 6. The

rates in each case were measured at 0.3 mm. pressure, hence this point is taken as 100% added gas.

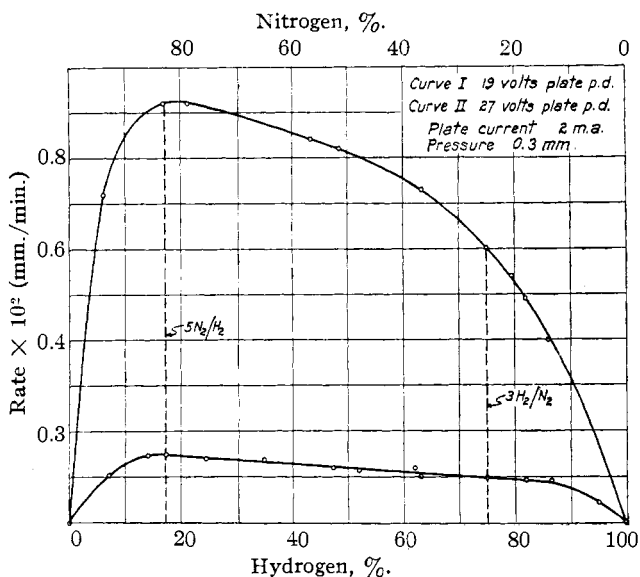


Fig. 5.

The helium and neon results could be duplicated without trouble, while argon, on the other hand, had a peculiar effect on the filament. After a run had been made with argon present, the rate for a pure $3\text{H}_2\text{-N}_2$ mixture

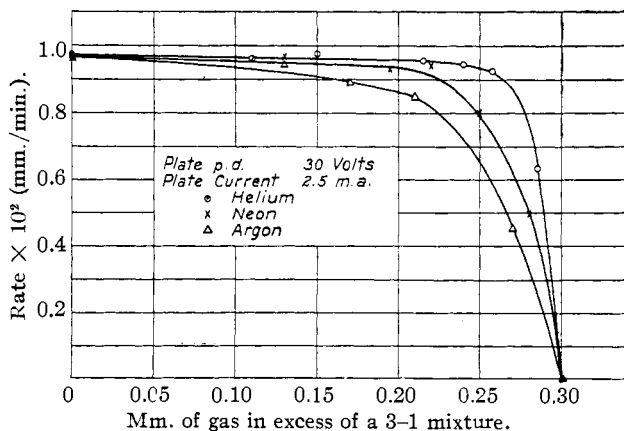


Fig. 6.

might be as much as twice that usually obtained; it returned to normal in the course of two or three runs in the absence of argon. For this reason the argon curve probably does not represent constant arc conditions.

The curve for helium is very similar to that obtained in the glow discharge, in that it shows no appreciable effect on the rate until the amount present is more than 80%. Argon in the glow discharge, however, slowed down the rate of reaction almost in proportion to the amount present.

Discussion of Results

The results just given are strikingly similar in nature to those presented previously for the glow discharge, in that the rate of synthesis (1) is proportional to the current flowing through the discharge, (2) is independent of the gas pressure over a wide range; and (3) is accelerated by excess nitrogen and retarded by excess hydrogen.

The similarities just mentioned necessitate the assignment of the same reaction mechanism to the two types of arcs. The fact that the electrochemical equivalence law ($dP/dt = \alpha I$) holds for the low voltage arc is definite proof that the reaction is initiated by ions formed in the discharge, since the rate of production of atoms and excited molecules is neither proportional to the current nor independent of the pressure.⁷

Recent experiments in the glow discharge⁸ have furnished direct proof that the oxidations of hydrogen, methane and carbon monoxide take place around positive ions formed in the discharge. Since the present reaction is similar in every respect, the mechanisms of reaction are evidently identical.

A comparison of line 1, Fig. 2, with similar lines for the glow discharge² shows that the synthesis may be carried to a much lower pressure in the low voltage arc, *i. e.*, 0.02 mm. for the arc as contrasted with 0.1 for the glow. This difference results from the fact that the life of an N_2^+ ion is much longer in the low voltage arc due to the absence of high fields driving ions to the electrodes and to the walls. The N_2^+ ion, therefore, is capable of making many more collisions with hydrogen molecules at a given pressure before becoming neutralized.

The acceleration in the rate of synthesis by the addition of excess nitrogen to the combining mixture, as shown in Fig. 5, is even more pronounced in the low voltage arc than in the glow discharge. This is again evidence in favor of the contention that the reaction is initiated primarily by N_2^+ ions and that H_2^+ ions are comparatively inert. The reason for the more pronounced effect of excess nitrogen in the present case lies in the fact, just pointed out, that the longer life of the N_2^+ ion enables the necessary collisions with hydrogen molecules to be made even when the partial pressure is very low.

The relationship between voltage and rate, as shown in Fig. 4, is a still

⁷ Lowe, *Trans. Roy. Soc. Canada*, **20**, 271 (1926); Hughes and Skellett, *Phys. Rev.*, **30**, 11 (1927); Crew and Hulbert, *ibid.*, **29**, 843 (1927); **30**, 124 (1927).

⁸ Brewer and Kueck, *J. Phys. Chem.*, **35**, 1281 (1931); **35**, 1294 (1931).

further proof that the reaction is initiated by N_2^+ ions, since no reactivity was detected under the ionization potential of nitrogen.

The present voltage-rate curves are in agreement with the results obtained by Kunsman⁹ for electron bombardment in that no reactivity was detected under the ionization potential of nitrogen. Wansbrough-Jones⁹ also obtained very similar results for the oxidation of nitrogen in the low voltage arc. The interpretation given his results is in complete agreement with that presented for the synthesis of nitrogen dioxide in the glow discharge.¹⁰

The results reported by Brett, however, are materially different from those presented in Fig. 4, not only in the presence of breaks but also in that he observed a clean-up even at zero voltage. The technique used in the two cases was not the same, which may account for the discrepancies. Brett made runs of but four minutes' duration; we were never able to obtain a temperature equilibrium under five minutes. His observed clean-up under 17 volts may have been due to temperature changes, or to an improperly reduced filament, or to oxygen in the $3H_2-N_2$ mixture. In regard to the breaks observed by Brett we have found that a given filament which has not had long use will be subject to changes even greater than those given. Further, no mention is made of the correction for contact potential, which is between -1.5 and -2.0 volts under the conditions of his experiments. Brett assumed breaks at 24.5 volts although his curves show near breaks only at 23.5 and 26.5 volts. The break at 23.5 volts is doubtless the one due to the second ionization potential of nitrogen; the other breaks, therefore, must be shifted by a similar amount. In this event the assigning of active states to the possible breaks and the attributing of chemical reactivity to these states is highly speculative.

Calculation of M/N Ratio.—The computation of the number of ions formed per electron of current involves uncertainties as to the percentage of the current carried by positive ions, as to the number of positive ions formed per electron, and as to the distribution of ions between the nitrogen and hydrogen. Neglecting the positive ion current, which probably does not introduce an error of more than a factor of two, the total number of positive ions formed per electron of current can be estimated from the data of Langmuir and Jones.¹¹ The distribution of ions between the two gases can be calculated from the probability of ionization per collision as given by Compton and Van Voorhis¹² and the collision frequency as given by Hughes and Klein.¹³

⁹ Wansbrough-Jones, *Proc. Roy. Soc. (London)*, **127**, 511 (1930).

¹⁰ Westhaver and Brewer, *J. Phys. Chem.*, **34**, 554 (1930).

¹¹ Langmuir and Jones, *Phys. Rev.*, **31**, 357 (1928).

¹² Compton and Van Voorhis, *ibid.*, **27**, 724 (1926).

¹³ Hughes and Klein, *ibid.*, **23**, 450 (1924).

The collision frequencies in nitrogen and hydrogen are of the ratio of 1.92 to 1.00; in a $3\text{H}_2\text{-N}_2$ mixture, therefore, an electron will make 1.56 collisions in hydrogen for every collision in nitrogen. A total of 1.5 ions for a 100 volt electron in a $3\text{H}_2\text{-N}_2$ mixture was taken as a standard from which the total number and distribution of ions was calculated from the probabilities of ionization for the various accelerating voltages. The results as computed from Fig. 4 are tabulated in Table I. $M/\text{min.}$ represents

TABLE I
COMPUTED RESULTS

Volts	$M/\text{min.}^a$	M/e	N_2^+/e	M/N_2^+
18	0.1366	0.0145	0.01127	1.288
20	0.5766	.0612	.0487	1.256
22	1.730	.1835	.0816	2.25
30	2.885	.306	.1945	1.57
40	4.350	.462	.345	1.34
50	5.770	.613	.487	1.258

^a $\times 10^{-17}$.

molecules per minute, M/e , molecules per electron, N_2^+/e , positive nitrogen ion per electron, and M/N_2^+ molecules of ammonia per nitrogen ion.

It will be seen from the table that the M/N ratio rises rapidly to a maximum near the second ionization potential of nitrogen and thereafter decreases slowly with increasing voltage. Below 20 volts the ratio is practically constant.

The increase in rate between 18 and 20 volts is evidently due to an increase in production of N_2^+ ions. The decrease in the M/N_2^+ ratio above the second ionization potential of nitrogen is interesting in that it shows the effect of dissociation of N_2^+ ions on the rate of synthesis. A 24.5 volt N_2^+ ion while showing only a very slight dissociation on the primary impact dissociates into $\text{N} + \text{N}^+$ upon collision with neutral molecules. Since the N^+ ion is capable of forming but one ammonia molecule while an N_2^+ ion can form two, the decrease in rate is to be expected. This is further evidence for the relative inactivity of neutral atoms.

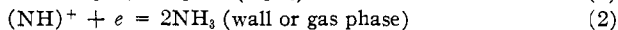
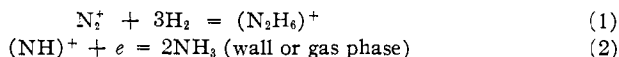
The value $M/\text{N}_2^+ = 2.25$ at 22 volts is evidently high since it is difficult to see how the ratio could exceed two on the basis of any mechanism that can be postulated. The error may be a general one arising from the manner of calculating N , or it may result from an added source of N_2^+ ions found above 18 volts, for instance, the ionization of nitrogen by collision of neutral molecules with the 18.2 volt hydrogen ion.

The Mechanism of Reaction.—The data presented in this paper, as well as correlative data obtained with the glow discharge, show clearly that the reaction mechanism may be divided into two parts: I, the formation of a positive nitrogen ion, and II, the interaction of the ion with neutral hydrogen molecules to form ammonia.

The evidence is definite regarding part I. It indicates that the reactivities of N_2^+ and N^+ are very great as compared to any other possible active state that might be present.

The process by which the ammonia molecule is built up around the positive ion is only indirectly indicated by the data in hand.

The results, on the whole, are entirely in line with the demands of a cluster mechanism, wherein hydrogen molecules are attached to the nitrogen ion. There is no indication of any intermediate compound formation. It seems probable from the M/N ratios obtained, that two molecules of ammonia are formed in the cluster about an N_2^+ ion, and one molecule about the N^+ ion cluster. This may be expressed by the equation for the N_2^+ ion



for the N^+ ion



It cannot be said that the above mechanism is the only one by which ammonia is formed in the arc. The results show definitely, however, that in the arc where atoms, excited molecules, metastables, and ions of both reactants are present, the reactivity around the nitrogen ions is so rapid that any possible reactivity of the other active states appears negligible in comparison. It is a matter of conjecture whether a mechanism of this type can be carried over to other conditions, such as the interaction of nitrogen and hydrogen on an iron catalyst. However, the possibility exists that the same work may be done by the surface forces in catalysis as is done by the electron in the arc.

The writers are indebted to Dr. C. H. Kunsman for the constructive interest he has taken in this research.

Summary

1. The synthesis of ammonia in the low voltage arc is shown to obey the electrochemical equivalence law, $dP/dt = \alpha I$, derived for the glow discharge, *i. e.*, the rate of ammonia formation is independent of the pressure between wide limits, and is proportional to the current flowing through the arc.

2. Synthesis does not take place for arc voltages under the ionization potential of nitrogen. Between 17 and 23 volts the rate increases rapidly with the voltage, while above 23 volts the increase is nearly linear.

3. A maximum rate of synthesis occurs in a mixture containing 83% nitrogen. The addition of hydrogen to a $3H_2-N_2$ mixture decreases the rate almost in proportion to the amount of hydrogen added.

4. The effect of various inert gases is discussed.

5. The results are interpreted as indicating that the reaction takes place around N_2^+ and N^+ ions. H_2^+ ions, neutral atoms, and excited molecules are relatively inactive.

6. A method of calculating the rate of ion formation, as well as the distribution of ions between the nitrogen and hydrogen, is presented.

7. A ratio of $M/N_2^+ \sim 2$ is obtained below 23 volts (24.5 volts when corrected for contact p. d.). A ratio for $M/N^+ \sim 1$ seems the most probable for the monatomic ion.

8. It is suggested that the reaction goes to completion in a cluster of hydrogen molecules around the nitrogen ions.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, No. 264]

VAPOR PRESSURES AND LATENT HEATS FOR THE SYSTEM: $BaCl_2 \cdot 8NH_3 - BaCl_2 - NH_3$

BY LOUIS J. GILLESPIE AND ELI LURIE

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Introduction

In the experimental study of the thermodynamic properties of ammonia in gaseous solutions of ammonia and nitrogen¹ the substances $BaCl_2 \cdot 8NH_3$ and $BaCl_2$ were chosen as the materials to be used to avoid the necessity of a semipermeable membrane, because the high ammonia content of the octammine, the high decomposition pressures at temperatures below 50° , as well as the formation by barium chloride of only one ammine, are very desirable properties from an experimental standpoint.

Hüttig and Martin² had studied the 0° isotherm of barium chloride and ammonia, and had shown that barium chloride forms only one ammine, the octammine. They also determined the decomposition pressures of the octammine in the temperature range between 0 and -15.5° .

The large deviations of ammonia from the ideal gas law make the equilibrium an interesting one to study, and we have determined the pressures of ammonia in equilibrium with barium chloride and its octammine from 0 to 50° . One of us has recently discussed equations for representing, as a function of the temperature, the decomposition pressure of solid compounds capable of evolving a gas that deviates from the ideal gas law;³ we have applied to our data the new equations for the pressures and the latent heats.

¹ Lurie and Gillespie, *THIS JOURNAL*, **49**, 1146 (1927).

² Hüttig and Martin, *Z. anorg. Chem.*, **125**, 269 (1922).

³ Gillespie, *Proc. Am. Acad. Arts Sci.*, **66** (No. 3), 153 (1930).