[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SYNTHESIS OF AMMONIA FROM ITS ELEMENTS IN THE LOW-VOLTAGE ARC[1]

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Heidemann[2] reported the synthesis of ammonia from its elements as being initiated by electrons of a velocity corresponding to more than 2 volts, and less than the ionization potential of either gas. His papers contain little or no description of apparatus, and practically no data.

Subsequently Andersen[3] studied the rate of reaction at various applied voltages. His plot of the change in pressure per unit of time against the accelerating voltage led him to the conclusion that the reaction did not commence until the ionizing potential (about 17 volts) of nitrogen was reached. Andersen's curves were of a wave type, the maxima and minima rising with increasing voltage. The distance between adjacent maxima or minima was 4–7 volts. No explanation of the shape of these curves was given beyond the vague suggestion that this might be due to some auxiliary resonance phenomenon.

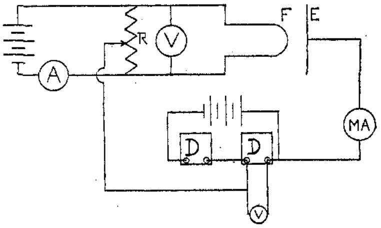

Fig. 1.—Electrical set-up

Andersen made no attempt to correct his voltages for the drop in potential along the tungsten filament used as a source of electrons. These drops were comparatively great, varying from 8 to 14 volts, and the corrections would, therefore, be of the order of magnitude of several volts.

In view of the unsatisfactory state of this problem, it seemed desirable to duplicate Andersen's apparatus, and attempt to find an explanation of the curves he obtained, using, however, much smaller potential drops across the cathode, and applying the accelerating potential at the center of the filament. The latter was done, as shown in Fig. 1, by applying the accelerating potential at the center of a resistance which was connected in parallel with the filament.

Experiments with an Apparatus Similar to that Employed by Andersen

The reaction chamber of the preliminary experiments was practically identical with that employed by Andersen.

It consisted of an 800cc. bulb into which were sealed 2 platinum plates to serve as anodes, and a tungsten filament acting as the source of electrons. Each anode was 1.5 sq. cm. in area, and the diameter and length of the filament were 0.050 and 2.5 cm., respectively. The filament was situated midway between the 2 platinum plates which were 1.5 cm. apart, thus making the distance between the cathode and anode 0.75 cm.

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[1] This paper was constructed from a thesis presented by H. H. Storch to the Faculty of the Graduate School of the University of California in May, 1923, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Heidemann, *Chem.-Ztg.*, **45**, 1073 (1921); **46**, 97 (1922).

[3] Andersen, *Z. Physik*, **10**, 54 (1922).

The total volume of the apparatus, including the McLeod gage and connections to the mercury vacuum pump, was approximately 1500 cc. A side tube containing 1 cc. of 98% sulfuric acid was attached to the bulb.

The electrical set-up is shown in Fig. 1. The voltmeters are designated by the letter V; A is an ammeter; MA a milliammeter; R is a 200ohm resistance; F represents the filament, and E the 2 anodes. The accelerating voltage was obtained from 4 sets of small lead storage cells, each set giving 50 volts, the 4 sets being connected in parallel. These batteries were short circuited through 2 dial resistance boxes (D, D), the sum of whose resistance was kept constant at 10,000 ohms. The accelerating voltage was controlled by connecting the tube electrodes to one of the dial resistance boxes, as a shunt circuit. The heating current for the filament was supplied by 2 sets of 5 Edison cells connected in parallel.

The hydrogen was obtained by the electrolysis of 10% potassium hydroxide solution, and was freed from oxygen by passage through a tube containing platinized asbestos. The nitrogen was prepared by removing the oxygen from air with alkaline pyrogallol. The gases were led into a mixing chamber and stored there over water. Before being admitted to the reaction chamber, the gas mixture was passed through a tube containing a glowing platinum wire, and through phosphorus pentoxide. The gas mixtures so prepared were found by analysis to contain only traces of oxygen, and no combustible gases other than hydrogen could be detected by the regular method of gas analysis.

The bulb was thoroughly "baked" and evacuated until the McLeod gage indicated a pressure of less than 10^{-4} mm. of mercury. The gas mixture (20% of hydrogen to 80% of nitrogen was used in this tube) was then admitted up to the desired pressure. Only one pressure was employed throughout, namely, about 0.17 mm. of mercury. The filament was kept at the temperature necessary to give a tube current (between E and F) of 0.6 milliampere at the particular voltage to be used in the determination. After having ascertained by pressure readings at 5-minute intervals that the pressure was not changing within the limits of the experimental error of reading the gage (which was ±0 0005 mm. of mercury at 0.17 mm. total pressure), the accelerating voltage was turned on and the drop in pressure in 5 minutes was observed. The residual gas was then pumped out, and more of the original mixture admitted, the pressure being adjusted to within a few per cent. of that in the previous determination. The tube current was kept constant at 0.6 milliampere for all determinations.

Blank tests were, of course, made, using the separate gases at pressures corresponding to the partial pressures of the gases in the mixture. The changes in the pressure in the pure gases were found to be negligible, being only 1 to 3 times the error of reading the McLeod gage.

It was soon discovered that there are two phenomena which must be carefully considered in the interpretation of pressure drops in vacuum tubes containing a mixture of nitrogen and hydrogen, metallic electrodes and hot tungsten filaments. First, cold metals such as tungsten, copper, and especially nickel or platinum, will adsorb active hydrogen (produced by the hot tungsten wire) with great rapidity until the metal surfaces are in equilibrium with the partial pressure of active hydrogen present in the tube. Second, the efficiency of the absorption of ammonia by a sulfuric acid surface of small area is very low as compared with its absorption by the large surfaces of the glass walls of the vacuum tube, these surfaces being coated with an adsorbed film of sulfuric acid. Thus it was found that the sulfuric acid tube could be sealed off, and for a short time the reaction rates observed were almost as great as with the sulfuric acid tube on.

It was further ascertained that wave curves of the type given by Andersen could be readily obtained when the glass surfaces were allowed to become saturated or nearly saturated with ammonia. This phenomenon will be referred to as the "fatigue" factor. For example, Curve I of Fig. 2 is of a wave type, and was obtained by measuring the change in pressure in 2 minutes at 17, 21, 25, 30, 36, 42 and 46 volts without evacuating the bulb after each determination. The observations were limited to 2 minutes and taken every 4 to 6 volts in order to avoid appreciable change in composition of the gas mixture. The drop in pressure for 5 minutes was calculated and plotted against the voltage.

When, however, the glass walls of the bulb were reheated, and the apparatus was thoroughly evacuated after each rate determination, the data indicated, as shown in Curve II of Fig. 2, that the rates were approximately constant for given voltage intervals, and that abrupt increases occurred at specific voltages. Hence, the explanation of the wave type of curve obtained by Andersen is obviously that the fatigue factor distorted what would otherwise have been a "step-like" curve. In the type of apparatus employed by Andersen the fatigue factor was found to be too rapid in its action to admit of any accurate determination of the voltage intervals corresponding to the sudden increases in reaction rate. Thus the individual points of Curve II were not accurately reproducible and, as will be shown later, the fatigue effect blurred out most of the breaks that exist in the region between 20 and 50 volts. Although a smooth curve approximately quadratic would fit the observations represented in Curve II, the results of later work made it seem more reasonable to draw the curve as shown. Curve III of Fig. 2 shows the pressure changes in the separate gases at various voltages.

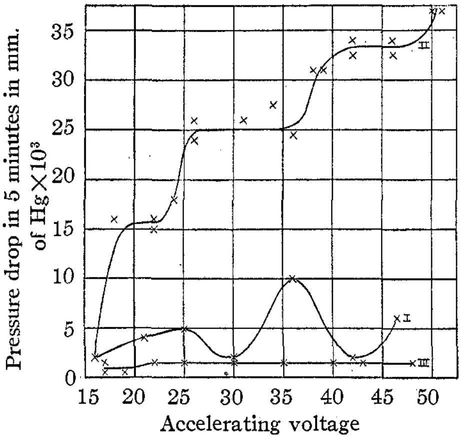

Fig. 2

The following facts were also established in the preliminary experiments. Positive tests for ammonia with Nessler's reagent were obtained at as low a voltage as was necessary to start an arc in the tube. With the distance between the filament and the platinum anodes at 0.75 mm., this voltage was usually 18 volts, but it was occasionally possible, by jarring the tube slightly, to start an arc at 16 volts, and obtain a satisfactory positive test for ammonia at this voltage. At voltages lower than 16–18 volts the pressure drops taken over periods of 2 minutes were found to be of the order of magnitude of those observed in the separate gases, and the tests for ammonia with Nessler's reagent were negative.

At the beginning of the preliminary experiments the tungsten filament was 0.050 cm. in diameter, but it gradually became thinner due to the spluttering and evaporation of tungsten. At the same time it was noted that the rate of the reaction at a given voltage increased slowly with the time. The possibility of a direct connection between these two observations led to an investigation of the effect of the diameter of the filament on the reaction rate. The results obtained are summarized in Table I. The 5 experiments were made with the same apparatus (similar to that used by Andersen, and as described above), but a different filament was employed for each experiment.

TABLE I

VARIATION OF RATE OF REACTION WITH THE DIAMETER AND TEMPERATURE OF THE FILAMENT AT CONSTANT PRESSURE

Pressure, 0.17 mm. of Hg; tube current, 0.6 milliampere; voltage, 18 volts.

Expt.	Diam. of filament Cm.	Length of filament Cm.	Potential drop across filament Volts	Current through filament Amperes	Pressure drop in 5 minutes Mm. of Hg
1	0.050	5.0	3.50	13.0	0.005
2	.030	6.25	3.95	4.9	.008
3	.030	3.13	2.45	6.5	.008
4	.0125	3.13	4.00	1.0	.010
5	.005	2.5	5.32	0.55	.013

It will be observed that the thinner filaments gave the higher rates of reaction, That this was not due to the higher temperature of the thinner wires is proved by comparing Expts. 2 and 3. In No. 3 the filament was hotter than in No. 2, but of the same diameter, and the reaction rates are identical. The explanation of these observations is probably that the potential gradient in the arc is very steep near the cathode, and hence the electrons acquire most of their energy at a very short distance from the filament, thus causing most of the ammonia to be formed in this region. The diameter of the wire, therefore, would largely determine the chance which an ammonia molecule has to escape decomposition by the hot filament, and in this way control the rate of the reaction.

In these experiments with excess of nitrogen (4 to 1) the total drop in pressure at any given voltage (above that necessary to start the arc) was much greater than could be accounted for by the complete removal of the hydrogen introduced for the experiment. This was due to the fact that the platinum anodes provided an additional supply of hydrogen by giving up their adsorbed hydrogen during the course of the reaction. Thus it was found that when a tube was used in which a mercury surface was the anode (see below), the total pressure drop was identical with that calculated from the composition of the gas mixture.

Experiments with a Mercury Anode and a Glass Wool Surface

The chief difficulties encountered in the type of apparatus similar to that used by Andersen were: (1) the fatigue of the absorption mechanism was rapid; (2) the quantities of hydrogen absorbed by the platinum anodes were relatively large, and hence the equilibration of the anodes before each determination was a very necessary and tedious procedure.

The apparatus shown in Fig. 3 was designed to eliminate both of these objections.

As indicated in the diagram, the mercury level (F) which served as the anode could be raised or lowered at will, thus making it possible to vary the distance between the electrodes without reconstructing the apparatus. The U-shaped filament is drawn in perspective to indicate its shape; the plane determined by the sides of the U was parallel to the mercury surface. The space A was filled with glass wool, in order to increase the adsorption surface and thus reduce the fatigue effect. The side tube E contained 1 to 2 cc. of 98% sulfuric acid. A condenser was attached below the reaction chamber in order to keep the temperature of the mercury constant. A 500cc. bulb was sealed into the line, in order to bring the total volume of the apparatus up to 1500 cc.

The clean-up of nitrogen during a 5- or 10-minute interval was found to be very small compared with the pressure drops in the gas mixture. (See similar data in Table V for a later apparatus.) The adsorption of hydrogen by the metal parts in this tube was very low, being practically within the experimental error of reading the gage. The other difficulty, namely, the fatigue effect, was, however, not entirely eliminated.

Before beginning the rate determinations the tube was thoroughly baked and evacuated as before, but it was found impossible to remove the adsorbed gas completely from the glass wool. However, after a few hours' baking and pumping it was found that the glass wool no longer gave off any measurable quantity of gas during the course of several hours with 0.17 mm. of mercury pressure of the gaseous mixture in the tube.

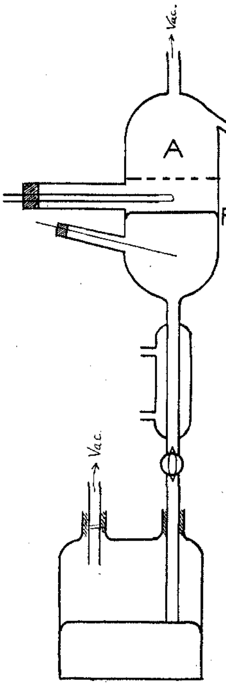

Fig. 3.—Mercury anode apparatus

The procedure used in making the rate determinations was the same as that outlined above for the first apparatus, except that a greater tube current, namely 1 milliampere, was used. In this latter apparatus the filament was 0.0125 cm. in diameter, and 1.25 cm. long.

As shown in Table II, the rate of reaction at 18 volts, with the electrodes 4 mm. apart, and with no sulfuric acid present, was found to be only $^1/_3$ as great as the rate with the sulfuric acid present. The glass wool was not in contact with the liquid sulfuric acid.

TABLE II

ADSORPTION OF AMMONIA BY THE GLASS WOOL SURFACE

Electrodes 4 mm. apart. Composition of gas: H_2, 32%; N_2, 68%. Initial pressure, 0.170 mm. of Hg; 18 volts accelerating voltage; tube current, 1.0 milliampere.

	Pressure drop in 5 minutes Mm. of Hg.	Filament Voltage Volts	Filament Current Amperes
No H_2SO_4	0.008	1.50	2.70
With H_2SO_4	.024	1.47	2.65

Since in this tube the clean-up of the separate gases was found to be negligible during a 5-minute interval, it follows from the data of Table II and the observations made with the first apparatus that the mechanism of the absorption of ammonia is 3-fold, namely, (1) adsorption by the glass surfaces; (2) reaction with the sulfuric acid adsorbed on the glass surfaces; (3) reaction with the sulfuric acid surface itself.

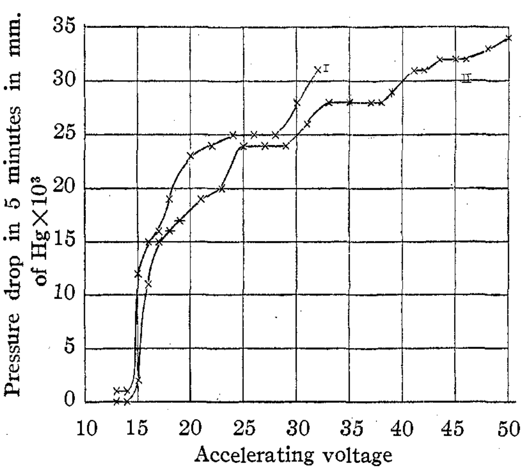

Fig. 4

The results obtained with this tube are sketched in Fig. 4. Curve I represents the data obtained with a 14.3–85.7% mixture of hydrogen and nitrogen and Curve II those with a 32–68% mixture. With the electrodes 3 mm. apart it was possible to start the arc at 15 volts, and a satisfactory positive test for ammonia was obtained at this voltage. With the electrodes 7 mm. apart the arc could not be started below 18 volts, and a negative test for ammonia was obtained below 18 volts. Hence, it seems that the formation of ammonia does not occur to any appreciable extent unless an arc is present.

A comparison of Curves I and II of Fig. 4 shows that the rate of the reaction is greater for a lower hydrogen content, which is in accord with the results obtained by Andersen. Curve II clearly indicates that the rate of ammonia formation remains approximately constant for definite voltage intervals, and increases abruptly at certain voltages. The individual points of this curve were not reproducible, but the general shape of the curve could be fairly well duplicated.

The individual points of the curves in Fig. 4 were not reproducible largely because of the fatigue effect. Reheating the glass wool after each determination caused erratic results because the glass surfaces could never be freed entirely of their adsorbed gases. Hence the curves of Fig. 4

were obtained by allowing the glass wool to become fatigued, that is, by not reheating after each determination. The fatigue factor was, however, slow enough in its action to prevent distortion into the wave type of curve.

Experiments with a Copper Gauze Anode, Using a Liquid-air Bath to Remove the Ammonia Gas

To avoid the fatigue factor it was decided to construct a discharge tube that could be entirely immersed in a liquid-air bath, so as to freeze the ammonia as fast as it was formed, thus making it possible to abandon the use of glass surfaces and sulfuric acid as the absorption device.

The apparatus consisted of a small tube containing a copper gauze anode and the tungsten filament. The tube was 2.5 cm. in diameter and 10 cm. long. The anode was made of 1 mm. mesh copper gauze, was cylindrical in shape, and was 8 cm. long. The tungsten filament was 0.0125 cm. in diameter and 1.25 cm. long. The distance from the center of the filament to the anode was approximately 10 mm. The total volume of the apparatus, including the McLeod gage, and a 750cc. bulb, was approximately 1500 cc. The tube containing the electrodes was completely immersed in liquid air during the rate determinations.

The copper anode was found to adsorb comparatively little hydrogen, but it was noted that the amount taken up was considerably greater than in the previous tube containing a mercury anode. As in the case of the first tube containing platinum anodes, the total pressure drop in this last tube was considerably greater than that calculated from the composition of the gas mixture, thus confirming the explanation of this phenomenon, given in a previous paragraph.

The pressure drops observed in the separate gases are given in Table III. It will be observed that the drops at the various voltages up to 50 volts are practically identical. This proves that the increases in rate observed with the mixture of the 2 gases were not due to abrupt increases in the adsorption of hydrogen by the metal and glass surfaces of the discharge tube, nor in the clean-up of nitrogen by the hot tungsten filament.

Table III

Blank Tests with the Separate Gases at Various Voltages, at Constant Tube Current

Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length of filament, 0.0125 cm. and 1.25 cm., respectively.

Initial pressure Mm. of Hg	Pressure drop in 5 minutes Mm. of Hg	Accelerating voltage Volts	Filament Volts	Filament Amperes
		Nitrogen		
0.104	0.001	20	1.7	1.90
.117	1	30	1.3	1.65
.117	2	41	1.23	1.60
.115	2	52	1.10	1.57
		Hydrogen		
.065	.002	20	1.23	1.70
.062	2	30	1.15	1.65
.062	2	40	1.10	1.60
.059	2	50	1.08	1.60

It was found necessary to bombard the copper gauze anode for about an hour with a heavy electron current (1 to 3 milliamperes) in a high vacuum before starting the rate determinations. If this precaution was not observed, the apparent rates of reaction were low, and not reproducible. This bombardment should be conducted at room temperature, or preferably at 300–400°, for at the temperature of liquid air the time necessary for the complete removal of all foreign gases from the anode was extraordinarily long.

TABLE IV

RATES OF REACTION AT VARIOUS VOLTAGES AT CONSTANT TUBE CURRENT

Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length of filament, 0.0125 cm. and 1.25 cm., respectively; filament current and voltage drop, 1.10–1.24 ampere, 1.03–1.30 volt. Composition of gas: H_2, 32%; N_2, 68%.

Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts	Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts
0.166	0.022	20	0.169	0.029	30
.167	.022	20	.167	.029	31
.165	.022	21	.167	.029	31
.169	.022	21	.168	.029	32
.169	.022	22	.168	.029	32
.169	.022	22	.169	.030	33
.162	.025	23	.168	.031	34
.167	.025	23	.168	.031	35
.169	.025	24	.168	.031	36
.167	.025	24	.167	.0315	37
.166	.025	25	.166	.0325	38
.166	.025	25	.168	.0325	39
.167	.027	26	.169	.0325	40
.170	.026	26	.167	.033	41
.162	.028	27	.169	.034	42
.166	.028	27	.168	.035	43
.165	.028	28	.170	.035	44
.166	.028	28	.169	.035	45
.169	.028	29	.168	.0365	46
.167	.028	29	.168	.0365	47
.166	.028	30	.168	.0365	48

Table IV gives the results of two series of determinations made with the same filament. The first series shows the rates taken at 1 volt intervals from 20 volts (the arc could not be started below 19 volts in this tube) up to 32 volts, and the second series up to 48 volts. The data were found to be reproducible within the experimental error of reading the pressure gage. These results are graphed in Curve I of Fig. 5. Table V gives a third series of measurements (plotted in Curve II of Fig. 5) up to 32 volts, using a different filament. The results, except for the 20–22 volt points, run uniformly higher than those of Table IV. This is probably to be explained by the variation in the diameters of the filaments, for the filament used in obtaining the data of Table V burned out shortly after the 32-volt determination was made, and hence it was probably thinner than the filament of Table IV. A comparison of the 2 curves of Fig. 5 shows that the voltages at which the abrupt increases in the rate of the reaction occur, are accurately reproducible, even when different filaments are employed.

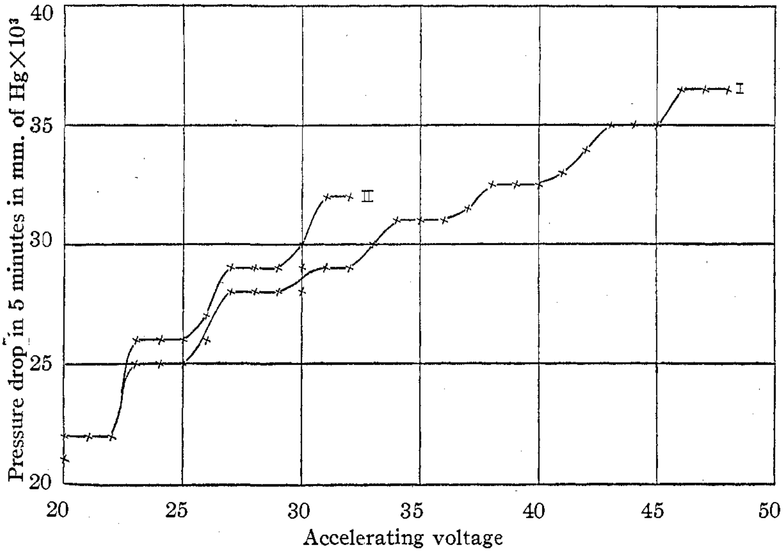

Fig. 5

TABLE V

RATES OF REACTION AT VARIOUS VOLTAGES AT CONSTANT TUBE CURRENT

Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length of filament, 0.0125 cm. and 1.25 cm., respectively; filament current and voltage drop, 1.48–1.51 ampere, and 1.05–1.22 volt. Composition of gas: H_2, 32%, N_2, 68%.

Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts	Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts
0.167	0.021	20	0.163	0.027	26
.174	.022	21	.172	.029	27
.173	.022	22	.166	.029	28
.173	.026	23	.169	.029	29
.170	.026	24	.169	.030	30
.170	.026	25	.173	.032	31
			.171	.032	32

Discussion

The data given in the last two tables indicate that the rate of the reaction, after the arc is once formed, increases abruptly at the following voltages: 23, 26–27, 30–31, 33–34, 37–38, 41–42 and 46. The intervals between these voltages are about 4 volts each. This phenomenon may be characteristic of the reaction, or it may be dependent upon the particular type of apparatus employed. The latter explanation seems improbable because the data obtained with the mercury anode apparatus also gave a "step-like" curve whose shape was reproducible. Moreover, the work on ionizing and resonance potentials shows that the voltage at which abrupt changes in the slope of current-voltage curves occur are characteristic of the gas employed.

The fact that an arc is essential for an appreciable formation of ammonia to occur makes it probable that ionized hydrogen or nitrogen, or both, are necessary before the reaction will proceed. Indeed, it is possible by various combinations of the critical potentials, observed in ionization tubes, for nitrogen and hydrogen, to account for the abrupt increases in the rates of reaction. Thus the 23-volt point may be due to increased ionization of nitrogen by electrons which have first produced resonance in nitrogen, and then gained sufficient energy to ionize nitrogen. However, these 4-volt points may be due to a critical point which is not directly observed in ionization tubes, such as the dissociation of molecular hydrogen or nitrogen.

In conclusion, therefore, we may state that the explanation of the phenomena presented in this paper must await such further research as a detailed study of the spectrum of the arc in a mixture of nitrogen and hydrogen, and the study of other reactions involving nitrogen or hydrogen.

This work was begun while one of the authors (A. R. O.) was a National Research Fellow in chemistry. We take this opportunity to express our appreciation to the National Research Council.

Summary

A study of the factors which control the rate of formation of ammonia from nitrogen and hydrogen in the low-voltage arc yielded the following results.

1. The results of the earlier work by Andersen in which a wave type of curve was obtained for the rate of reaction as a function of the accelerating voltage are explained by the preliminary experiments described in this paper. The curve obtained by Andersen was found to be due to a superposition of the curve described in 2 (below), and a "fatigue" factor in the mechanism used for absorbing the ammonia gas.

2. The variation of the rate of the reaction, at constant tube current with the accelerating voltage, is such as to give abrupt increases in the rate of the reaction at specific voltages which are about 4 volts apart.

3. The formation of ammonia in sufficient quantity to be detected by Nessler's reagent does not occur unless an arc is present.

4. The magnitude of the rate at any given voltage, and at constant tube current, depends primarily on the diameter of the hot filament used as the source of electrons.

5. An increased nitrogen content favors a higher rate of reaction.

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