

## ORIGINAL PAPERS

PREPARATION OF NITROGEN AND HYDROGEN MIXTURE BY DECOMPOSITION OF AMMONIA<sup>1</sup>

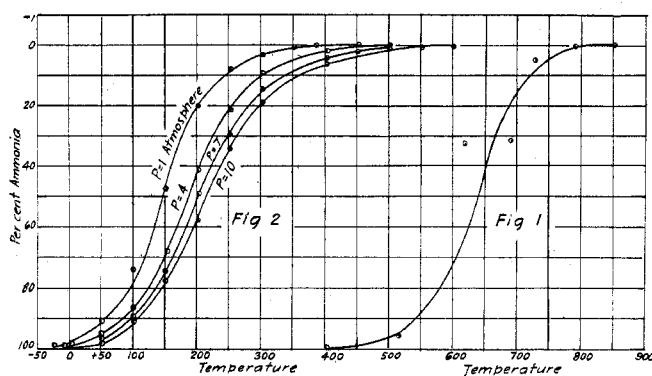
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In work in the Bureau of Soils laboratory on the synthesis of ammonia done in cooperation with the Nitrate Division of the War Department, it was necessary to obtain a mixture of hydrogen and nitrogen in the ratio of  $3\text{H}_2$  to  $\text{N}_2$  in amounts of several hundred cubic feet per day. This gas should be free from impurities, especially carbon monoxide and oxygen. Anhydrous ammonia being easily obtained, it was decided to build an electric furnace to decompose it and use the decomposed gases as the required mixture of nitrogen and hydrogen.

## HISTORICAL

Investigations on the decomposition of ammonia were made in 1884 by Ramsay and Young<sup>2</sup> at temperatures of  $500^\circ\text{C}$ . and  $830^\circ\text{C}$ . They found that decomposition began under most favorable circumstances slightly below  $500^\circ\text{C}$ . Though decomposition occurred below  $500^\circ\text{C}$ . the rate of reaction was too slow to observe in the time of the test. The tests were made in tubes of porcelain and iron with pieces of broken porcelain as catalyst. Decomposition was found to be one and a half to two times greater in an iron tube than in a porcelain one.



The curve in Fig. 1 shows the quantities of ammonia found in the iron tube starting with pure ammonia. Decomposition was complete only at about  $780^\circ\text{C}$ . Haber<sup>3</sup> found that the velocity of reaction when  $t = 700^\circ\text{C}$ . was still so small that equilibrium could not be established with certainty. Plank<sup>4</sup> discusses the theoretical values at one to 10 atmosphere pressures. These values are shown in the curves of Fig. 2. These theoretical equilibria would exist only after months or years as the velocity of reaction is very slow.

Perman and Atkinson<sup>5</sup> made tests between  $t = 677^\circ\text{C}$ . and  $1111^\circ\text{C}$ . with a reaction vessel of porcelain.

<sup>1</sup> Published by permission of Chief of Ordnance.

<sup>2</sup> *J. Chem. Soc.*, 45 (1884), 88.

<sup>3</sup> *Z. Electrochem.*, 40, 2144.

<sup>4</sup> *Z. ges. Kalt-Industrie*, March and May 1916, p. 8; reviewed in *Am. Soc. Refrig. Eng. J.*, 2 (1915), 34.

<sup>5</sup> *Proc. Roy. Soc. London*, 74 (1905), 110.

Mercury, platinum, and iron as catalysts were all found to accelerate the reaction.

Bodenstein and Kranendiech<sup>1</sup> operated between  $790^\circ\text{C}$ . and  $880^\circ\text{C}$ . using quartz glass for catalyzer and reaction vessel. Their results verify those of other investigations. From their experiments it is shown clearly that iron acts as a catalyzer toward this reaction in both directions.

## DESCRIPTION OF FURNACE

The furnace devised by us for carrying out this reaction is shown in Fig. 3.

A diagrammatic sketch of the furnace shows the outer tube *a* to be a piece of 5-in. standard wrought iron pipe 4 ft. long closed at the ends with flanges *c*, and the upper 34 in. wound with nichrome ribbon, *k*. Inside this pipe is a piece, *b*, of 2.5-in. standard iron pipe, 35 in. long, wound with nichrome wire, *k*. A pyrometer tube, *n*, extends 14 in. into the upper end of this inner pipe and the vacant space *f* (about  $\frac{1}{4}$  cu. ft.) is filled with the catalyst (in this case iron turnings or steel wool). Automobile spark plugs were adapted to carry the leads through the flanges. The lower portion is the heat interchanger *g* which actually consists of three coils of  $\frac{1}{8}$  in. pipe connected in parallel. The anhydrous ammonia enters the interchanger through the lower flange, passes upward over the interchanger coils, through the catalyst between the heaters, then passes down through the catalyst inside the inner pipe, through the interchanger coils, and emerges as a mixture of  $3\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$ , the percentage of  $\text{NH}_3$  depending upon the temperature and rate of flow. The gases are passed through a water scrubbing tower to remove the remaining ammonia and then through a meter to the gas holder. The ammonia remaining in the scrubbed gases rarely exceeded 0.2 per cent and quite often is nil.

It will be seen that the inner heater is very favorably situated since it operates in a reducing atmosphere. It consumes about 65 per cent and the outer coil about 35 per cent of the total energy. The source of current is a 25 cycle, 40 volt transformer. It was originally intended to use copper turnings as a catalyst and the furnace was wound inductively. With iron as catalyst the power factor is reduced to 92 per cent. The coils are connected so that their magnetic fluxes are opposed. The maximum power consumption at 40 volts is 2 k. v. a. which is inadequate to maintain the furnace at the proper temperature for a flow of ammonia as great as the catalyst can decompose. In a new furnace of similar design, the length is increased one foot and the diameter one inch. The inner coil is wound non-inductively on 3.5-in. cold drawn boiler tube and has a carrying capacity of 4 k. v. a. at 40 volts. The outer coil is also wound non-inductively with a maximum capacity of 3 k. v. a. The voltage is adjusted so that the inner coil will dissipate about 80 per cent of the energy. The capacity of the heat interchanger

<sup>1</sup> *Festschrift, W. Nernst* (1912), pub. by Knapp, Halle; *Chem. Abs.*, 7 (1913), 1647.

is considerably increased, and the inlet and outlet gases travel through about 10 ft. of double pipe in counter-current flow. Fine steel wool is used for catalyst.

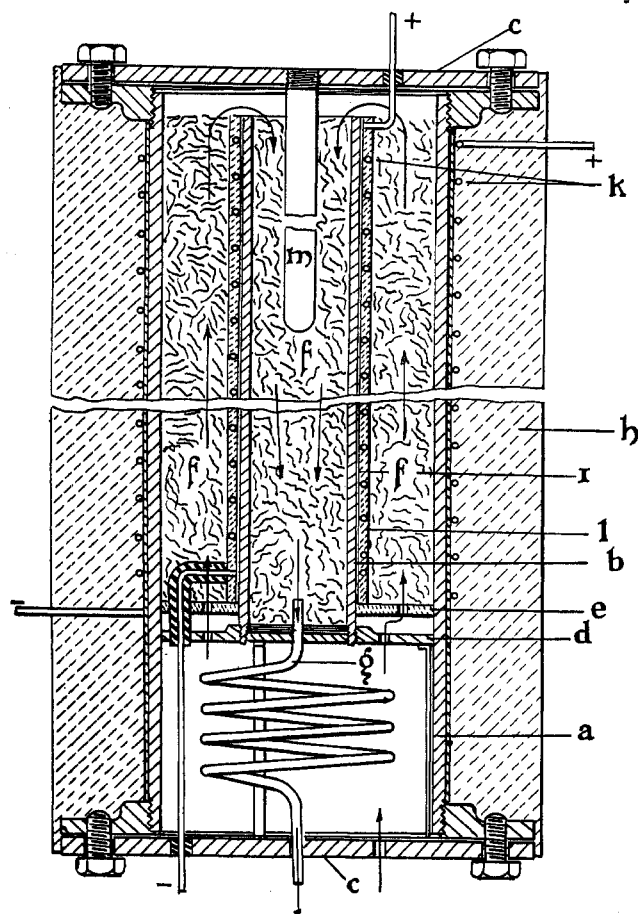


FIG. 3.—FURNACE FOR THE DECOMPOSITION OF AMMONIA

- a—5-in. iron pipe  
 b—2.5-in. iron pipe  
 c—flange ends  
 d—flange end to inner pipe  
 e—perforated asbestos board  
 f—catalyst space  
 g—heat interchange coil  
 h—insulating material  
 i—alundum sheath  
 k—resistance coil of chromel wire  
 l—alundum cement  
 m—pyrometer well

The weight of the furnace is partially supported from above to prevent deformation and the sides and top are covered with 7 in. of infusorial earth.

#### RESULTS

Table I shows some results obtained in the furnace using iron shavings as catalyst. The flow is measured by the decomposed gas free from  $\text{NH}_3$  which passes through the meter.

TABLE I—DECOMPOSITION OF AMMONIA  
 (Catalyst: Iron. Space: 0.22 Cu. Ft.)

Temp. ° C.	Flow Cu. Ft. per Min.	Decomposition Per cent
370	0.01	73.0
470	0.15	84.0
540	0.01	94.0
600	0.20	97.0
600	2.00	94.5
610	0.50	93.5
650	0.62	99.6
650	1.50	97.4
675	0.50	99.7
675	1.00	99.5
700	1.50	99.7
710	2.00	99.6
735	0.82	99.7

For ordinary operation a temperature of 675° C. is maintained which enables one to obtain about 100 cu. ft. per hr. of the hydrogen-nitrogen gas mixture with a power consumption of 2 k. v. a. with loss

of 0.3 to 0.4 per cent of ammonia. The equilibrium of a system of  $\text{H}_2$ - $\text{N}_2$ - $\text{NH}_3$  at that temperature and atmospheric pressure theoretically should be about 0.02 per cent  $\text{NH}_3$ . The average time of contact in the catalyst space is about 5 sec. This time could probably be reduced considerably.

A small preliminary furnace in which copper chips and turnings were used for catalyst was employed before this one was constructed. Table II shows results obtained with this.

TABLE II—DECOMPOSITION OF AMMONIA  
 (Catalyst: Copper. Space: 0.11 Cu. Ft.)

Temp. ° C.	Flow Cu. Ft. per Min.	Decomposition Per cent
750	0.01	96.0
750	0.25	75.0
800	0.05	97.3
850	0.01	99.7
850	0.22	99.4
850	0.95	90.5
900	0.85	96.2
925	0.50	99.3
925	1.00	97.5

It will be seen that copper requires a temperature about 200° C. higher than iron, and a longer contact. The figures are not strictly comparable for the iron surface was probably of the order of ten times that of the copper. Beilby and Henderson<sup>1</sup> emphasize the fact that ammonia decomposes less rapidly in contact with copper than with iron.

Because of the lower operating temperature and cheapness, iron was chosen in preference to copper as a catalyst.

The furnace with steel shavings was in operation for about 6 mo. when the outer coil burned out. On taking apart the iron, shavings were found to have sintered into a compact mass and to be attached firmly to the sides of the iron pipe. The pipe itself, which had operated continuously in an atmosphere of hydrogen and nitrogen, showed attack from within to such a degree that it was granular and cracked about two-thirds the distance through the wall (0.25 in. thick) and crystallized the other third. The metal was very brittle and the pipe was readily broken up with a hammer. Beilby and Henderson<sup>2</sup> and Henderson and Galletly<sup>3</sup> found a similar deterioration of metals exposed to ammonia at high temperatures. Probably this was due to the formation of iron nitride or hydride, or both. The nichrome wire used as resistance winding seemed to be in as good condition as when first wound. The maximum temperature to which the furnace had been subjected was not over 900° C., and this temperature was reached inadvertently and maintained for a very short time.

#### THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER<sup>4</sup>

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Since the introduction of the use of organic substances to assist in, or to accelerate, the vulcanization

<sup>1</sup> *J. Chem. Soc.*, 79 (1901), 1245.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *J. Soc. Chem. Ind.*, 27 (1908), 387.

<sup>4</sup> Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.