

## XX.—*The Synthesis of Ammonia at High Temperatures.*

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IF the equilibrium between nitrogen, hydrogen, and ammonia be examined thermodynamically, it will be seen that whereas at moderate temperatures, such as are employed for the catalytic synthesis of ammonia, an increase in temperature leads to a rapid decrease in the amount of ammonia in equilibrium with nitrogen and hydrogen, this amount passes at higher temperatures through a minimum and, with increasing temperature, begins to rise with increasing velocity.

For a rough preliminary calculation, either of the following formulæ, which have been worked out by Haber (*Zeitsch. Elektrochem.*, 1914, **20**, 597; "Thermodynamics of Technical Gas Reactions," p. 204) for the ammonia equilibrium at temperatures below 1000°, may be extended to higher temperatures in order to demonstrate this reversal, but it will be shown that more ammonia is actually obtained at, for instance, the temperature of the oxy-hydrogen flame than can be accounted for by either formula.

We have, accordingly, if  $K = \frac{P_{\text{NH}_3}}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$

$$(a) \log_{10} K_p = 2215/T - 3.625 \log_{10} T + 0.000307T + 0.29 \times 10^{-6}T^2 + 4.82.$$

$$(b) \log_{10} K_p = 2098/T - 2.5088 \log_{10} T - 0.0001006T + 0.186 \times 10^{-6}T^2 + 2.1.$$

The calculated variation of  $K$  with temperature is given in the following table.

TABLE I.

Temperature.	Value of $K \times 10^4$ .	
	By equation (a).	By equation (b).
1000° Abs.	5.7	5.7
2000	0.78	0.26
3000	3.03	0.28
4000	152.0	1.5

It was accordingly to be assumed that mixtures of nitrogen and hydrogen, at high temperatures, contain ammonia which by rapid cooling might be brought, without complete decomposition through the temperature zone at which ammonia becomes unstable into that region of temperature in which it is once more capable of stable existence.

The subject has been examined experimentally, first for not extremely high temperatures, by rapidly cooling mixtures of nitrogen and hydrogen from the temperature of the oxy-hydrogen flame to the ordinary temperature, yields of ammonia amounting to more than 1 per cent. by volume under atmospheric pressure being obtained. The result is of special interest if one considers that such a yield is only possible otherwise below 350°, a temperature at which the formation of ammonia, even in the presence of catalysts, does not proceed with measurable velocity.

The method of heating and suddenly cooling employed in the work about to be described consists in injecting the mixture of nitrogen and hydrogen into an oxy-hydrogen flame burning under water, or, in a second series of experiments, into an oxy-hydrogen flame burning in a water-cooled silica tube, the amount of ammonia formed being estimated in some cases by direct titration with  $N/10$ -acid and in others colorimetrically by Nessler's solution. The reaction mixture contained, therefore, in addition to nitrogen and hydrogen, a volume of steam depending on the proportion of the mixture of nitrogen and hydrogen injected into the flame. It was noted, further, that the yield of ammonia recovered at the ordinary temperature was considerably greater when direct cooling with water was employed than when the flame was cooled by contact with a water-cooled quartz tube.

#### EXPERIMENTAL.

For the first series of experiments, the reaction chamber consisted of a silica tube 6.5 mm. in diameter and 7.5 cm. long, completely immersed in about 900 c.c. of distilled water contained in a glass vessel fitted with an efficient glass cooling coil through which

a rapid current of water was passed, the vessel having a capacity of slightly more than 1 litre. Into the quartz reaction chamber, nitrogen, hydrogen, and oxygen, at rates determined by velocity meters, were injected and ignited, the flame gases passing out of the open end of the reaction chamber and bubbling through the water, by the action of which the ammonia, recovered from the flame by sudden cooling, was retained. In some cases the water was replaced by dilute acid, without, however, any appreciable difference in the results, provided that the water was kept cool. The amount of oxygen passed into the reaction chamber was in every case regulated in such a way as to leave uncombined hydrogen equal to three times the volume of the nitrogen passed in.

In order to make a comparison of the results obtained at various temperatures and at varying partial pressures, that is, by the increasing dilution of the oxy-hydrogen flame with a mixture of nitrogen and hydrogen, advantage was taken of the known fact that for small percentages of ammonia the volume formed at a given temperature is directly proportional to the pressure, so that the volume of ammonia which would be formed at the temperature of the flame but under atmospheric pressure may be calculated by dividing the value observed by the corresponding partial pressure of the nitrogen, hydrogen, and ammonia in the nitrogen, hydrogen, ammonia, and steam reaction mixture. In this way, it becomes possible easily to compare the relative amounts of ammonia formed at different temperatures and under varying partial pressures. In this series of experiments, the ammonia in the resulting solution was estimated colorimetrically by Nessler's reagent, care being taken to use distilled water free from ammonia for cooling the flame. In those cases in which dilute acid was used for cooling, this was made up by dissolving 40 c.c. of ammonia-free  $N/10$ -sulphuric acid in each litre of distilled water.

Table II summarises the results obtained by direct cooling with water or dilute acid.

It will be noticed that the percentage of ammonia by volume in the mixture of nitrogen and hydrogen recovered by suddenly cooling (reduced for uniformity to one atmosphere pressure) rises from 0.0027 to 1.23 as the reaction temperature approaches that of the oxy-hydrogen flame. The flame temperatures are calculated from Féry's observed values for the oxy-hydrogen and air-hydrogen flames.

#### *Experiments with Indirect Cooling.*

The reaction chamber employed for this series of experiments consisted of a vertical quartz tube 90 cm. long and 8 mm. in

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TABLE II.

No. of expt.	Velocity in litres per hour of gases passed into reaction chamber.			Duration of expt. in minutes.	Cooling agent.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Partial pressure of system nitrogen- hydrogen- ammonia in flame.	Estimated temperature of flame. ° Abs.	Percentage volume of ammonia formed at absolute pressure of 1 atm.
	Nitrogen.	Hydrogen.	Oxygen.						
1	60	220	20	15	Acid	0.00235	0.86	1280	0.0027
2	60	260	40	15	Water	0.005	0.75	1500	0.0067
3	60	360	90	15	Water	0.013	0.57	1830	0.023
4	30	270	90	15	Water	0.018	0.4	2120	0.045
5	20	240	90	15	Water	0.0205	0.31	2260	0.066
6	20	300	120	10	Acid	0.0366	0.25	2350	0.146
7	20	460	200	5	Acid	0.07	0.167	2470	0.42
8	10	430	200	5	Acid	0.112	0.091	2580	1.23

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internal diameter. This was cooled by making it the inside tube of a long Liebig's condenser. The flame gases, which in this case were cooled only by contact with the cold walls of the silica tube, were allowed to pass from the bottom of the tube through a known quantity of *N*/10-acid, which was afterwards titrated with alkali in the usual manner. As was to be expected from the less rapid cooling, the amount of ammonia produced at high temperatures was less than that obtained by directly leading the flame into cold water. At lower temperatures, the divergence became less marked until, at the lowest temperature studied, approximately equal values for the yield of ammonia were observed. The results obtained by indirect cooling in the above manner are summarised in table III.

TABLE III.

No. of expt.	Duration in minutes.	Partial pressure of system nitrogen- hydrogen- ammonia in flame.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Estimated temperature of flame, ° Abs.	Percentage volume of ammonia at absolute pressure of 1 atm.
1	30	0.86	0.0026	1280	0.003
2	30	0.57	0.0068	1830	0.012
3	30	0.25	0.0134	2350	0.054
4	30	0.167	0.0196	2470	0.118
5	30	0.091	0.019	2580	0.21

*Summary.*

It may be shown thermodynamically that the ammonia equilibrium first sinks with increasing temperature, then passes through a minimum, and finally rises again. By suddenly cooling mixtures of nitrogen and hydrogen, much of the ammonia contained therein may be obtained at the ordinary temperature, and the ammonia formed is, if we assume Féry's measurements for the temperature of the oxy-hydrogen flame to be correct, greater than corresponds with Haber's equation for the ammonia equilibrium at temperatures below 1000°. With direct cooling of flames by means of water, volumes of ammonia amounting for atmospheric pressure to 1.23 per cent. of the mixture of nitrogen and hydrogen have been obtained. With indirect cooling, less ammonia is recovered, the maximum volume per cent. obtained at atmospheric pressure being 0.21.

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