XIV.—*The Decomposition of Ammonia by Heat.*

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It has long been known that when ammonia gas is passed through a red-hot porcelain tube, or when it is exposed to the electric spark for some time, decomposition into nitrogen and hydrogen ensues. Attempts have also been made to bring about the combination of free nitrogen and hydrogen, but these have been attended with but slight success. Thus Deville noticed that when ammonia gas is exposed to the electric spark in a closed tube, there always remains a small quantity of the compound undecomposed, for by the introduction of a little hydrochloric acid gas a cloud is produced (*Annalen*, **135**, 104). He also found that the presence of hydrochloric acid hindered the decomposition of ammonia. An attempt to bring about the synthesis of ammonium chloride by the passage of hydrochloric acid gas, nitrogen, and hydrogen, through a tube heated to dull redness, led to no result, even when spongy platinum was placed in the tube (*Annalen*, **127**, 281). Deville, however, found that when the electric spark was passed through a mixture of nitrogen, hydrogen, and hydrochloric acid, a certain quantity of ammonium chloride was formed, and, in his ingenious apparatus designed to imitate the action of the spark, and consisting of a porcelain tube heated to redness, along the axis of which was placed a metal tube cooled by a stream of cold water, he succeeded in bringing about the same result. The quantity of sal-ammoniac formed was, however, very small (*Annalen*, **135**, 104).

Donkin, also, has recently shown that ammonia may be formed in small quantity by the passage of the silent discharge through a mixture of nitrogen and hydrogen (*Proc. Roy. Soc.*, **21**, 281). This has recently been confirmed by E. Johnstone (*Chem. News*, Dec., 1883). It is stated in *Watts's Dictionary*, vol. i, p. 183, that ammonia is decomposed by passage through a red-hot porcelain tube containing copper or iron wire, and to a less extent when gold, silver, or platinum wire is employed.

But little, however, is known as regards the temperature at which decomposition takes place, or as to the influence of the material of the vessel or tube containing the gas. It appeared interesting, therefore, to study these points more carefully than has yet been done.

The ammonia gas was generated by gently warming a concentrated aqueous solution of ammonia, and was dried by passing it through

three bottles containing quicklime, and then led through a tube heated by a Fletcher's furnace. The undecomposed ammonia was estimated by absorption in a known quantity of standard sulphuric acid and subsequent titration of the unsaturated acid, while the mixed nitrogen and hydrogen were collected in a suitable vessel and their volume measured. The temperature of the furnace was ascertained approximately by the fusion of salts placed on small pieces of platinum-foil lying on the surface of the tube. Thus, according to Carnelley, calcium chloride melts at 719° , and potassium chloride at 734° , and if the former salt liquefied, while the latter remained solid, the temperature was taken to be between 719° and 734° .

The percentage of ammonia decomposed was calculated as follows:—

v = volume of standard sulphuric acid taken.

v' = volume of standard soda solution required to neutralise the excess of acid.

1 c.c. of standard acid contains 0.0468 gram H_2SO_4 , and therefore neutralises 0.0162 gram NH_3 .

Therefore the amount of undecomposed ammonia = 0.0162 ($v - v'$) = x .

The volume of the mixed gases at t° and p mm. = V c.c.

The tension of aqueous vapour at t° = τ .

Therefore the volume of mixed gases at 0° and 760 mm. =

$$\frac{V(p - \tau)}{(1 + 0.003665t)760} = V'.$$

1 c.c. of nitrogen at 0° and 760 mm. = 0.0012562 gram.

3 c.c. of hydrogen at 4° and 760 mm. = 0.002668 gram.

Therefore 4 c.c. of the mixed gases weigh 0.0015250 gram, and 1 c.c. of the mixed gases weighs 0.00038125 gram.

Hence the weight of ammonia decomposed = 0.00038125 $V' = y$.

And the percentage of ammonia decomposed = $\frac{y \times 100}{y + x}$.

In the first series of experiments a porcelain tube filled with broken pieces of porcelain was employed with the following results:—

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
500°	0.00678	0.43902	1.52 }	1.575
„	0.00907	0.54756	1.63 }	
520	0.00946	0.35316	2.61 }	2.53
„	0.00923	0.32902	2.73 }	
„	0.00703	0.28188	2.43 }	
„	0.00720	0.29970	2.35 }	

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
600°	0·04493	0·19880	18·43	18·23
„	0·04486	0·20250	18·14	
620	0·04182	0·13446	23·72	25·58
„	0·04503	0·11502	28·79	
„	0·04560	0·14255	24·24	
680	0·04517	0·08586	34·47	35·01
„	0·04636	0·08910	34·22	
„	0·04629	0·08100	36·36	
690	0·04542	0·05832	43·78	47·71
„	0·04542	0·04212	51·88	
„	0·04542	0·05022	47·49	
810 to 830° ..	0·04431	0·02754	61·67	69·5
„ „ ..	0·04772	0·01620	74·66	
„ „ ..	0·04613	0·01134	80·27	
„ „ ..	0·34285	0·14256	70·63	
„ „ ..	0·34561	0·20412	62·87	
„ „ ..	0·36264	0·15390	67·04	

The want of uniformity in the results at the higher temperatures appears to be due to two causes—(1) the difficulty in keeping the temperature of the tube constant; thus in the last series the tube was at one time very nearly at 810°, and at another at about 830°; (2) The variable rapidity of the current of gas, which was found subsequently to exercise great influence on the amount of decomposition, and this might be anticipated, since there is practically no recombination of nitrogen and hydrogen to form ammonia.

A second series of experiments was made with an iron tube filled with broken pieces of porcelain.

Temperature.	Weight of NH_3 decomposed.	Weight of NH_3 undecomposed.	Percentage of ammonia decomposed.	Mean.
507—527°	0·04432	1·01410	4·19	4·15
„	0·02303	0·53622	4·12	
600° (a).....	current very fast.			
„	0·04644	0·17658	20·82	21·36
„	0·04540	0·17344	20·76	
„	0·04527	0·15522	22·49	
„ (b).....	current much slower.			
„	0·04527	0·08586	34·44	34·44
628	0·04733	0·02268	67·61	65·43
„	0·04558	0·02592	63·75	
„	0·04558	0·02106	68·40	
„	0·34980	0·21465	61·97	

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Temperature.	Weight of NH ₃ decomposed.	Weight of NH ₃ undecomposed.	Percentage of ammonia decomposed.	Mean.
676—695°	0·35407	0·16524	68·02	66·57
„	0·36473	0·19926	64·67	
„	0·35762	0·17334	67·35	
„	0·35941	0·18306	66·25	
730	0·34840	0·02268	93·89	93·38
„	0·35459	0·02106	94·39	
„	0·35034	0·02268	93·92	
„	0·35850	0·03402	91·33	
780	vol. = 1 litre	—	100	100
„	„	—	100	

It is to be remarked that in all these experiments with broken porcelain, the surface became blackened, owing, doubtless, to the reduction of the lead used in the enamelling. The surface was consequently blistered, and possibly to some extent porous.

The gas was then passed through a plain glass combustion tube lying in the iron tube, which was heated to 780°.

Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.
0·00571	2·4056	0·24

That the small quantity of gas collected was really a mixture of nitrogen and hydrogen was proved by its burning quietly with a colourless flame as usual.

The ammonia was then passed through a glass tube quite filled with fragments of broken combustion tubing to increase the surface. The temperature was again 780°, but rose slowly.

Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
0·01016	0·7776	1·29	1·72
0·01020	0·6042	1·66	
0·01040	0·5540	1·84	
0·01720	0·8019	2·10	

A glass tube was then filled with strips of ignited asbestos card-board, which being porous should expose a large surface to the gas.

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
520°	0·00788	0·2641	2·90	2·90
780	vol. = 1 litre	—	100	100
„	„	—	100	

On passing dry ammonia through a plain iron tube heated to 780° the whole of the ammonia was decomposed, as far as could be ascertained by volumetric analysis.

If, however, the tube was partially oxidised, water was formed, and only about 95 per cent. of the gas was decomposed.

The effect of metallic surfaces on the decomposition of ammonia was further studied by placing several lengths of iron and copper wire in a glass combustion-tube. With the iron wire at 760° , 76 and 74.3 per cent. of ammonia was decomposed, while with the copper wire, under similar conditions and at the same temperature, only 2.0 per cent. was decomposed.

A glass combustion-tube was then filled with copper oxide, and a current of ammonia passed until the whole was reduced. After complete removal of the water, the temperature was raised to 780° , when it was found that the percentage of ammonia decomposed in four experiments was 49.3, 42.6, 57.3, and 51.6, or, as a mean, 50.2. Of course in this case the amount of surface exposed was very large.

The results obtained may be summed up as follow:—

1. When ammonia-gas is passed through a porcelain tube, or an iron tube, or a glass tube filled with asbestos cardboard, the amount of decomposition at 500 — 520° is nearly equal and very small. It may be fairly assumed, therefore, that the temperature at which ammonia begins to decompose, under the most favourable circumstances, lies a little below 500° .

2. In contact with a glass surface, the temperature at which decomposition begins lies much higher.

3. The amount of decomposition depends partly on the rate of passage of the gas, or, in other words, on the time of exposure to heat.

4. The nature of the surface heated has an enormous influence on the extent of decomposition, as is shown by the difference between the effects of copper and of iron wire, and of glass and porcelain.

5. The extent of the surface also influences the amount of decomposition, as shown by the experiments with copper wire and reduced copper.

6. Attempts were also made to ascertain the influence of pressure and of time by heating ammonia to high temperatures in sealed glass tubes; but at the temperatures attained no decomposition ensued, while at the higher temperatures the tubes invariably burst, though protected by coiled copper wire, copper electrolytically deposited, and sheet copper. In one case, however, a glass tube containing ammonia was successfully heated to 780° or a little lower for six hours, without any appreciable decomposition of the gas.

It has been stated that in several cases the decomposition of the

ammonia was complete: this is, however, not strictly correct, since, although no ammonia could be recognised by volumetric analysis, even when a litre of mixed nitrogen and hydrogen was collected, yet the issuing gas had always a faint ammoniacal smell and an alkaline reaction sufficiently powerful to turn a piece of red litmus-paper blue.

In order to make quite certain of this point, an iron tube was heated to very bright redness with the blast, but even in this case the issuing gas contained a trace of ammonia.

From this result, together with Deville's observation that decomposition is never complete when the spark is passed, it appears certain that recombination of the nitrogen and hydrogen must take place, if only to a very minute extent; when, however, a mixture of dry nitrogen and hydrogen was passed through a red-hot glass tube containing iron filings, or through an iron tube, the presence of ammonia could not be recognised. When the mixed gases were moist, a trace of ammonia was formed, possibly due to the decomposition of water by iron and the formation of nascent hydrogen.