fluorescent light. It is true that it would not depend upon the amplitudes of the vibrations; but if new free periods are excited as I have described, the intensity and the absorption would both depend upon the number, and the duration of the periods thus produced, and it is this which, I think, the change of absorption in fluorescence most distinctly proves.

The Direct Synthesis of Ammonia.

By Edgar Philip Perman, D.Sc., Assistant Professor of Chemistry at University College, Cardiff.

(Communicated by Principal E. H. Griffiths, F.R.S. Received January 3, and in revised form, March 4,—Read March 30, 1905.)

It was shown in a recent paper on "The Decomposition of Ammonia by Heat,"* that ammonia is decomposed almost (if not quite) completely when heated in a porcelain vessel at about 800° to 1100°, and that there is no sign of equilibrium between the ammonia and its decomposition products at any of the temperatures employed, 677° to 1111°.

In order to discover if there is any such state of equilibrium, it was thought better to attempt to reach that state by synthesising ammonia instead of decomposing it, as the testing for and estimation of the ammonia could then be carried out with much greater accuracy.

Preparation of the Mixed Gases.—In the first series of experiments, the mixture of nitrogen and hydrogen was made by passing ammonia gas, from a strong aqueous solution, through a red-hot iron tube heated in a gas furnace, and the resulting gases were collected in a large gasholder and stored over dilute sulphuric acid. It may be objected to this method of preparation that carbon monoxide, hydrogen, and other gases would percolate through the iron, and contaminate the product obtained. In order to test this point, a careful analysis of the gases was made, with the result that no carbon monoxide could be detected by the blood test; no carbon dioxide was found after exploding the gases with oxygen; and the ratio of nitrogen to hydrogen was found to be correct. The mixture of gases made by this method will be referred to as "Mixed Gases I."

It was thought, nevertheless, that traces of foreign gases might have escaped detection, and might possibly have influenced the results. Consequently a second series of experiments was carried out with a mixture of

* 'Roy. Soc. Proc.,' vol. 74, p. 110, 1904.

nitrogen and hydrogen made in an entirely different way. Nitrogen gas was made by heating gently a solution of equivalent quantities of ammonium chloride and sodium nitrite, and hydrogen was prepared from a concentrated potash solution heated with metallic aluminium, the gas being passed through two Drechsel flasks containing potassium permanganate solution.

Each gas was stored in a gasholder, and a mixture of the two was then made, in the proportion of 1 volume nitrogen to 3 volumes hydrogen, in a third gasholder. The volume of gases was measured by the volume of water drawn off, due regard being paid to the "head" of water. This mixture will be called "Mixed Gases II."

Attempted Synthesis by Heat. (Mixed Gases I, and II, separately.)—The mixture was proved to be free from ammonia by testing with Nessler's solution. It was then passed through a hard glass tube heated in a combustion furnace. Glass was chosen as likely to have no chemical action on ammonia or its constituents. The temperature was varied from about 600° to 1000° C. The resulting gases were bubbled through dilute hydrochloric acid solution; this was afterwards made alkaline with potash, and Nessler's solution added. The result was that *no ammonia could be detected*, whatever the temperature or state of gases as to moisture.

In some experiments the mixture was freed from traces of oxygen by bubbling through alkaline pyrogallate solution, and then dried by strong sulphuric acid; in other experiments these precautions were omitted, but the result was always the same, and was obtained many times.

The experiment was varied by filling a porcelain globe with nitrogen and hydrogen (Mixed Gases I), and heating it in a furnace to a bright red heat for about 1½ hours. The gases were then tested for ammonia in the usual way, but not a trace was found. We may conclude, therefore, from these experiments, that ammonia cannot be synthesised from nitrogen and hydrogen by heating in vessels of glass or porcelain, or that, if it is formed, it is not in sufficient quantity to be detected by Nessler's solution.

Synthesis by Heat in the Presence of Iron. (Mixed Gases I.)—Some of the mixed gases were then passed through an iron tube heated to redness, or in some cases a glass tube containing iron nails, and it was found that, when moisture was present, traces of ammonia were formed; if, however, care was taken to exclude moisture by passing the gases through alkaline pyrogallate solution and sulphuric acid, and reducing any iron oxide, then no ammonia could be detected. This result was obtained also by Ramsay and Young.*

In order to form an idea of the amount of ammonia produced, known

* 'Chem. Soc. Journ.,' vol. 44, p. 88, 1884.

volumes of the mixed gases were passed through a hard glass tube packed with "French nails," and the ammonia was estimated by Nessler's solution, as in the method used in water analysis. The following results were obtained :—

Vol. of mixed gases. c.c.	Approximate rate. litres per hour.	Ammonia. milligrammes.
500	10	0·03
500	10	0·06
250	3	0·08
250	3	0·10

No ammonia could be detected in any case unless the iron was at a bright red heat, about 800° to 900°. With Mixed Gases II :—

Time. ′ ″	Vol. of mixed gases. c.c.	Ammonia. milligrammes.
8 20	250	0·20
2 45	250	0·20
0 42	250	0·17

It will be noticed that the maximum amount of ammonia was formed when the gases were passed at the middle rate, indicating that the mixture had come into equilibrium. More than twice as much ammonia per litre of mixed gases was formed in this series as in the first, and it appeared to be formed at a lower temperature. Moreover, when the gases were carefully dried by sulphuric acid, traces of ammonia were still found. Whether this difference was due to greater purity of the gases or to any other variation in the conditions (*e.g.*, the new French nails) I am unable to say.

My attention has been called to a paper by Haber and van Oordt* in which some very similar experiments are described. The proportion of ammonia formed in the experiments of these investigators was about 0·2 to 1000 possible (if completely converted), which is considerably less than obtained by me, but the temperature and other conditions were different in the two cases.

Haber and van Oordt have attempted to find the dissociation constant at different temperatures, but it appears to me that the available data are entirely insufficient for the purpose. Moreover, the part played by the iron is not yet completely understood.

My experiments show that the quantity of ammonia formed depends on the amount of moisture present, but Haber and van Oordt appear to have overlooked this point, and say simply that their gases were dry.

* 'Zeits. für anorg. Chemie,' vol. 43, p. 111, 1905.

Synthesis by Heat in the Presence of other Substances.—Similar experiments were made with a number of other metals. Copper, zinc, nickel, cobalt, palladium, aluminium, and magnesium, all gave traces of ammonia, but usually less than iron. Platinum sponge yielded traces, whilst platinised asbestos and platinum foil produced very minute and scarcely perceptible quantities. Zinc and copper in contact gave no more than when present separately. In all these cases, which were made with "Mixed Gases I," no attempt was made to exclude moisture.

Effect of Large Surface.—(Mixed Gases I.) The following substances were selected in order to test the influence (if any) of large surfaces, on the synthetical formation of ammonia: pipe stems, pumice, broken porcelain, asbestos. A hard glass tube was packed with the substance, and the experiment conducted in the usual way. As the result, traces of ammonia were found in each case, except with the porcelain. All these substances, except the porcelain, contained a notable quantity of iron, and I believe that it is owing to its presence that the ammonia was formed. The porcelain was from a broken globe, see former paper.* The pipe-stems altered in colour, under the influence of the gases, from a yellowish tint to a dull grey, which I ascribe to the reduction of the iron present. Although my conclusion may be questioned, I believe that (in this case) the extent of surface has no effect, unless the substance with which the gases are in contact reacts chemically with them.

Synthesis by Explosion.—It was noticed that if an explosion of the mixed gases and air took place in the hard glass tube, traces of ammonia were formed, and the effect was further investigated by exploding the gases with oxygen in a eudiometer and testing the resulting gases for ammonia.

The following are the results:—

Mixed gases.	Oxygen.	Result.
c.c.	c.c.	
10·5	2	Trace of ammonia
15	5·2	ditto (but less)
16	3·5	ditto
16·3	3·4	ditto
16	9	ditto (but less)

It will be seen that the quantity of ammonia formed diminishes if the oxygen is in excess. The quantities were very small, but nevertheless considerably greater, in proportion to the volume of gases taken, than those

* *Loc. cit.*

produced by the action of iron. Similar effects have been noticed by other investigators.*

Synthesis by Sparking.—It is well known that ammonia can be synthesised in small quantities with the aid of high potential electric discharges, and I have now attempted to bring the gases into a state of equilibrium during sparking, *i.e.*, into such a state that the rate of decomposition is equal to the rate of formation of the ammonia, and to reach that condition from each direction.

Mixed Gases I. The experiments were carried out in a glass bulb of about 250 c.c. capacity, provided with two tubes and stop-cocks, and with platinum wires for sparking, the sparking distance being about 25 mm

The bulb was placed in a thermostat and maintained at a temperature of 40° C., it was filled with the mixed gases, and the platinum wires connected with the terminals of an induction coil capable of giving an 8-inch spark.

After the sparking the gases were aspirated into dilute hydrochloric acid solution and nesslerised. The various results are put together in the following tables:—

Pressure.	Time of sparking. mins.	Ammonia formed. milligrammes.	Remarks.
Atmospheric	5	0·02	moist gases
„	15	0·06	„
„	15	0·02	very thin spark
„	5	0·02	gases dried
„	10	0·03	by H_2SO_4
„	15	0·06	„
„	20	0·07	„
„	30	0·10	„
„	45	0·10	„
2 atmospheres	60	0·19	„
„	30	0·19	„

From these results it will be seen that:—

(1) Under atmospheric pressure equilibrium (as before defined) was reached when 0·1 milligramme ammonia had been formed.

(2) Under a pressure of two atmospheres equilibrium was reached when 0·19 milligramme was present.

(3) The amount of ammonia formed depends on the quantity of electricity passing, thus a very thin spark produced only one-third as much ammonia as a "fat" spark in the same time.

* See Watts' Dictionary, 1st ed., **Art. "Ammonia."**

Decomposition of Ammonia by Sparking.—Attempts were made to reach the same equilibrium points by starting from the opposite end of the reaction. It was found to require long sparking before equilibrium was nearly reached. The following are the results :—

Pressure.	Time of sparking. hrs.	Ammonia remaining. milligrammes.
Atmospheric, allowed to blow off every few minutes	2·5	0·13
Atmospheric, rising to two atmos. at end	5	4·2
Two atmos., commencing with a mixture of N and H (1 : 3), and 2 per cent. NH_3	2	0·56
Two atmos., commencing with a mixture of N and H (1 : 3), and 1 per cent. NH_3	2·5	0·32

At atmospheric pressure decomposition was rapid, and the equilibrium point was very nearly reached, synthesis giving 0·10 milligramme and analysis 0·13 milligramme. When the volume was kept constant, decomposition was very slow and the point of equilibrium was approached only by starting a long distance from the beginning of the decomposition. Starting with a mixture containing 1 per cent. of ammonia, after $2\frac{1}{2}$ hours' sparking, 0·32 milligramme ammonia remained instead of 0·19 milligramme by the synthetical method.

Mixed Gases II.—In this series the length of the spark was 11 mm., and the capacity of the globe 262 c.c. At the conclusion of the experiment the gases were pumped out through dilute acid. The temperature was 39°·8 C.

Time. mins.	In primary coil. Current. ampères.	Voltage.	Ammonia. milligrammes.
15	2	4	0·08
30	2	4	0·30
15	1·5	4	0·25
30	5·5	4	0·44
45	5·5	4	0·37
22·5	5·5	4	0·41
15	2·75	2	0·07
	Decomposition of ammonia by sparking.		
68	5·5	4	0·41

From these results it is seen that—

(1) Equilibrium was reached in about 22 minutes, the gases then containing 0·41 milligramme ammonia. On sparking ammonia at atmospheric pressure exactly the same point of equilibrium was reached.

(2) More ammonia is formed than in the first series, owing to the shorter spark; also the rate of decomposition and the rate of formation are quicker.

(3) Other conditions remaining the same, the amount of ammonia formed is roughly proportional to the current strength.

(4) If the current strength remains the same, the quantity of ammonia formed is much influenced by the voltage. (It must be remembered that the electrical measurements here mentioned are those of the primary coil.)

Since writing the above, I have discovered that Berthelot carried out experiments of a somewhat similar nature. He found that, starting either with ammonia or with nitrogen and hydrogen, sparking left finally a minute quantity of ammonia which was "of the same order" in the two cases.* Using the silent discharge, he obtained the same point of equilibrium, starting from either direction, viz., a mixture containing 3 per cent. ammonia. Reference should be made also to the work of Hemptinne, who has investigated the synthesis of ammonia under various conditions.†

Summary.

(1) So far as can be shown by one of the most delicate tests known to chemists, ammonia cannot be synthesised by heat (except under special conditions specified below). The decomposition of ammonia by heat may, therefore, be regarded as an irreversible reaction.

(2) Ammonia may be synthesised in small quantities from its constituent elements (*a*) by heating with many of the metals; (*b*) by exploding with oxygen; (*c*) by sparking. These are reversible reactions.

(3) It would appear that the synthesis of ammonia is effected only when the gases are ionised; the ionisation would be brought about by sparking, or by the high temperature of an explosion of hydrogen and oxygen. The immediate decomposition of the ammonia formed would be prevented by its sudden cooling. The metals in the presence of moisture also produce "nascent" or ionised hydrogen.

(4) It does not appear that nitrides of the metals form an intermediate stage in the formation of ammonia, for it was found that metals readily forming nitrides, *e.g.*, magnesium, did not produce more ammonia than the others.

* 'Mécanique chimique,' vol. 2, p. 358, 1879.

† 'Bull. Acad. Roy. Belgique,' 1902, p. 28.

(5) There is a close analogy between ozone and ammonia with regard to their synthesis and decomposition; both are formed by sparking, and both are completely decomposed by heat.

In conclusion, I wish to express my thanks to Mr. G. A. S. Atkinson, B.Sc., and to Mr. J. H. Davies, B.Sc., for valuable assistance rendered during the earlier and later portions of the work respectively.

Determination of Vapour-pressure by Air-bubbling.

By Edgar Philip Perman and John Hughes Davies.

(Communicated by Principal E. H. Griffiths, F.R.S. Received March 8,—Read March 30, 1905.)

It was shown recently by one of us* that the vapour-pressure of water can be determined with a considerable degree of accuracy by bubbling a current of air through water in a thermostat, and estimating the amount of water evaporated by absorbing it in strong sulphuric acid.

The accuracy of the method has since been questioned,† supersaturation being specially suggested as likely to cause error. We have therefore made experiments in order to discover what error (if any) is introduced by supersaturating the air with moisture before it enters the water in the thermostat. The effect of dust in the air and of electrification have also been investigated. In each case the arrangement of the apparatus was as described in the previous paper.

Supersaturation.—Before passing into the flasks in the thermostat, which was maintained at 70°, the air was bubbled through a large wash-bottle containing water at about 85°. The wash-bottle was connected by a short rubber tube with the flasks at 70°. Otherwise the experiment was conducted as already described. The following results were obtained:—

W.	P.	T.	V.	*p.*	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0·6757	753·2	286·1	2·005	736·4	234·7
0 6706	749·3	288·1	2·005	730·2	234·8

The numbers obtained in the previous experiments were 234·2, 233·2, 234·5, 235·0, 233·5, and 233·5, while Regnault's number (corrected as described

* 'Roy. Soc. Proc.,' vol. 72, p. 72, 1903.

† 'Journ. Phys. Chem.,' vol. 8, pp. 299 and 313, 1904.