

Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $\text{KMnO}_4$ . Grams.	Weight of $\text{K}_2\text{SO}_4 \cdot 2\text{MnSO}_4$ . Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Grams.	Per cent. of $\text{KMnO}_4$ .
55°	25	9.960			3.216	16.198
	25	9.995		2.4404		16.212
	25	8.675			2.802	16.203
	17	12.090*			3.904	16.199
	17	8.481*		2.0685		16.193
	17	8.675*			2.802	16.203
Average,						16.201
65°	4	7.801		2.3531		20.028
	4	6.987			2.744	19.988
	4	9.049			3.607	19.994
	4	7.810*		2.3597		20.060
	4	6.763*		2.0382		20.010
	4	6.809*		2.0555		20.043

Average, 20.021

Temperature. Degrees.	Per cent. of $\text{KMnO}_4$ .	Parts of $\text{KMnO}_4$ to 100 parts of water.
0	2.75	2.83
9.8	4.13	4.31
19.8	5.96	6.34
24.8	7.06	7.59
29.8	8.28	9.03
34.8	9.64	10.67
40.0	11.16	12.56
45.0	12.73	14.58
50.0	14.45	16.89
55.0	16.20	19.33
65.0	20.02	25.03

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## THE NITRIDES OF ZINC, ALUMINIUM AND IRON.

BY ALFRED H. WHITE AND L. KIRSCHBRAUN.

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THE action of ammonia at high temperatures upon metals has already been investigated by Beilby and Henderson<sup>2</sup> who showed that almost all metals are profoundly modified in their physical properties upon exposure to ammonia gas at a red heat. In their experiments nitrides of approximately definite composition were formed from some metals, but in more cases the percentage of

<sup>1</sup> These determinations were prepared by Mr. Hubbard, the remainder by Mr. Boylston.

<sup>2</sup> J. Chem. Soc. 79, 1245.

nitrogen fixed was small and variable, and frequently the only evidence that there had been combination between the nitrogen and metal was obtained from the porous structure after the operation.

We have studied the action of ammonia gas upon zinc, aluminum, and iron in as nearly a quantitative manner as possible and present here the results which are new. The apparatus and methods were in general the same as those previously employed by one of us in measuring the decomposition of ammonia at high temperatures.<sup>1</sup>

*Zinc Nitride and the Action of Ammonia upon Zinc.*—We have found no record in the literature of a previous study of this reaction. When ammonia was passed over granulated zinc at a temperature of 500° or below, no evidence of appreciable fixation of nitrogen could be detected on solution of the treated metal in acid. The most favorable temperature for the absorption of nitrogen seemed to be 600°, granulated zinc at this temperature taking up 2 per cent. of nitrogen in thirty minutes. The percentage absorbed was not increased by a longer stay in the furnace. Higher temperatures caused much volatilization of zinc without fixation of nitrogen. Sheet zinc at 600° gave only a trace of nitride. When ammonia was bubbled through molten zinc, fine particles were thrown up which stuck to the walls of the test-tube and contained as high as 3.7 per cent. of nitrogen. Zinc dust fixed a larger amount of nitrogen and the resulting product contained as much as 10.6 per cent. nitrogen, with a zinc content of 86.83 per cent. Although the temperatures employed were ordinarily 200° above the melting-point of zinc, zinc placed in a combustion tube heated to this temperature in a current of ammonia did not melt but retained the form of the material as it was placed in the tube. It became brown and dust-like on the surface and as the percentage of nitrogen increased became blacker. The nitride obtained from the zinc dust and which contained 10.6 per cent. of nitrogen was a powder, mostly black but mixed with a brown material. It was found possible to remove considerable of the brown powder by washing in alcohol, the brown powder staying in suspension and being poured off with the alcohol. The black powder remaining was washed with ether and dried *in vacuo* but it was noticed that the odor of ammonia was very

<sup>1</sup> This Journal, 27, 373.

noticeable when the desiccator was opened, and the percentage of nitrogen had not been increased by the washing process.

The decomposition of the ammonia in the synthesis of this nitride at  $600^{\circ}$  was only from 1.0 to 1.5 per cent. so that it did not seem that the hydrogen would have caused any very important reversal of the reaction. The stability of the nitride when heated in an atmosphere of nitrogen was tested at different temperatures. Samples heated to  $650^{\circ}$  and  $700^{\circ}$  for an hour did not change appreciably in appearance or in percentage of nitrogen. However, sublimed zinc in the cooler parts of the tube showed that there had been decomposition, but that it had proceeded no more rapidly than the sublimation of the zinc. The following series of experiments was then undertaken.

Duration of heating.	Temp.	Loss of weight of nitride. Per cent.
20 min.	$800-840^{\circ}$	60.1
1 hr.	750	63.0
1 hr.	700	26.0
1 hr.	600	6.3

These experiments show that the decomposition of zinc nitride begins below  $600^{\circ}$ , which is the temperature at which it may best be formed by the action of ammonia upon the metal, and that therefore it will not be possible to synthesize in this way a nitride of theoretical composition. The closest approach to it will be made by offering the greatest extent of metallic surface to the action of the ammonia, and thus accelerating the reaction. The higher absorption of nitrogen when the zinc was in the form of dust agrees with this view. The instability of the nitride at relatively low temperatures also indicates that it is useless to hope to bring about any considerable formation of nitride by direct union of the elements, although from the close relationship of zinc and magnesium in the periodic system, it had been hoped that zinc like magnesium could be made to combine directly with nitrogen.

Arons<sup>1</sup> has noted a slight combination of zinc and nitrogen between the poles of an electric arc maintained between zinc electrodes in an atmosphere of nitrogen, and Rossel<sup>2</sup> has observed a similar phenomenon when zinc and calcium carbide are heated in the air, but the only record which we have found of the preparation of a

<sup>1</sup> Chem. Centr. 11, 643 (1899).

<sup>2</sup> Compt. rend. 121, 941.

nitride of definite composition is that of Frankland,<sup>1</sup> who by heating zinc amide to 200° obtained a nitride to which he gave the formula  $Zn_3N_2$ . This theoretically contains 12.52 per cent. nitrogen. The highest percentage obtained in our experiments was 10.6 per cent., but in view of the facts just noted concerning the difficulty of preparing a nitride of theoretical composition by the action of ammonia upon metallic zinc, it seems probable that the nitride obtained in our experiments should be regarded as  $Zn_3N_2 + xZn$ . Whether this diluting zinc is to be regarded as a mechanical mixture or a solid solution is a point upon which we have no evidence except the fact that it was not possible by fractional solution to isolate either a definite nitride or to dissolve the nitride and leave a residue of zinc. Apparently, the nitride and its diluting zinc dissolved together which is, so far as it goes, an indication that the nitride is dissolved in the zinc as has been shown to be the case with nitride of chromium by Baur and Voerman.<sup>2</sup> The properties of our nitride of zinc agree with those given by Frankland.

*The Action of Ammonia upon Aluminium.*—The action of dry ammonia upon metallic aluminium was studied in the same way. The most favorable temperature for the absorption of nitrogen seemed to be higher than was the case with zinc and only relatively slight amounts of nitrogen were fixed. Only a trace of nitrogen was found in aluminium dust which had been heated for an hour and three-quarters at 600° in a stream of ammonia whose decomposition was only 0.4 per cent. At 750° in an hour and a quarter 1.54 per cent. of nitrogen was fixed, the decomposition of the ammonia being 1.0 per cent. The highest percentage of combined nitrogen was obtained at a temperature of 700°. After three hours the amount of nitrogen was 1.80 per cent. The nitride is decomposed by boiling water with evolution of ammonia. The fixation of nitrogen by aluminium was so small that it was not deemed practicable to determine its temperature of initial decomposition in an atmosphere of nitrogen.

*Nitride of Iron and Action of Ammonia upon Iron.*—The formation of nitride of iron through the action of ammonia upon metallic iron has received a great deal of attention in recent years. The very interesting experiments of Baur and Voerman before alluded

<sup>1</sup> Phil. Mag. [4] 15, 149.

<sup>2</sup> Z. physik. Chem. 52, 467.

to have shown that the dissociation pressure of the nitride at the lowest temperature at which ammonia will react with iron is many atmospheres, and that therefore it will never be possible in this way to attain a nitride of theoretical composition. It would be expected from analogy with the other bivalent elements, magnesium, barium, zinc and others, that the formula for the iron nitride would be  $\text{Fe}_3\text{N}_2$ . The usually accepted formula is  $\text{Fe}_2\text{N}$ , based entirely upon the analytical results, which show as the highest amount of combined nitrogen which has been obtained a trifle less than the 11.11 per cent. required for the compound  $\text{Fe}_2\text{N}$ . Our experiments have been no more successful than those of others in synthesizing a nitride with a higher percentage of nitrogen. The best results were obtained from iron reduced by hydrogen which, from its large surface, absorbed nitrogen rapidly.

This spongy iron begins to decompose ammonia below  $400^\circ$ , and at  $412^\circ$  in spite of a rapid stream of gas flowing through the apparatus, 1.0 per cent. of the ammonia was decomposed. That nitrogen was being absorbed was shown by the fact that the gas passing the acid of the nitrometer was 87.6 per cent. hydrogen instead of the 75 per cent. obtained when  $\text{NH}_3$  is decomposed by heat alone. The next gas analysis made when the furnace temperature was  $440^\circ$ , showed that the ammonia was decomposed to the amount of 3.4 per cent. and that the nitrogen was being almost quantitatively absorbed, the gas collected containing 96.2 per cent. hydrogen. The next test was made at a temperature of  $513^\circ$  and showed that nitrogen was being given off more rapidly than it was being absorbed, the gas in the nitrometer containing only 70.2 per cent. hydrogen. The proportion of ammonia decomposed was 12.8 per cent. The furnace was then allowed to cool with the ammonia passing through it. The nitride obtained contained 8.26 per cent. nitrogen. The most successful temperature was found to be  $450\text{--}475^\circ$ , but our best preparation yielded only 10.1 per cent. nitrogen, which is a few tenths of a per cent. less than some others have obtained. Varying percentages below this could be obtained according to the conditions.

Each of the preparations was analyzed by solution in dilute acid with measurement, and in many cases analysis of the gas evolved, titration of the dissolved iron, and distillation of the ammonia. The gases were always found to be pure hydrogen

and the sum of the iron and nitrogen to be above 99 per cent. If the hydrogen evolved during solution be calculated to free iron, and the difference between this figure and 100 per cent. called nitride, and the total amount of nitrogen be figured as being contained in this nitride, it will bring the percentage of nitrogen in the nitride to 14.5 per cent. as the average of determinations on nine samples, with a maximum of 15.1 and a minimum of 14.2. The percentage of nitrogen calculated on the total weight varied in these samples from 2.25 to 10.04, so that as far as analytical results show there is no break in the series, whose members may be regarded as either a mechanical mixture or a solid solution of iron and nitride of iron. The nitride of iron mentioned above corresponds closely to  $\text{Fe}_3\text{N}_2$  containing 14.35 per cent. nitrogen. The series might then probably be considered as  $\text{Fe}_3\text{N}_2 + x\text{Fe}$ , but so far as percentage calculations go, might equally well be considered  $\text{Fe}_2\text{N} + y\text{Fe}$ .

An analogy suggests itself between the nitride of iron and the carbide of iron. It is impossible to prepare the theoretical  $\text{Fe}_3\text{C}$  by direct union of carbon and iron. The resulting compound invariably carries a lower percentage of carbon. The theoretical carbide may however be isolated from any sample of slowly cooled iron which contains carbon, and we know that all such samples of slowly cooled steels are mechanical mixtures of iron and carbide of iron. This has been shown for steel in several ways but unfortunately the methods which have proven themselves most valuable in the investigations of the reactions of carbon and iron are inapplicable in the study of the nitrides, whose spontaneous decomposition prevents the study of cooling curves, and whose physical state as brittle fine wires or powder prevents the polishing necessary for a microscopic investigation. The impossibility of getting a solid bar of iron containing a high percentage of nitrogen prevents the application of the electrolytic method by which iron is dissolved away, leaving a pure carbide. An experiment was tried with a piece of sheet iron containing about 4.0 per cent. of nitrogen but no nitride could be isolated by electrolytic solution.

Solutions of the double chlorides of copper and potassium both neutral and slightly acid have proved useful in isolating some of the constituents of steel and their effect was tried on the nitrides. A qualitative test with nitrides containing 1.0 and 2.5 per cent. of

nitrogen showed them to be quickly attacked by a neutral solution. A sample with 6.2 per cent. nitrogen was slowly attacked while one with 8.0 per cent. of nitrogen was apparently unchanged even after two weeks. A quantitative experiment with a sample containing 8.2 per cent. nitrogen made from iron reduced in hydrogen was carried out by placing 0.100 gram of the nitride in a beaker with 10 cc. of neutral 30 per cent. potassium copper chloride. No copper was deposited nor was other sign of reaction visible, and after standing for six days at room temperature the residue was removed and analyzed. It had lost only 3 mg. in weight and contained 7.9 per cent. nitrogen as compared with the original 8.2 per cent. A parallel experiment made with a solution to which hydrochloric acid had been added until it was a decinormal solution, showed more marked action. After six days the powder had lost about 37 mg. in weight and its percentage of nitrogen was 7.05. Similar experiments with other nitrides confirmed these results. Nitrides with higher percentages of nitrogen were very slowly attacked, those with smaller percentages more quickly, but the concentration of nitrogen in the undissolved residue was practically unchanged. It seems almost impossible that this fine porous nitride could contain free mechanically mixed iron which would not be dissolved by neutral or slightly acid potassium copper chloride, reagents which will disintegrate and remove completely the iron even from white cast iron. The results far rather point to the conclusion that the material is practically homogeneous and that the nitrogen is probably present as a solution of nitride of iron in iron.

#### SUMMARY.

By the action of dry ammonia gas upon zinc dust at the most favorable temperature of 600° a nitride of zinc is formed. This has a marked dissociation pressure even at its temperature of formation and hence must always have a lower percentage of nitrogen than theory requires. Preparations were obtained with varying nitrogen content, the highest being 10.6 per cent. The formula  $Zn_3N_2$  requires 12.5 per cent. nitrogen. The properties of our nitride agree with those of the  $Zn_3N_2$  which Frankland obtained by heating zinc amide and it is to be regarded as a mixture, or solid solution, having the general formula  $Zn_3N_2 + xZn$ .

When ammonia gas acts upon aluminium powder small amounts

of nitrogen up to 1.8 per cent. may be made to combine with the metal. The most favorable temperature is  $700^{\circ}$ .

The most favorable temperature for the formation of nitride of iron is  $450-475^{\circ}$ . On account of the high dissociation pressure of the nitride at this temperature the nitride formed must always contain less than the theoretical percentage of nitrogen. Preparations with 10 per cent. of nitrogen were scarcely appreciably attacked by neutral potassium copper chloride and although slowly attacked by acid solutions did not change their percentage composition. They can not therefore be mechanical mixtures of free iron and nitride and are preferably to be regarded as solid solutions, as is the case with nitride of chromium and chromium. From analogy with other bivalent elements iron should form the nitride  $\text{Fe}_3\text{N}_2$  and the preparations may be represented by the formula  $\text{Fe}_3\text{N}_2 + x\text{Fe}$ .

UNIVERSITY OF MICHIGAN,  
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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 100.]

## THE ELECTROLYTIC PRECIPITATION OF GOLD WITH THE USE OF A ROTATING ANODE.<sup>1</sup>

BY JAMES RENWICK WITHROW.

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THE electrolytes used in this investigation were solutions of auric chloride in the presence of (1) potassium cyanide and (2) sodium sulphide. The rate of precipitation of the metal was especially studied. The results show that pure potassium cyanide is evidently a better electrolyte than sodium sulphide for this particular purpose.

The apparatus used in the experiments was similar to that described by Ingham.<sup>2</sup> The first series of experiments with the cyanide electrolyte was made under conditions prescribed by Exner.<sup>3</sup> They were as follows:

<sup>1</sup> From the author's thesis for the Ph.D. degree.

<sup>2</sup> This Journal, 26, 1269.

<sup>3</sup> Ibid. 26, 1256.