L.—*Electrolysis of the Nitrogen Hydrides and of Hydroxylamine.*

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THE present communication forms part of a comprehensive research I have undertaken in order to examine the behaviour of nitrogen compounds under the influence of the electric current, and therefore only a short account of the experimental facts will be given, leaving general considerations to a future occasion.

The electrolyses of ammonia, hydrazine, azoimide, hydroxylamine, and their salts were carried out at different current densities, tem-

peratures, and concentrations, and the conditions were determined under which, by electrolytic decomposition, ammonia, hydrazine, or azoimide yields its two components in the proportion contained in the molecule.

The experiments were carried out in an apparatus which admitted of the gases liberated at the two electrodes being collected and measured separately. An adjustable resistance ampèremeter, a copper and a gas voltmeter were in the circuit, and a voltmeter in shunt.

Ammonia.

Solutions of ammonia and its mixtures with sodium chloride were electrolysed by Losanitsch and Jovitschitsch (*Ber.*, 1896, **29**, 2436), who found that secondary reactions almost invariably take place, the nitrogen liberated at the anode being less than that required by the proportion $N_2 : 3H_2$. An exceptional case occurs when the mixture $9NaCl : NH_3$ is electrolysed at 100° ; the gases are then liberated in the proportion $N_2 : 3H_2$, and no secondary products are formed.

My experiments (Table I.) show that if sufficiently high current densities are employed, ammonium hydroxide, either alone or mixed with sodium chloride, on electrolysis even at the ordinary temperature, yields its two component elements in the proportion contained in the molecule, unaccompanied by secondary reactions; only traces of nitrites and nitrates could be detected in the electrolysed liquid.

TABLE I.

Exp.	Solution.	D_a .	D_c .	c.c. at 0° and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	20 per cent. ammonia...	352.1	352.1	5.6	16.9	20.1°
2	" "	246.5	246.5	10.2	30.8	22.2
3	" "	153.6	153.6	11.7	35.5	21.7
4	" "	156.8	156.8	9.7	29.2	98.9
5	10 per cent. ammonia, 20 per cent. NaCl	301.8	301.8	4.7	14.2	21.5
6	" "	260.1	260.1	6.6	20.1	22.4
7	" "	211.8	211.8	8.1	24.5	22.2
8	" "	148.7	148.7	11.4	34.4	21.7
9	" "	147.1	147.1	7.8	23.5	99.3

In the columns D_a and D_c respectively, the current densities on the anode and cathode are given, the numbers being calculated in ampères per square decimetre of electrode surface.

Hydrazine.

Solutions of the base in water, containing the hydrazine hydrate, are very bad conductors of electricity.

TABLE II.

Exp.	Solution.	D_a .	D_c .	c.c. at 0° and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	50 per cent. of hydrazine	20.2	20.2	3.7	7.4	22.2°
2	" "	50.6	50.6	4.4	8.8	21.7
3	" "	117.7	117.7	4.7	9.4	23.8
4	" "	20.7	20.7	9.2	18.4	99.3
5	" "	52.1	52.1	6.1	12.2	99.6
6	" "	110.2	110.2	4.3	8.6	99.1
7	25 per cent. of hydrazine	21.7	21.7	6.7	13.4	22.2
8	" "	48.8	48.8	6.6	13.2	23.4
9	" "	120.1	120.1	5.3	10.6	25.1
10	" "	119.2	119.2	8.1	16.2	98.7
11	12 per cent. of hydrazine	19.3	19.3	12.2	24.4	22.1
12	" "	56.4	56.4	7.3	14.6	22.4
13	" "	118.1	118.1	6.1	12.2	25.3
14	" "	116.2	116.1	5.4	10.8	99.2

From this table, it can be seen that the hydrazine is resolved by the electric current into $N_2:2H_2$, and that this proportion remains unchanged, however much the experimental conditions are varied. The reaction may be explained by assuming that the hydrazine hydrate is ionised by the current, the two hydroxyls being carried to the anode, forming 1 molecule of water and evolving 1 atom of oxygen, which oxidises the hydrazine to water, nitrogen being liberated. On the cathode, the free base reacts with 2 mols. of water, the hydrate being reformed and hydrogen liberated.

The sulphate and chloride of hydrazine were also electrolysed; the results are given in Table III (p. 606).

When collected and examined, the gases were found to be pure nitrogen at the anode, and pure hydrogen at the cathode. No secondary products were detected in the electrolysed liquid. The chlorine liberated on the anode reacts with the hydrazine, forming hydrochloric acid with liberation of nitrogen. An analogous reaction takes place when hydrazine sulphate is electrolysed; it is remarkable that no trace of the oxidation products of nitrogen could be detected in the liquid.

TABLE III.

Exp.	Solution.	$D_a = D_c$.	c.c. at 0° and 760 mm.		Temp.
			Nitrogen.	Hydrogen.	
1	25 per cent. ehloride.....	25·1	2·2	4·4	22·1°
2	" " 	30·0	3·1	6·3	98·6
3	" " 	116·4	3·4	6·8	22·3
4	" " 	150·6	2·7	5·5	98·9
5	10 per cent. chloride.....	30·6	3·9	7·8	21·5
6	" " 	122·3	2·7	5·4	22·3
7	3 per cent. sulphate	22·1	2·3	4·6	21·4
8	" " 	156·7	3·1	6·2	21·7
9	About 35 per cent. sulphate	20·3	5·3	10·6	99
10	" " 	164·1	7·2	14·4	99

Azoimide.

Before proceeding to a description of the experiments with azoimide, some details may be given concerning the preparation of this compound in considerable quantities, as this has always been considered a rather difficult and dangerous operation.

With the exception of that of Wislicenus, the methods of different authors were found to give very poor yields; Wislicenus' method, if a suitable apparatus is employed, allows of the preparation of azoimide on a large scale with comparative ease.

The apparatus I used was a circular, thick-walled cast iron vessel with a straight iron outlet tube screwed in the shoulder at an angle of about 45°. The mouth of the vessel was closed by an iron plug which screwed down closely on an inner ledge, giving a gas-tight joint. An iron leading tube was fitted through the plug reaching nearly to the bottom of the vessel. The wall of the vessel was drilled with a vertical tube to carry a thermometer. The dimensions of the apparatus were such that 50 grams of sodium could be worked with in one operation. This amount was converted into the amide at a temperature of 360—390°. The amide was then converted into sodium azoimide by passing nitrous oxide over the fused product. For this part of the process the most favourable temperature was found to be from 190—220°. A yield of as much as 56 per cent. of the theoretical amount was obtained, this being about 6 per cent. higher than that recorded by Wislicenus. It was surprising to find cyanide in the product, the only possible explanation being that the cast iron contained carbon which, at about 400°, in presence of sodium, reacted with the ammonia, forming sodium cyanide. The best way

to eliminate this impurity is to precipitate the crude sodium azoimide with alcohol, the sodium cyanide remaining in solution.

In the following table, the results of the electrolysis of the acid and its sodium salt are formulated :

TABLE IV.

Exp.	Solution.	D_a .	D_c .	c.c. at 0° and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	20 per cent. azoimide...	270	270	33.1	11.1	15°
2	" "	150	150	22.3	7.5	"
3	" "	112	112	25.2	8.5	"
4	" "	85	85	27.4	9.2	"
5	32.5 per cent. sodium salt	281.2	140.6	70.35	23.6	20
6	" "	162.5	81.2	86.40	29.4	"
7	" "	162.5	81.2	85.8	29.4	"
8	" "	119	59.5	88.8	30.45	"
9	" "	56.2	112.5	77.2	25.6	"
10	" "	462.5	231.2	78.2	26.2	"
11	40 per cent. sodium salt	250	125	39.3	13.21	10—12
12	" "	438	219	40.0	13.4	8—9
13	" "	182	91	39.6	13.35	10—12
14	" "	188	94	38.8	13.1	13—14
15	" "	115.6	51.8	39.18	13.2	6—10
16	20 per cent. sodium salt	112.5	56.2	39.21	13.3	10
17	" "	112.5	56.2	39.4	13.3	10
18	" "	250	125	39.18	13.21	10—15
19	32 per cent. sodium salt	100	100	48.2	16.2	24
20	" "	165.6	165.6	39.6	13.1	24
21	" "	168.7	168.7	21.4	7.3	24
22	" "	259.4	259.4	31.2	10.6	30
23	" "	275	275	84.9	28.3	40

Slight traces of ammonia, but no oxidation products of nitrogen, were found in the electrolysed liquid. In some of the experiments, the ratio of hydrogen to nitrogen was found to be less than that required by the expression $H_2 : 3N_2$. The deficiency of nitrogen seemed to indicate that some condensation of this element to a polymericide of the type N_3 or N_6 had taken place on the anode during the electrolysis. In order to test this possibility, density determinations of the gas evolved under two sets of conditions were made, but in each case the values obtained proved it to be pure nitrogen.

As an extension of these experiments, it is my intention to electrolyse mixtures of azoimide with its salts at very high current densities and low temperatures, thereby hoping to effect a condensation of nitrogen in a process which is analogous to that in which percarbonates and persulphates are produced.

Hydroxylamine.

I have made several attempts to electrolyse the base, but failed owing to the difficulty of preventing the spontaneous transformation of hydroxylamine into ammonia.

Solutions of the sulphate of this base were electrolysed under varying conditions ; the results show that secondary reactions always take place, the base being reduced on the cathode to ammonia and oxidised at the anode to oxygen compounds of nitrogen. Under certain conditions, the whole of the hydrogen is absorbed in the reaction.

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