

ART. XXXVI.—*On Methylamine*; by M. CAREY LEA.(1.) *Production and Separation of Methylamine.*

IN a previous paper I have pointed out that ammonias in which hydrogen is replaced by methyl are obtained by the action of nitrate of methyl upon ammonia at ordinary temperatures.* Nitrate of methyl, obtained by the distillation of methylic alcohol with nitric acid and urea, is placed in well stoppered bottles filled only about one quarter, together with a little more than its own bulk of thoroughly saturated aqueous ammonia, and is left till the nitrate of methyl disappears, or until only a few brown oily drops remain, a reaction which requires from three to six days, according to the temperature. The liquid is then distilled with caustic alkali and the gaseous products are conducted into water.

In this solution we should by analogy expect to find ammo-

* This Journal, March, 1862.

nia, methylamine, dimethylamine and trimethylamine, and it remains to separate these bases. This is a matter of extraordinary difficulty, much surpassing that of the separation of the ethyl bases. In the ethyl series the bases differ from each other and from ammonia by C_2H_5 , whereas in the methyl series the successive terms acquire the addition of C_2H_5 only. Naturally therefore we must look for greater similarity in character and corresponding difficulty in separation. Accordingly, the methods which give such satisfactory results with the ethyl-ammonias, fail entirely with the methyl bases. Ammonia cannot be separated from them by a difference in the solubility of the sulphates in alcohol: when the mixed solution is neutralized with sulphuric acid and exhausted with alcohol, little or nothing is removed by it. Nor can the separation be effected by means of picric acid, although that substance may be used in one particular case mentioned below.

This problem I have as yet been able to resolve only in part. Two steps I have accomplished:—first, the complete removal of the ammonia from the mixed methyl bases, and second, the isolation of the methylamine in a state of purity. The separation of the more substituted bases still remains to be accomplished.

It is however, satisfactory to have a process for obtaining perfectly pure methylamine without resorting to the troublesome reaction of the cyanate of methyl, and that much has been effected. After the compound ether has been completely decomposed by the ammonia, the contents of the bottles are to be distilled with caustic alkali or lime. The solution of the mixed bases and of ammonia is to be exactly neutralized with oxalic acid and the water driven off as far as possible by being heated over the water-bath. The resulting mass is transferred to a flask, and boiled a few minutes with a large quantity of alcohol of density 42° B., and after cooling and standing some hours, it is filtered. The whole of the ammonia remains as oxalate upon the filter. The filtrate by spontaneous or gentle evaporation separates into two layers. The lower, which is much the least in quantity, becomes very soon crystalline, indeed this change takes place so rapidly that the fluid stage may easily pass unnoticed. More oxalate of methylamine remains in the mother liquid and separates on further evaporation.

After the fluid has crystallized, the resulting pearly white laminae are purified by boiling with absolute alcohol, or with a mixture of equal parts of alcohol of 42° B. and ether, and this is repeated three or four times, allowing a thorough cooling to take place between each operation. The oxalate of methylamine finally crystallizes out quite pure, and methylamine may be obtained from it directly by distillation with caustic alkali. But the distillation is extremely unpleasant, exhibiting the phenomenon of percussive ebullition to such a degree as to endanger the whole

apparatus, and to drive the liquid out of the Woulfe's bottle in strong jets through the safety tube. It is therefore advisable to treat the oxalate with nitrate of baryta or chlorid of barium, leaving them in contact for a day, to evaporate the filtrate and then distill. I give the preference to the nitrate of baryta, because the nitrates of the ammonias distill more quietly than any of the others of these salts.

The methylamine thus obtained was converted into chloroplatinate and analyzed.*

1.0105 grms. gave of Pt,	-	-	-	·4216
This corresponds to, per cent,	-	-	-	41.72
Theory requires for C_2H_3	}			
H				
H				
H				
		NCl, PtCl ₂ ,	-	41.62

The residue after the greater part of the oxalate of methylamine had crystallized out, was evaporated, exhausted with absolute alcohol, treated with nitrate of baryta, distilled with caustic soda and neutralized with picric acid. From this solution there crystallized out beautiful amber-colored bevelled prisms and hexagonal plates greatly resembling the picrate of ethylamine and apparently isomorphous with it. These were converted into chloroplatinate and analyzed with the following result.

·7265 grms. chloroplatinate gave of Pt,	-	·3025
This corresponds to, per cent,	-	41.65
Chloroplatinate of methylamine contains,	-	41.62

The substance was therefore picrate of methylamine.

The residue appeared to be a mixture. Analyses of different portions, from different crystallizations gave respectively 39.85, 40.14, and 40.23 per cent of platinum in the chloroplatinate, nor could any satisfactory means of separation be found.

Reactions of Methylamine.

Many of the reactions of methylamine have been already described by its discoverer, M. Wurtz. To these may be added the following.

Cerium, protochlorid,	A white precipitate insoluble in an excess of the precipitant.
" nitrate of proto-peroxyd,	Dirty white, insoluble in excess of precipitant.

* It is scarcely necessary to observe that if platinum salts are recrystallized, the results of their analysis cannot be taken as a proof of the accuracy of the mode of separation used. In the analyses here published care was taken to use in all cases an excess of bichlorid of platinum, and to include the whole precipitate in the analysis.

Zirconium, sulphate of zirconia,	White, insoluble in excess.
Aluminium, alum,	A white precipitate which redissolves in an excess of the precipitant.
Antimony, terchlorid,	A red brown precipitate insoluble in excess of precipitant.
Glucinum, sulphate of glucina,	A white precipitate insoluble in excess of precipitant.
Molybdenum, protochlorid,	No precipitate.
“ bichlorid,	Reddish precipitate insoluble in excess of precipitant.
Palladium, protochlorid,	Abundant flesh-colored precipitate, insoluble in excess of precipitant.
Ruthenium, sesquichlorid,	Brown precipitate, insoluble in excess of precipitant.
Platinum, protochlorid,	No precipitate.

In describing the reactions of diethylamine I pointed out* that the remarkable property of dissolving alumina, hitherto considered as characteristic of ethylamine, amongst the ammonias, was shared by diethylamine. It now appears that it is possessed also by methylamine, and it would not be surprising if it was found to extend to the other methyl and ethyl bases, and even to the bases containing other alcohol radicals, a point which I propose hereafter to examine.

The deportment of methylamine towards solutions of protochlorid of molybdenum is characteristic, and differs from that of ammonia, ethylamine and diethylamine.

Methylamino-chlorid of Palladium.

When aqueous methylamine is added in excess to solution of protochlorid of palladium, or to a solution of the following salt, at the first moment no precipitation takes place, but in a few moments a quantity of flesh-colored needles are formed. These were dried over sulphuric acid and ignited.

·2049 substance gave metallic palladium ·0969.

From which we find:—

		Calculated.	Found.
2C,	12	9·32	
5H,	5	3·88	
N,	14	10·88	
Pd,	53·3	41·38	42·45
Cl,	35·5	27·56	
HO,	9	6·98	
	128·8	100·00	

leading to the formula $C_2H_5N^{\wedge}PdCl + HO$.

* This Journal, Jan., 1862.

The palladium is a little in excess because with the small quantity of material at command, it was impossible to wash out the not entirely insoluble precipitate thoroughly, without too great a loss.

Chloro-palladite of Methylamine.

When methylamine is added, not in excess, to an acid solution of protochlorid of palladium, or when the foregoing salt is treated with an excess of the same acid solution, a deep brown red liquid is obtained, which by concentration yields beautiful brown red laminæ, very soluble in water and in alcohol. The quantity at command was insufficient for analysis, but judging from analogy, their constitution must be



Picrate of Methylamine.

This is a very beautiful salt. It crystallizes in bright yellow laminæ grouped in fine arborescent clusters, or by somewhat slower crystallization, in amber-colored bevelled prisms and hexagonal plates. Heated on platinum foil it deepens in color, melts to a clear red liquid apparently without decomposition, and when the heat is further raised, burns with a vivid white light leaving a carbonaceous residue. It is moderately soluble in water and in alcohol.

Other combinations of methylamine will be described at a future time.