

and the two divisions have a tendency to rotate in opposite directions. The character of these two forms of electrical discharge can always be determined by the magnet.

The author concludes his paper in the following words :—"I refrain for the present from any observations as to the action of the magnet on the discharge. The intimate relation of magnetic and electric action has long since been shown ; but the curious effect of the power of a magnet to draw out the stratifications from the positive terminal, and in some instances its powerful action on that portion of the discharge which exhibits the phosphorescent light in its greatest intensity, are worthy of further examination. In the preceding experiments my object was directed to the examination of the stratified and of the dark band discharge ; at present I am inclined to the opinion that the stratifications in the positive, and the dark band between it and the negative glow, although apparently similar, are effects arising from distinct causes—the former from pulsations or impulses of a force acting in a highly attenuated but resisting medium, the latter from interference. I am at this time engaged in making further experiments for the elucidation of this novel and remarkable phenomenon."

March 11, 1858.

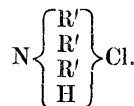
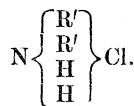
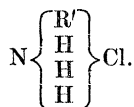
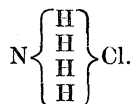
Dr. HOOKER, Vice-President, in the Chair.

The following communications were read :—

- I. Notes of Researches on the Poly-Ammonias. By AUG. W. HOFMANN, Ph.D., F.R.S. &c. Received February 4, 1858.

Former investigations had led me to some general conclusions regarding the molecular constitution of the organic bases, which I have communicated to the Royal Society, and which have been published in the 'Philosophical Transactions' (1850, p. 93 ; 1851, p. 357). My experiments had proved that each equivalent of hydrogen in

ammonium may be replaced by an equivalent of a mono-atomic electro-positive radical, such as methyl, ethyl, &c. ;—a series of compound ammoniums being produced, the salts of which may be thus formulated :—



R' representing a mono-atomic electro-positive radical.

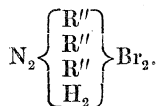
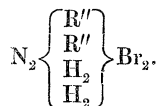
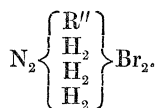
These successive substitutions were accomplished by the action of ammonia upon the bromides and iodides of the alcohol-radicals, which since that time have become most valuable agents of substitution in the hands of chemists.

All the bases produced by this process being derived from 1 equiv. of ammonium, contain 1 equiv. of nitrogen ; they differ in this respect essentially from the majority of the alkaloids extracted from plants, and more particularly so from those which, like quinine, morphine, strychnine, &c., specially claim our interest. By far the greater number of the vegetable alkaloids contain 2 equivs. of nitrogen. In some vegetable and animal bases we find even 3 and 4 equivs. of nitrogen. The molecular construction of these bodies is still obscure, but it is extremely probable that they are derived from 2, 3 or 4 ammonia equivs., in which the hydrogen is more or less replaced by poly-atomic molecules, and that the stability of such complicated

structures essentially depends upon the substituting capacity of their replacing molecules.

It was long my intention to extend my researches to the poly-ammonium bases. But my attention has been specially called to the subject by the beautiful results obtained of late, especially in France, by the study of the poly-acid alcohols, by the experiments of M. Berthelot, and more particularly by the classical researches of M. Wurtz, which enable us to take a general view of this subject.

Taking as a point of departure the neutral compounds which are formed by the action of ammonia upon bibasic and tribasic acids, the *diamides* and *triamides*, derived respectively from 2 or 3 eqivs. of ammonia, it became extremely probable that the action of ammonia upon poly-acid alcohols would give rise to poly-ammonium bases. In the conception of this analogy there appeared but little doubt that ammonia, under the influence of the bromides and iodides of bi-acid alcohols, would furnish a series of bi-ammonium bases, exactly as treatment of ammonia with the analogous compounds of mono-acid alcohols has given rise to the formation of the mon-ammonium bases above referred to. In other words, it was to be expected that a compound ether $R'' Br_2$ or $R'' I_2$ (R'' representing a bi-atomic electro-positive radical) would act upon two equivalents of ammonia, producing a series of salts expressed by the following formulæ :—



In endeavouring experimentally to verify this idea, it became necessary

to examine what had hitherto been done in this direction. Science possesses already some very interesting observations on the ammonia derivatives of bi-acid alcohols. About five years ago, soon after the publication of my experiments upon the action of ammonia upon bromide and iodide of ethyl, M. Cloëz* obtained a series of bases, on submitting ammonia to the action of the brominetted Dutch liquid ($C_4H_4Br_2$). Two of these bodies he described under the name of formylia and acetylia, whilst a third body subsequently obtained is designated by the term propylia†.

To these three bodies M. Cloëz attributes the following formulæ :—

Formylia	C_2H_3N
Acetylia	C_4H_5N
Propylia	C_6H_7N

At a later period M. Natanson has studied the action of ammonia on the chlorinetted Dutch liquid ($C_4H_4Cl_2$). This reaction produces analogous results, but the number of bases is smaller, the chief product being a chloride, which contains a base either identical or isomeric with the acetylia of M. Cloëz.

When carefully considering the results obtained by M. Cloëz, it appeared to me probable that the bases which he describes, are in fact the di-ammonium compounds for which I was searching. The constitution assigned by M. Cloëz to his substances is not very probable. It is difficult to understand how the action of ammonia upon a compound like the Dutch liquid can produce simultaneously three bodies belonging to three different homologous families, the formyl-, acetyl-, and propyl-series. Our doubts are, however, increased if we examine into the physical characters of these bodies, especially if we consider their high boiling temperatures, and the differences between the boiling-points of the three bases :—

Formylia . . .	C_2H_3N	123°	} difference 47.
Acetylia . . .	C_4H_5N	170°	
Propylia . . .	C_6H_7N	210°	} difference 40.

Methylamin, C_2H_5N , which contains only 2 equivalents of hydrogen more than formylia, is at the common temperature a gas, and

* Instit. 1853, 213.

† Cahours, Leçons de Chimie Générale, t. ii. p. 654.

liquefies only considerably below the freezing-point of water. Again, the differences of the boiling-points of substances, related in the way that the formulæ of M. Cloëz suppose, do not often exceed 20° , and very rarely rise to 40° and 47° .

All these difficulties disappear by submitting the formulæ of M. Cloëz to a slight alteration, and by regarding formylia, acetylia and propylia as the di-ammonium bases of the same series, of the ethylene series. If we adopt this view, the three bodies are derived from 2 of ammonia, in which 2, 4 or 6 equivalents of hydrogen are replaced respectively by 1, 2 or 3 equivalents of the bi-atomic molecule ethylene; and the formylia, acetylia and propylia of M. Cloëz present themselves as monethylene-diamine, diethylene-diamine and triethylene-diamine.

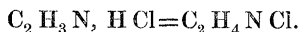
I have endeavoured experimentally to solve this question. The analysis of acetylia, which is remarkable for the definite character of its salts, appeared to promise an answer to it.

When repeating the beautiful experiments of M. Cloëz, I had occasion to confirm all the indications given by this able chemist, regarding the formation of the bases derived from bibromide of ethylene. The analysis, however, furnished a discrepant result.

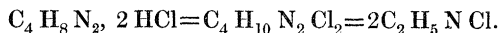
M. Cloëz represents formylia by the formula



when the hydrochlorate becomes



When considered as a di-ammonium compound, this salt has the composition



The two formulæ only differ by one equivalent of hydrogen.

The analysis of a magnificently crystallized hydrochlorate has furnished me the following results:—

	Formula of M. Cloëz— $\text{C}_2 \text{H}_4 \text{N Cl}.$		New formula— $\text{C}_4 \text{H}_{10} \text{N}_2 \text{Cl}_2.$		Mean of analysis.
Carbon . . .	18·32	18·04	17·87
Hydrogen..	6·10	7·51	7·55
Chlorine ..	54·19	53·38	53·17

On preparing the free base by the action of hydrate of potassa

upon the hydrochlorate, I was surprised to find that this body retains hydrogen and oxygen in the proportion in which they exist in water, which cannot be separated by prolonged contact with, or by repeated distillation over, anhydrous baryta.

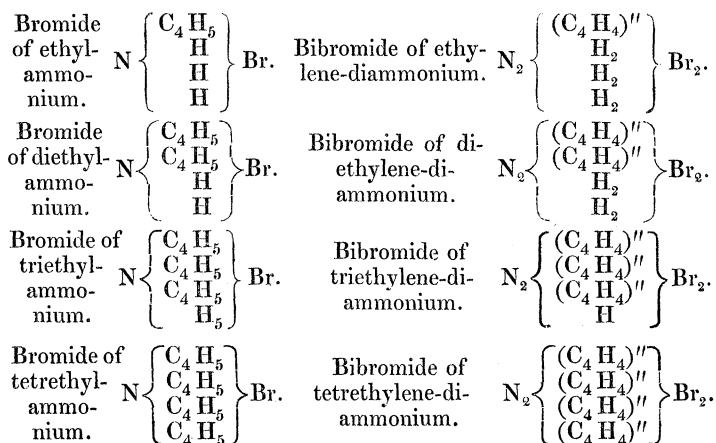
The analysis of the free base has given the following result:—

	Formula of M. Cloëz— $C_2 H_4 N O.$		New formula— $C_4 H_{10} N_2 O_2.$		Analysis. Mean.
Carbon . . .	31·58	30·76	30·67
Hydrogen..	10·52	12·82	12·97
Nitrogen ..	36·84	35·90	36·32

These numbers appear to me in favour of the formula which I propose for formylia; there remains but little doubt that acetylia and propylia are analogously constituted.

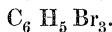
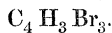
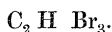
There remains yet to find the last term of the series, the tetrethylene-diammonium compound. Up to the present moment I have only established by experiment that the three lower bases are powerfully attacked by bibromide of ethylene, a non-volatile compound being produced possessing properties in every respect analogous to the character of tetramethyl- and tetrethylammonium.

If further experiments confirm the hypothesis which I have advanced, the action of ammonia on bi-bromide of ethylene would give rise to four compounds analogous to the bases which I have obtained by the action of bromide of ethyl.

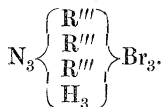
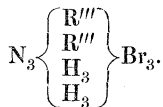
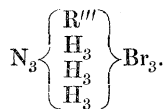


The conception of diammonium-compounds has suggested to me

the idea to extend my observations also to the triacid-alcohols, and to submit ammonia to the action of the bodies



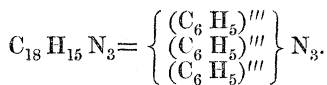
Analogy suggested the formation in this reaction of a series of triammonium-bases, the salt of which might be thus formulated:—



I have not yet succeeded in realizing these compounds by treating under several conditions ammonia by the above chlorides and bromides of triacid-alcohols. The processes which I have as yet tried have led to other transformations. A different result is, however, obtained by replacing the ammonia in these processes by amidogen-bases. In this reaction, and especially with aniline and chloroform, a series of beautifully crystallized alkaloids is formed, the study of which engages at present my attention.

In conclusion, I may remark that several of the known basic compounds appear to belong to the triammonium-type.

The cyanethine of Kolbe and Frankland may be viewed as such a compound—



This substance appears to me to be derived from 3 equivs. of ammonia, in which 3 equivs. of hydrogen are replaced by 3 equivs. of the tri-atomic radical which chemists assume in glycerin-alcohol.