

side, the visible effect is a drying up and clearing of the air, with a rising barometer and falling thermometer; while on the equatorial side, overpowering quantities of warm moist air—rushing from comparatively inexhaustible tropical supplies—push towards the north-east as long as their impetus lasts (however originated), and are successively chilled, dried, and intermingled with the always resisting, though *at first* recoiling, polar current. After such struggles these two currents unite in a *varying* intermediate state and *direction*, one or other prevailing gradually.

Very plain and practical conclusions are deducible from these considerations :—

One, and the most important, is that in a gale which seems likely to be near the central part of a storm, that should be (of course) avoided by a ship which has sea room : a seaman, facing the wind, knows that the centre is on his *right* hand in the northern hemisphere, on his *left* in the southern; he therefore is informed *how to steer*.

Another valuable result is that telegraphic communication can give notice of a storm's approach, to places then some hundred miles distant, and *not otherwise forewarned*.

The Society adjourned to January 12, 1860.

January 12, 1860.

Sir BENJAMIN C. BRODIE, Bart., President, in the Chair.

The Right Hon. Edward Lord Stanley was admitted into the Society.

The following communications were read :—

- I. "Notes of Researches on the Poly-Ammonias."—No. VII.
On the Diatomic Ammonias. By A. W. HOFMANN, LL.D.,
F.R.S. Received December 14, 1859.

In continuing my inquiries into the nature of the organic bases, I was led in the commencement of the year 1858 to repeat some experiments on the action of dibromide of ethylene upon ammonia,

which M. Cloëz* had published in 1853. The repetition of these experiments compelled me to contest not only the formulæ of M. Cloëz, but also the general interpretation which he had given to his results.

I have not hesitated to communicate my conclusions to the Royal Society†.

M. Cloëz‡ shortly afterwards discussed my observations, and pointed out the arguments which induced him to maintain his formulæ and his interpretations.

I have not replied to these remarks. M. Cloëz having stated in the same note that he was still engaged with his experiments and that his inquiry was nearly completed, I discontinued my experiments on the action of dibromide of ethylene upon ammonia, fully persuaded that the chemist, to whom we are indebted for the first observation of this reaction, in continuing his experiments would arrive at the same results which I had myself obtained.

In discontinuing the discussion with M. Cloëz, I was not freed from the obligation of proving the general thesis of my note, viz. the formation of diatomic bases by the action of diatomic bromides on ammonia. I have given the proof in several communications§ addressed during the last two years to the Royal Society, and especially in a note|| describing some new derivatives of phenylamine and ethylamine published during last summer. The formation of these bodies, their analysis and their transformations, have, I believe, settled the question at issue in a satisfactory manner.

These researches have been the subject of some remarks on the part of M. Cloëz¶, from which it appears that this chemist has interpreted my silence as a tacit admission of defeat; he rejects the formulæ which I have given for the diatomic derivatives of phenylamine and ethylamine, and blames me for having continued my researches on the diatomic bases without having previously replied to his observations.

Under these circumstances I have been compelled to resume the investigation of the action of dibromide of ethylene upon ammonia, and to reply, after nearly two years have elapsed without M. Cloëz's paper having been published, to the series of objections which this chemist has raised against the theory of the diatomic bases.

* L'Institut, 1853, p. 213.

† Proceedings, vol. ix. p. 150.

‡ Comptes Rendus, xlv. p. 255.

§ Proceedings, vol. ix. pp. 277, 287, 651.

|| Proceedings, vol. x. p. 104.

¶ L'Institut, 1859, p. 233.

Since this continuation of my experiments throws considerable light upon this new class of compounds, I beg leave to submit them to the judgment of the Royal Society.

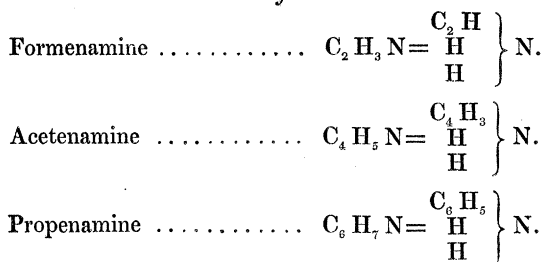
In order to render more intelligible the line of argument which M. Cloëz has brought forward against the diatomic notions, it will be useful to recapitulate in two words the subject of our controversy.

M. Cloëz admits that in the action of dibromide of ethylene upon ammonia, the molecule of ethylene splits into radicals belonging to three distinct groups, viz. the formic, acetic, and propionic series; these radicals acting upon *one* molecule of ammonia, in which each of them replaces one equivalent of hydrogen, give rise to the formation of three *primary monamines*, viz. Formenamine, Acetenamine, and Propenamine.

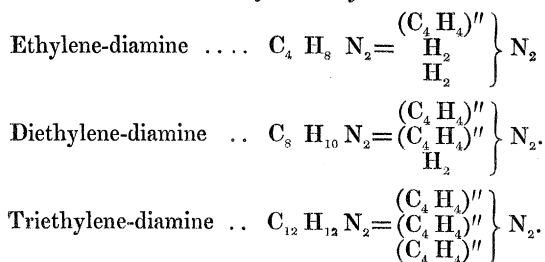
According to the view which I defend, the molecule of ethylene remains intact in the reaction, acting upon *two* molecules of ammonia in which 2, 4, or 6 equivalents of hydrogen are replaced respectively by 1, 2, or 3 diatomic molecules of ethylene; the dibromide of ethylene gives rise to the formation of three diamines belonging to the same family, a primary, a secondary, and a tertiary diamine.

Expressed in formulæ the two views may thus be represented:—

Formulæ of M. Cloëz.

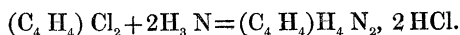


Formulæ of Dr. Hofmann.

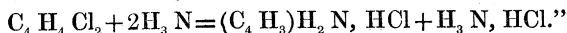


It was by careful examination of the physical properties of the bases under consideration, and more especially by the absence of simple equations capable of explaining the formation of the first and of the third terms of the series, that I had first been led to doubt the correctness of M. Cloëz's formulæ; but I would not have expressed this doubt, if, on repeating the analysis of the first base, of formenamine, the slightest doubt on the subject had remained in my mind. I did not at the time investigate the two other bases, and I limited myself to stating that the constitution of these bodies would probably be found analogous to that which I had experimentally established for the first term of the series.

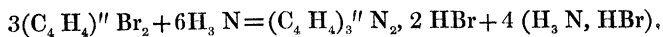
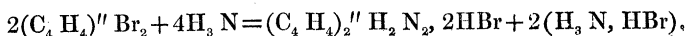
Let us now examine the objections which M. Cloëz has brought forward against my argument. "*According to the hypothesis of M. Hofmann,*" says he, "*the action of ammonia on the chlorinated and brominated hydrocarbons cannot give rise to the formation of chloride or bromide of ammonium; the reaction consists simply in a combination of the two substances, without the separation of a third compound: it is a case of symmorphosis or addition,*



Experiment proves, however, that the reaction involves the elimination of hydrochloric acid and the fixation of the elements of amidogen: apomorphosis and symmorphosis are accomplished side by side, as indicated by the following equation:—



M. Cloëz would be perfectly right if during the reaction no other base were formed except the first one. But he forgets altogether that in the process under examination—exactly as in the mutual reaction between bromide of ethyl and ammonia—several other bases of more advanced substitution are produced. The equations which I give for the formation of these bodies likewise involve the elimination of bromide of ammonium, and in fact of considerable quantities of this compound.



The bromide of ammonium then, which separates in considerable quantity in the action of dibromide of ethylene upon ammonia, be-

longs to the second and third portions of the reaction ; it has nothing whatever to do with the formation of the first base. M. Cloëz, as I have pointed out, does not admit the simple equation which I have given for the formation of this body ; he denies that it is simply formed by the union of the two compounds reacting upon each other. According to his opinion it is produced in a secondary reaction, occasioned by the intervention of heat. My experiments do not confirm this opinion. A mixture of dibromide of ethylene and alcoholic ammonia allowed to stand for some time at the ordinary temperature, deposited a quantity of crystals, from which I was enabled to extract, without distillation, simply by successive crystallizations, absolutely pure salt of ethylene-diamine, as proved by the analysis of the bromide, the chloride, and the platinum-salt.

In discussing the numbers which I have obtained in analysing the hydrate and the hydrochlorate of the first base, M. Cloëz quotes the results on which he founds his own formula. A glance at these figures will show unmistakably that they agree much better with my formula than with the one which he defends. The following are the analytical details of our analyses, together with the theoretical values required by each formula :—

	Formula of M. Cloëz.	Analysis of M. Cloëz.	Formula of Dr. Hofmann.	Analysis of Dr. Hofmann.
Carbon . . .	31·58	31·12	30·76	30·67
Hydrogen . .	10·52	12·77	12·82	12·97

Every experimentalist has incontestably the first right of interpreting his analytical results ; knowing, as he does, his methods, he will do it generally much better than any other person. In the case before us, however, I believe very few chemists would have interpreted the results of analysis as M. Cloëz has done. As far as I am concerned, I would always prefer to admit having lost 0·2 per cent. of hydrogen, to calculating a formula requiring 2·25 per cent. of hydrogen less than had been obtained by experiment. I would prefer this especially in analysing a substance like ethylene-diamine, attracting carbonic acid with the utmost avidity—a trace of which would very appreciably lower the experimental hydrogen—and containing so high a percentage of hydrogen, that the presence even of a small quantity of water would produce a somewhat similar effect.

The results which M. Cloëz has obtained in the analysis of the hydrochlorate are not less in favour of my views. He finds 1·28 per cent. of hydrogen more than required by his formula, whilst admitting my theory, he would not have lost more than 0·13 per cent.

I have since examined several other salts of ethylene-diamine, and the results fully confirm the conclusions drawn from my former analyses. It would be useless to quote these additional experiments, but I will mention the characteristic numbers furnished by the analysis of the anhydrous base, since the diminution of the equivalent exhibits in a more striking manner the differences between the theoretical values of the two formulæ. Ethylene-diamine retains the water with the greatest energy, and it is in fact only by protracted contact with metallic sodium that it is possible to obtain this body in the anhydrous condition. I give the numbers obtained by combustion, side by side with the theoretical values of the two formulæ :

	Formula of M. Cloëz, C_2H_3N .	Formula of Dr. Hofmann, $C_4H_8N_2$.	Analysis.
Carbon	41·37	40·00	40·13
Hydrogen	10·34	13·33	13·31

These numbers require no commentary.

It is not, however, in the results of analysis that M. Cloëz finds the chief support of his views ; he quotes an observation which at the first glance appears fatal to the diatomic notions.

“ *But there is,*” continues M. Cloëz, “ *a capital fact (un fait capital) which completely settles the question at issue : this is the vapour-density of the free base.*”

This density has been found by experiment to be 1·42.

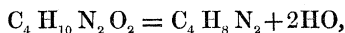
“ *The theoretical density calculated for my formula, referred to 4 volumes, is 1·315 ; the modified formula of M. Hofmann, likewise referred to 4 volumes, gives the theoretical density of 2·699.*

“ *These results appear to me decisive, and I do not hesitate to maintain the formula of the new series of bases, of which I first pointed out the formation.*”

I entirely agree with M. Cloëz as to the importance of the determination of the vapour-densities, but I certainly arrive at a very different interpretation of his result.

In repeating the experiment of this able chemist, I have arrived, as might have been expected, at exactly the same number. But this number refers to the *hydrated base*, and it is easily seen that the hydrated molecule, when in the state of vapour, must occupy 8 volumes. In calculating the theoretical density corresponding to the diatomic formula when referred to 8 volumes, we arrive at the number 1.35, which coincides in fact with the number obtained by experiment.

It is obvious that under the influence of heat the hydrated base splits into anhydrous base (4 volumes) and water (4 volumes),



and that, instead of taking the vapour-density of the intact hydrated molecule, M. Cloëz has determined the density of a mixture of anhydrous base and water, which on cooling combined again, reproducing the hydrated compound. And here I must recall the observations of several chemists, especially those of M. Bineau, of M. Kekulé, and of M. H. Saint-Claire Deville, each of whom has had the opportunity of explaining the anomalous vapour-densities in the transitory decomposition of the compounds submitted to experiment; and I would quote particularly a note by Professor Kopp*, in which this distinguished physicist has treated the question of anomalous vapour-densities in a general manner.

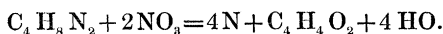
In the case before us, there is a very simple experiment, calculated to remove all hypothesis from the above explanation,—the determination of the vapour-density of the *anhydrous base*.

The experiment made with a substance the purity of which had previously been proved by analysis, led to the number 2.00, which indeed absolutely coincides with the theoretical density of the diatomic formula $\text{C}_4 \text{H}_8 \text{N}_2$ referred to 4 volumes. This theoretical density is 2.07, whilst the formula of M. Cloëz, likewise referred to 4 volumes, requires the theoretical density of 1.00.

The molecule of *ethylene-diamine* (formenamine) then, like those of all other well-examined organic compounds, corresponds to 4 volumes of vapour; and the vapour-density of the base, far from militating against the molecular value which I assign to this body, furnishes on the contrary an additional and incontestable argument in its favour.

* Ann. de Chem. et de Pharm. cv. 390.

The preceding remarks are, I hope, sufficient to establish the formulæ of the diatomic ammonias upon a solid basis. I will therefore only briefly allude to some results which I have obtained in studying the products of decomposition of ethylene-diamine, and which are not less characteristic. Submitted to the action of nitrous acid, this base is decomposed with evolution of nitrogen; in the first stage of the reaction an indifferent crystalline body is produced, and the final result of the process is a large quantity of pure oxalic acid. The nitrogen evolved during the transformation is accompanied by a very volatile liquid, the odour of which is somewhat similar to that of aldehyde. At the time when I made these experiments I really believed the liquid to be aldehyde, but since I failed in obtaining the crystalline compound with ammonia and in transforming it into acetic acid, I abstained from mentioning this reaction in my note to the Royal Society. I have now scarcely a doubt that the volatile liquid was the oxide of ethylene, isomeric with aldehyde, since discovered by M. Wurtz. The transformation would be



In preparing the ethylene-diamine for my experiments, I obtained as a secondary product a small quantity of the second base, which M. Cloëz has described as acetenamine, and for which I now propose the term diethylene-diamine. This base has exactly the same percentage composition, whether viewed as a diamine or considered as the monatomic acetenamine of M. Cloëz. The analysis of the base itself, and of some of its salts, fully confirms the results obtained by that chemist. But this base is no primary monamine; it does not contain the radical acetyl, $\text{C}_4 \text{H}_9$, as supposed by M. Cloëz; it is a secondary diamine containing two molecules of ethylene. Acetenamine, as conceived by M. Cloëz, should be formed by the action of chloride, bromide, and iodide of vinyl ($\text{C}_4 \text{H}_3 \text{Cl}$, $\text{C}_4 \text{H}_3 \text{Br}$, $\text{C}_4 \text{H}_3 \text{I}$) upon ammonia. These reactions do not furnish a trace of the base in question. But there is a more conclusive proof of the diatomic nature of this body, the evidence of which will not be contested by M. Cloëz,—this is the determination of the vapour-density. Experiment gave the number 2·7. The diatomic formula, $\text{C}_8 \text{H}_{10} \text{N}_2$, referred to 4 volumes of vapour, requires 2·9. According to the monatomic view, a vapour-density of 1·45 should have been found.

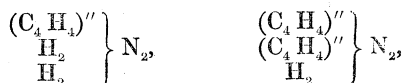
The preceding experiments, although fixing in a satisfactory manner the composition and the equivalents of the two diammonias, do not unveil their molecular constitution—their degree of substitution.

I have endeavoured to solve this problem by submitting them to the action of iodide of ethyl, a process which I have first used for similar purposes, and which has since become of general application. This process, moreover, could not fail to furnish a final decision between the two theories.

In considering with M. Cloëz the two bases as primary monamines belonging respectively to the formic and to the acetic groups,



it is evident that each of them must be capable of absorbing successively 1, 2, or 3 equivalents of ethyl, and of yielding *three* ethylated bases, two volatile, and one fixed. On the contrary, if the bases were products of the successive substitution of the same molecule for the hydrogen of two equivalents of ammonia, if they were respectively a primary and a secondary diamine,



the first of the two must likewise give rise to the formation of *three* bases, whilst the second one would produce only *two*.

Experiment has verified this latter anticipation. In submitting ethylene-diamine to the alternate action of iodide of ethyl and oxide of silver, I have succeeded in obtaining two volatile ethylated bases, and a third one, which is fixed. These compounds are well defined; their composition was established by the analysis of their iodides or their platinum-salts. Represented as salts, these bases contain—

Salt of ethylene-diammonium $[(\text{C}_4\text{H}_4)'' \quad \text{H}_6\text{N}_2]'' \text{I}_2.$

Salt of diethylated ethylene-diammonium. . $[(\text{C}_4\text{H}_4)'' (\text{C}_4\text{H}_5)_2\text{H}_4\text{N}_2]'' \text{I}_2.$

Salt of tetrethylated ethylene-diammonium $[(\text{C}_4\text{H}_4)'' (\text{C}_4\text{H}_5)_4\text{H}_2\text{N}_2]'' \text{I}_2.$

Salt of hexethylated ethylene-diammonium $[(\text{C}_4\text{H}_4)'' (\text{C}_4\text{H}_5)_6\text{N}_2]'' \text{I}_2.$

On repeating the same experiments with diethylene-diamine, perfectly analogous phenomena were observed, but the reaction yielded only one volatile base, which was immediately converted into a fixed base. Analysed in a similar manner, and represented as salts, these bases exhibit the following composition :—

Salt of diethylene-diammonium $[(C_4 H_4)''_2 H_4 N_2]'' I_2$.

Salt of diethylated diethylene-diammonium $[(C_4 H_4)''_2 (C_4 H_5)_2 H_2 N_2]'' I_2$.

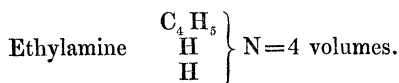
Salt of tetrethylated diethylene-diammonium $[(C_4 H_4)''_2 (C_4 H_5)_4 N_2]'' I_2$.

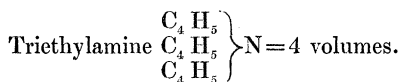
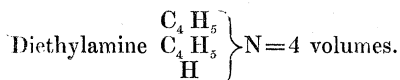
The same result is accomplished, but in a shorter and more elegant manner, by substituting iodide of methyl for its ethylated homologue. Already, at an earlier period, I have shown that iodide of methyl has a remarkable tendency to yield the last product of substitution. Thus, on treating iodide of methyl with ammonia, the iodide of tetramethylammonium is alone obtained, together with a very large proportion of iodide of ammonium. The action of iodide of methyl with the ethylenated bases is perfectly analogous. The last product of substitution is formed at once in notable quantity, and may be purified by a simple crystallization. I have obtained in this manner, without being embarrassed by the intermediate compounds, the iodide of hexmethylated ethylene-diammonium and of tetramethylated diethylene-diammonium.

These results require no further explanation.

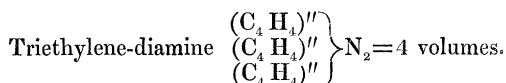
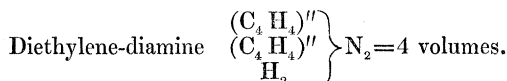
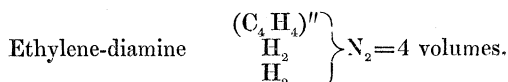
In the present state of science we rely upon a certain number of considerations which guide us in the construction of a chemical formula. These are,—the study of the origin of a body ; analysis ; observation of the physical properties, and especially of the boiling-point ; the determination of the vapour-density ; and lastly, the examination of its metamorphoses. I have endeavoured to look at the question under discussion from these several points of view ; experiment has given invariably the same reply.

It follows from this controversy that the diatomic alcohols imitate the monatomic alcohols in their deportment with ammonia. Ethyl alcohol produces, as is well known, three ethylated ammonias, the molecules of which occupy 4 volumes of vapour.





In a similar manner we find that glycol, the diatomic alcohol of ethylene, the discovery of which we owe to the remarkable labours of M. Wurtz, gives rise to three diatomic bases, corresponding to 2 molecules of ammonia, and representing likewise 4 volumes of vapour.



The two first terms of this series are the bases which M. Cloëz discovered about six years ago, but the true nature of which he failed to recognize. To complete the series, it remains only to examine the third volatile base and the oxide of tetrethylene-diammonium.

The observations which I have the honour of submitting to the Royal Society coincide in every point with the first note upon this subject which I presented nearly two years ago. I have simply carried out somewhat more in detail the sketch traced in my former communication.

In conclusion I may state a fact which has also been observed by M. Cloëz, viz. that the action of dibromide of ethylene upon ammonia gives rise to the formation of bases not directly belonging to the series which we have discussed. In searching for the method of purifying the ethylene bases, I have been obliged to examine also the terms of the other group; but since these substances do not necessarily belong to this part of the inquiry, I omit for the present to enter more fully into their examination.