

pendulum-apparatus, to construct a portable instrument by means of which a large number of observations can be made upon a few square inches of paper. They reserve the description of their instrument for a future occasion.

IV. "Notes of Researches on the Poly-Ammonias.—No. XXI.
On Paraniline." By A. W. HOFMANN, LL.D., F.R.S.
Received December 2, 1862.

In a short paper submitted to the Royal Society about a year ago *, I called attention to some of the by-products which are obtained in the manufacture of aniline upon a large scale, and more especially to toluylene-diamine, the primary diamine of the toluyl-series.

MM. Collin and Coblenz, aniline manufacturers at Labriche, near St. Denis, Paris, to whose kindness I had been indebted for the material used in these researches, immediately after their publication transmitted to me with the utmost liberality a large quantity of basic oils boiling at temperatures higher than the boiling-point of aniline, which are separated from the pure aniline by rectification, and are known in the language of the laboratory as *queues d'aniline*. The investigation of this complex mixture has been interrupted by numerous engagements arising from the International Exhibition; and it was only within the last two months that I was enabled to resume the inquiry.

This inquiry is far from being finished; but some of the results already obtained are sufficiently definite for publication.

Submitted to distillation, the *queues d'aniline* begin to boil at about 182°, considerable quantities of pure aniline passing over; the temperature gradually rises without any indication of a fixed boiling-point, until it becomes necessary to remove the thermometer; in fact the last bases are volatilized only at temperatures not very far short of a red heat. By collecting separately what distils between 200° and 220°, and again what comes over between 270° and 290°, basic oils are obtained from which, by appropriate treatment, very considerable quantities, respectively, of toluylamine (toluidine) and toluylene-diamine may be separated. The former of these bases more

* Proceedings, vol. xi. p. 518.

especially is obtained in so large a quantity from this source, that M. Eugen Sell, a young chemist working in my laboratory, was enabled to engage in a more minute investigation of this substance.

The bases which accompany the monamine and diamine of the toluyl-series being liquids, their separation is by no means easily accomplished. Theory suggests that this mixture consists chiefly of the higher homologues of the toluyl-bases. These substances being far more easily prepared from their pure hydrocarbons*, I have for the present refrained from entering very minutely into the examination of these oils. The following remarks are therefore exclusively devoted to the fraction of the bases which boils at the highest temperature.

On collecting separately what comes over above 330°, a brown, viscid, scarcely mobile liquid is obtained, which at the first glance appears to present scarcely sufficient interest for a more minute examination. This liquid proved to be a mixture of several compounds. Treated with dilute sulphuric acid it solidified into a semisolid crystalline mass, which by filtration separated into a crystalline sulphate almost insoluble in water, and a sulphate easily soluble, the base of which forms the subject of this communication.

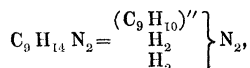
Decomposed by means of caustic soda, this sulphate yielded a viscid basic oil, which after some days solidified into a semisolid crystalline mass. This was purified from adhering oil by pressure between folds of bibulous paper, and crystallized first from water, and subsequently once or twice from boiling alcohol. Long white silky needles were thus obtained easily soluble in alcohol and ether, difficultly soluble in water, fusible at 192°, and boiling beyond the range of the mercurial thermometer, but distilling without decomposition.

When submitted to combustion, this substance was found to contain



and thus to have exactly the same composition as aniline, from which

* I may mention in passing, that dinitrocumol, $\text{C}_9 \text{H}_{10} (\text{NO}_2)_2$ obtained by submitting cumol to the action of a mixture of nitric and sulphuric acids, when distilled with iron and acetic acid, yields cumylene-diamine, a beautiful crystalline base,



fusible at 47°, the composition of which was determined by the analysis of the base itself and of the platinum-salt.

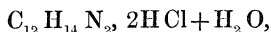
it differs in all its properties. I propose for this new compound the name of *paraniline*.

Paraniline forms a series of splendidly crystallized salts, the study of which proved that the above expression must be doubled, and that the true molecular value of this compound is represented by the formula

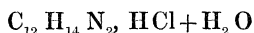


The molecule of paraniline is capable of fixing either one or two equivalents of acid. The salts with one equivalent of acid are most readily obtained; they are of a light yellow colour, and their solution exhibits in an unusual degree the phenomenon of green fluorescence.

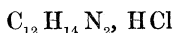
From a solution in concentrated hydrochloric acid a beautiful hydrochlorate crystallizes in transparent yellow six-sided plates, containing at 100°



which on treatment with water are immediately converted into yellow needles sparingly soluble in water, more soluble in alcohol, insoluble in ether, containing

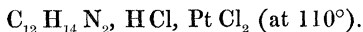


at 100° , and



at 115° .

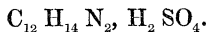
The *platinum-salt* crystallizes in yellow difficultly soluble needles,



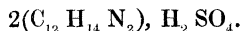
I have analysed only one *nitrate*, which crystallizes in short, yellowish, starlike-grouped needles, containing



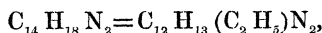
but two *sulphates*. One of them is readily obtained by dissolving paraniline in dilute sulphuric acid, when spherical aggregates of small needles are separated, easily soluble in water, less soluble in alcohol, which have the composition



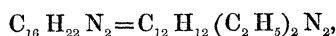
Digested in aqueous solution for some time with an excess of paraniline, the sulphate just described assimilates a second equivalent of the base, a salt being formed very similar to the previous one, but containing after crystallization from alcohol



What is the constitution of this diamine? For the decision of this question I must wait till MM. Collin and Coblenz have kindly supplied me with a fresh quantity of their *queues d'aniline*. As yet I have only ascertained that iodide of ethyl gives rise to the formation of two ethylated bases, viz.,

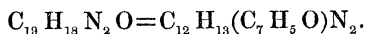


the composition of which I have fixed by the analysis of the chloride, iodide, and platinum-salt, and



of which I have only examined the platinum-salt. The saline solutions of the ethylated bases are likewise remarkable for their fluorescent properties.

Chloride of benzoyl furnishes with paraniline small needles, insoluble in water but soluble in alcohol, of the formula



Paraniline, it cannot be doubted, is the product of the action of heat upon aniline; and its formation suggests the existence of a series of similar bodies, similarly related to the other ammonias, which the progress of science cannot fail to reveal.

Experiments made in search of these bodies have hitherto been rewarded only by partial success. Nevertheless I have already succeeded in converting several ammonias into higher bases, and I intend to pursue the direction of research which is indicated by these results.

V. "Additional Observations on the Proximate Principles of the Lichens." By JOHN STENHOUSE, LL.D., F.R.S. (See p. 263.)

VI. "Letter to Professor STOKES, Sec.R.S., containing Observations made at Malta on a Planetary Nebula." By WILLIAM LASSELL, F.R.S. (See p. 269.)

PLATE

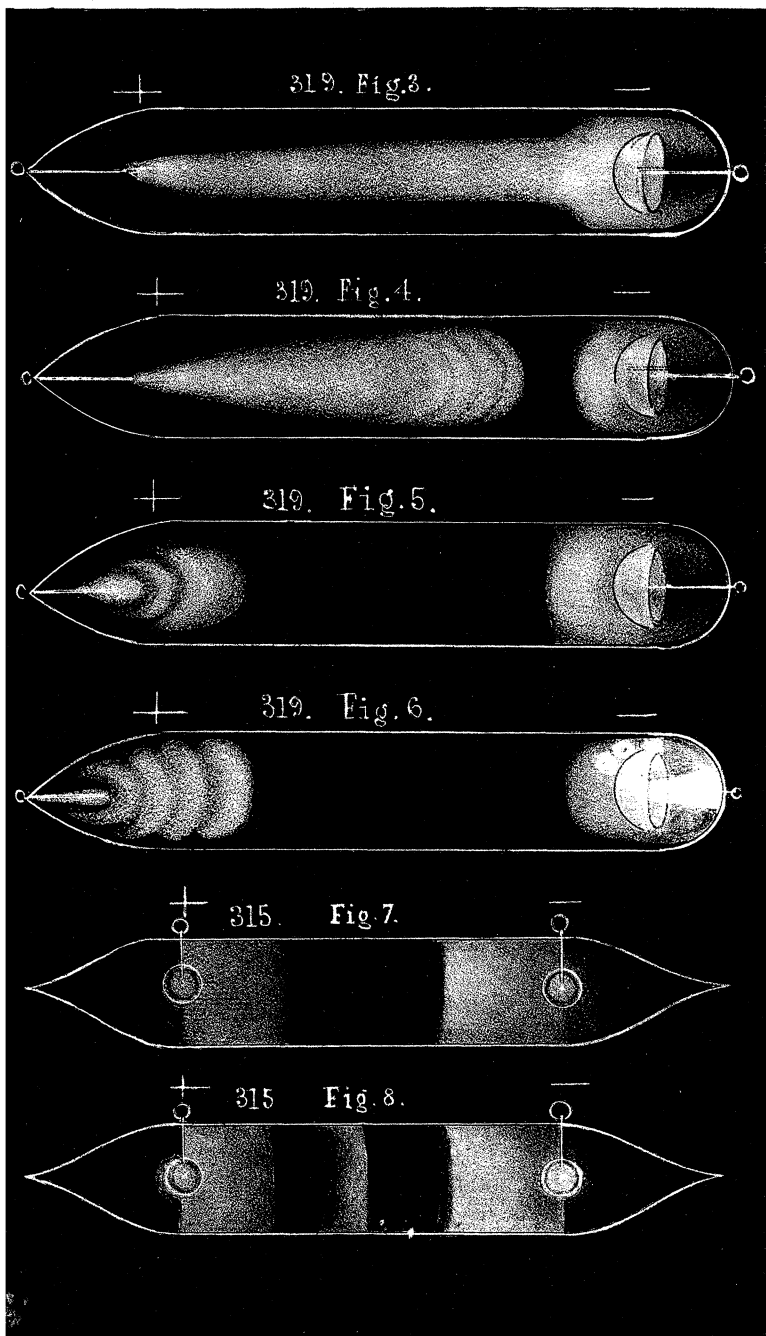
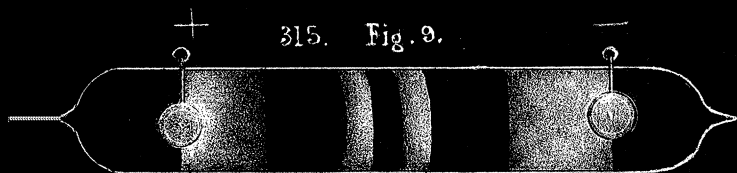
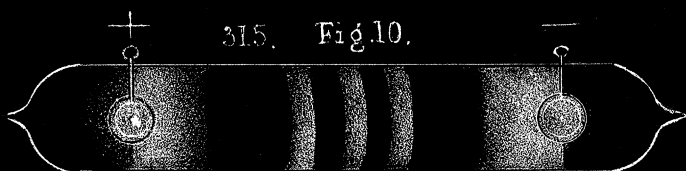


PLATE II

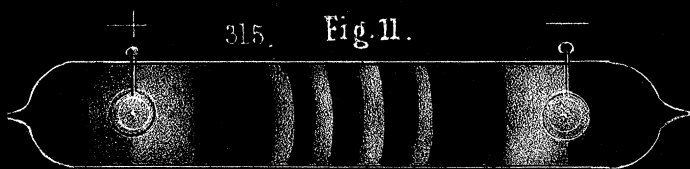
315. Fig. 9.



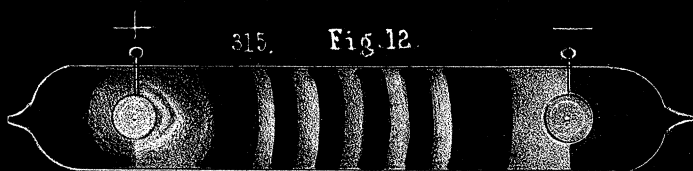
315. Fig. 10.



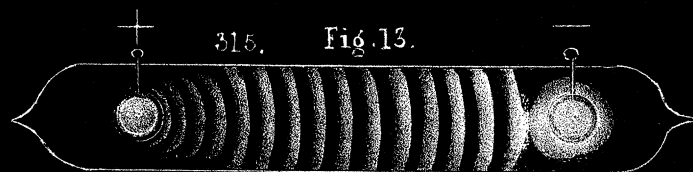
315. Fig. 11.



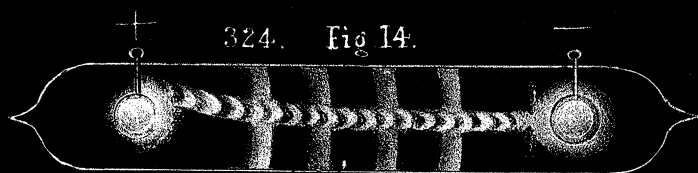
315. Fig. 12.



315. Fig. 13.



324. Fig. 14.





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Fig. 7.

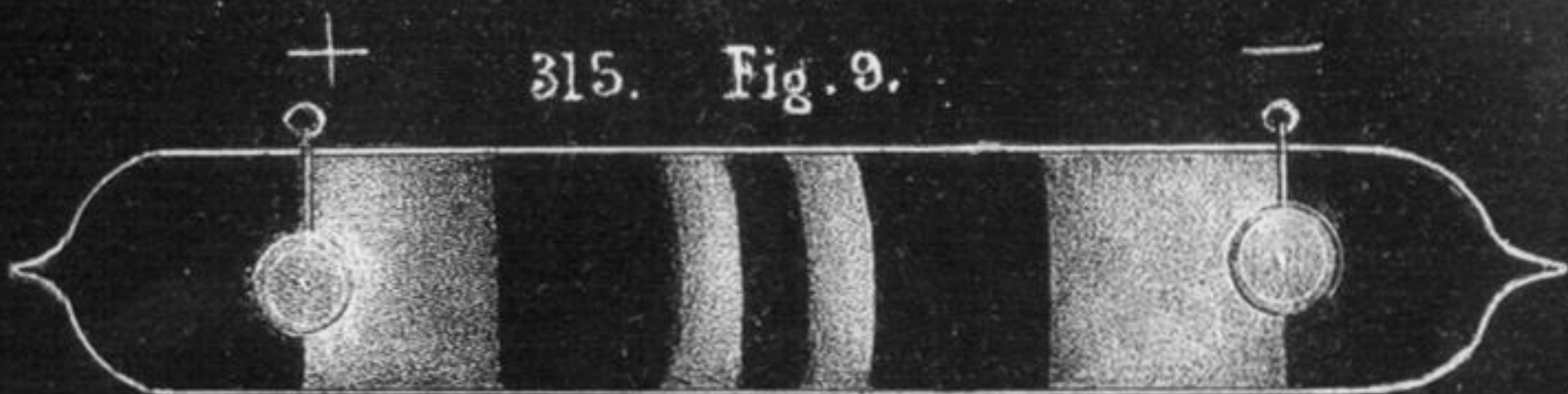


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Fig. 8.



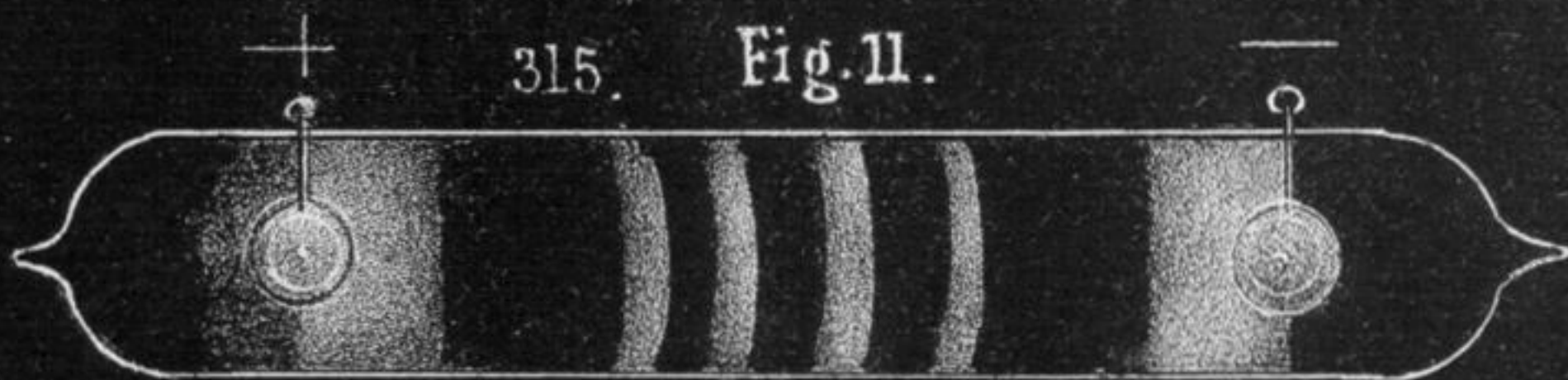
315. Fig. 9.



315. Fig. 10.



315. Fig. 11.



315. Fig. 12.



315. Fig. 13.

