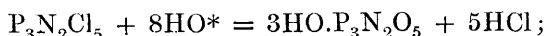


XXVII.—On Chlorophosphuret of Nitrogen, and its Products of Decomposition.

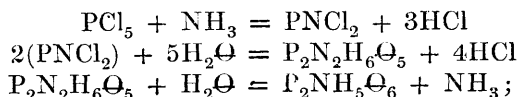
By J. H. GLADSTONE, Ph. D., F.R.S., and J. D. HOLMES, Esq.

UNDER this same title, two papers were communicated by one of us to the Chemical Society in 1850, and were published in vol. iii. of the Quarterly Journal, pp. 135 and 353. The general result was to confirm the formula $P_3N_2Cl_5$ assigned to chlorophosphuret of nitrogen by its discoverers, Wöhler and Liebig, to describe the substance more fully, and especially to show that, under the influence of aqueous ether, alkalies, and even of water, it was capable of giving rise to two new acids, named respectively *deutazophosphoric* and *azophosphoric* acids. The first was believed to be produced by the simple decomposition :



but neither the acid nor its salts could be obtained in a state to give trustworthy analyses. The second—azophosphoric acid—is produced from a solution of a deutazophosphate by heating it with different metallic salts, when a precipitate containing the new acid falls. The most remarkable of these is a ferric salt, insoluble in dilute acids, and soluble in ammonia; but several others were prepared, described, and analysed, and the common formula found for them was $3MO.P_2NO_5$, combined with from two to five equivalents of water.

But these formulæ were soon challenged. Laurent, in the *Comptes Rendus* for Sept. 9, 1850, considers that chlorophosphuret of nitrogen must have the formula $PNCl_2$, and the two acids derived from it must be respectively $P_2N_2H_6O_5$ and $P_2NH_5O_6$, according to the following schemes of decomposition :



and he views these acids as amidated acids, giving them correspond-

* In this paper we have been obliged to employ both the systems of notation, therefore when the equivalent of oxygen is 16, we have distinguished it by the bar frequently used for that purpose.

ing names, while their discoverer regarded them as $3\text{HO} \cdot \text{PO}_5$ conjugated with PN and 2PN .

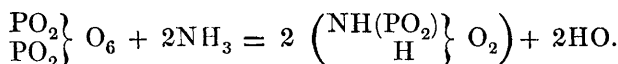
The opposite views of their composition are therefore as follows, giving only empirical formulæ:

GLADSTONE.		LAURENT.	
Chlorophosphuret of nitrogen	$\text{P}_3\text{N}_2\text{Cl}_5$	PNCl_2	Chlorophosphuret of nitrogen
Deutazophosphoric acid	$\text{P}_3\text{N}_2\text{H}_3\text{O}_8$	$\text{P}_2\text{N}_2\text{H}_6\text{O}_5$	Pyrophosphodiamic acid
Azophosphoric acid	$\text{P}_2\text{NH}_3\text{O}_8$	$\text{P}_2\text{NH}_3\text{O}_6$	Pyrophosphamic acid

Laurent did not examine the substances himself, and the results of the analysis published in the Quarterly Journal, were almost as compatible with the one view as with the other; but the following considerations led the original discoverer of the acids to retain confidence in his own formulæ:—It was hardly conceivable that the chlorophosphuret of nitrogen was produced by so simple a reaction as that given in Laurent's equation; for in that case the whole of the pentachloride would have suffered that transformation; or if some other reaction had been set up, the amount of chlorophosphuret would have varied with different conditions, whereas the proportion actually found is very small, and apparently very uniform. Again, in the conversion of deutazophosphoric into azophosphoric acid, on the first theory, only two-thirds of the phosphorus should be found in the new precipitate, while, on the supposition of Laurent, the whole should be found there; but in a recorded experiment the proportion so found was just two-thirds.

Yet the subject was evidently one that deserved re-examination, and Dr. Gladstone always intended to revert to it at some time or other; but the difficulty of preparing a quantity of the substances, and of analysing them when prepared, caused him to defer this in favour of more promising lines of research.

In the mean time Schiff,* examining the action of ammonia on anhydrous phosphoric acid, found the principal product to be an acid, which he considered to be identical with deutazophosphoric acid; but he gave it a third name—phosphamic acid, and expressed the reaction thus:—



* Ann. Ch. Pharm., ciii, 168.

He prepared and analysed the salts of barium, calcium, iron, and nickel, and described some others, giving them the general formula PNHMO_4 , sometimes with 2HO .

In relating the experiments we have recently made on this subject, we shall give first the synthetical, and afterwards the analytical results :—

SYNTHETICAL RESULTS.

Chlorophosphuret of Nitrogen.—Our first attempt was to discover some more productive method of preparing chlorophosphuret of nitrogen than those hitherto known, viz., saturating pentachloride of phosphorus with ammoniacal gas, or heating it with chloride of ammonium. In this we were unsuccessful, though we found one reaction by which its preparation is rather more easily effected. If “white precipitate” ($\text{NHg}_2\text{H}_2\text{Cl}$) be intimately mixed with the pentachloride of phosphorus in a flask, and gently heated, a brisk action ensues, and chlorophosphuret of nitrogen is formed, mixed with chlorophosphamide, chloride of mercury, and chloride of ammonium. When treated with water, the two latter substances dissolve, and from the residue when dry the chlorophosphuret may be extracted by means of ether, chloroform, or bisulphide of carbon.

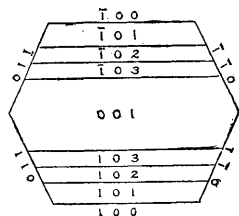
We are enabled to add to the description of the physical properties of this body previously given, the following account of its crystalline form and optical properties, kindly furnished by Prof. W. H. Miller, of Cambridge.

“Prismatic : $101, 001 = 61^\circ 38'$; $110, 100 = 66^\circ 14'$.

Observed forms : $001, 100, 103, 102, 101, 401, 110, 210$.

Angles :

401,	$\bar{4}01$	$164^\circ 38'$
101,	$\bar{1}01$	$123^\circ 16'$
102,	$\bar{1}02$	$85^\circ 36'$
103,	$\bar{1}03$	$63^\circ 22'$
110,	$\bar{1}10$	$47^\circ 32'$
210,	$\bar{2}10$	$82^\circ 44'$
001,	401	$82^\circ 19'$
001,	101	$61^\circ 38'$
001,	102	$42^\circ 48'$
001,	103	$31^\circ 41'$



001,	110	90° 0'
001,	210	90° 0'
001,	100	90° 0'
100,	401	7° 41'
100,	101	28° 22'
100,	102	47° 12'
100,	103	58° 19'
100,	110	66° 14'
100,	210	48° 38'

"An appearance resembling cleavage parallel to the face 0 0 1, was observed in one crystal ; but as no cleavage could be detected in the other crystals examined, it was probably due to the existence of a plane of union.

"Approximate values of the optical constants were obtained by observing the apparent angle between the optic axes, as seen through two opposite faces of the form 110; the minimum deviations of the brightest part of the solar spectrum ; and the planes of polarization of the refracted rays through the faces 1 0 0, $\bar{1}$ 1 0, and through the faces 0 0 1, 1 0 0, the crystal being immersed in oil. It appears from these observations that, for a ray in the plane 0 0 1, and polarized in that plane, the index of refraction is between 1·616 and 1·617; that of the two rays in the plane 0 1 0, the more refrangible is polarised in that plane, and its index is between 1·633 and 1·634; and that the optic axes lie in the plane 0 0 1, making with one another an angle of 23° 20', which is bisected by the line 0 1 0. Hence of the two rays in the plane 1 0 0, the less refrangible is polarised in that plane, and its index is a little less than 1·616."

We have determined the specific gravity of the chlorophosphuret of nitrogen to be 1·98. Yet small crystals or a film of the melted substance will float on water, doubtless from its inability to be wetted.

The specific refractive energy of this compound, *i.e.*, the refractive index minus unity, divided by the density, will be ·316, a number approximating to that calculated from the specific refractive energies of its constituents, *viz.*, ·332, taking that of phosphorus at ·58, of nitrogen at ·238, and of chlorine at ·242.

Deutazophosphoric Acid.—We have been more successful in obtaining this acid in considerable quantity ; chlorophosphuret of nitrogen when decomposed by an alcoholic solution of an alkali,

yields its full amount of the acid, mixed with an alkaline chloride. By two other methods it is more easily prepared in abundance.

The first is that discovered by Schiff, by the action of ammonia on anhydrous phosphoric acid. The white salt thus obtained, when dissolved in water, yields a neutral or slightly acid solution. This solution contains abundance of deutazophosphoric acid; as is shown by the formation of the very characteristic ferric azophosphate, when it is boiled with an iron salt, and by its agreement in every respect with the known properties of deutazophosphoric acid, as obtained from chlorophosphuret of nitrogen; but we could not obtain it free from metaphosphoric and possibly other acids.

The second process is by the action of dry ammonia on oxychloride of phosphorus, taking care that the temperature does not rise to any great extent. The action should be stopped as soon as the oxychloride is converted into a solid white substance. This substance, first observed by Wurtz, is perfectly soluble in water, the solution containing hydrochloric and deutazophosphoric acids partly as ammonium-salts. If this solution be exactly neutralized with ammonia, it produces precipitates of deutazophosphates with several metallic salts.

Azophosphoric Acid.—This acid is prepared from any solution containing free deutazophosphoric acid by simply heating it, but in this process the decomposition is apt to go too far, and phosphate of ammonium may be the only result. The preferable method is to prepare some azophosphate, which is insoluble in dilute acids, such as the ferric or copper salt, by simply heating an alkaline deutazophosphate with some acid solution of the metal. In this way azophosphoric acid may be obtained from chlorophosphuret of nitrogen, anhydrous phosphoric acid, or oxychloride of phosphorus.

ANALYTICAL RESULTS.

In approaching the question of the true composition of these bodies, it seemed desirable to repeat the crucial experiment, which appeared to show that, in the conversion of a deutazophosphate into an azophosphate, only two-thirds of the phosphorus was capable of passing into the new compound. This was tried as follows :—

·483 grm. chlorophosphuret, dissolved in alcohol, decomposed
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by ammonia, the solution mixed with ferric sulphate, acidified, and boiled, yielded ·518 grm. azophosphate of iron, dried at 100° C.

On the one theory ·483 grm. $P_3N_2Cl_5$ contain ·150 grm. P,
and ·518 grm. $Fe_2O_3, P_2NO_5, 4HO$, contain ·139
grm. P ;

and on the other theory ·483 grm. $PNCl_2$, contain ·129 grm. P,
and ·518 grm. $Fe_2P_2NH_2O_6, H_2O$ contain
·129 grm. P.

It would appear therefore that when the experiment is made with every precaution to ensure the complete conversion of the one body into the other, the whole of the phosphorus passes from the chlorophosphuret, through the deutazophosphate, into the azophosphate—a result fatal to one at least of the formulæ originally assigned to these bodies, and rendering imperative a revision of the analyses.

Chlorophosphuret of Nitrogen.—The difficulty formerly experienced in analysing chlorophosphuret of nitrogen consisted in the estimation of the nitrogen and phosphorus, but we have found a process which is easy and gives satisfactory results. The crystals dried at 100° C. are dissolved in alcohol, and treated with a very strong aqueous solution of ammonia; this produces chloride and deutazophosphate of ammonium; the solution is evaporated to dryness and redissolved in water; the chlorine may then be thrown down by a silver salt in the presence of nitric acid. After separating the excess of silver by hydrochloric acid, the solution is boiled for some hours, to convert the deutazophosphoric acid into tribasic phosphoric acid, which may be determined in the usual manner. It is necessary to assure oneself that the phosphoric acid has been entirely converted into the tribasic condition. To determine the nitrogen, the alcoholic solution is decomposed by pure soda, the solution boiled with excess of hydrochloric acid, and the ammonia precipitated as platinum-salt.

I.—·9255 grm. gave 2·2715 grm. AgCl, and ·8715 grm. $Mg_4P_2O_7$.

II.—·603 grm. gave 1·4905 grm. AgCl, and ·5605 grm. $Mg_4P_2O_7$.

III.—·441 grm. gave 1·088 grm. AgCl, and ·418 grm. $Mg_4P_2O_7$.

IV.—·4866 grm. gave ·9065 grm. $PtCl_2NH_4Cl$.

The following are the percentage results compared with the

rival formulæ $P_3N_2Cl_5$ and $PNCl_2$. It will be seen that they agree best with that of Laurent:—

	Calculated.		Found.			
	$P_3N_2Cl_5$	$PNCl_2$	I.	II.	III.	IV.
Phosphorus	31·15	26·72	26·29	25·96	26·44	
Nitrogen	9·38	12·07	—	—	—	11·73
Chlorine	59·46	61·21	60·72	61·15	61·02	
	100·00	100·00				

The formula, or atomic weight, of this body cannot be controlled by the analysis of a compound, as none are known to exist, but two determinations of its vapour-density gave the following results:—

	I.	II.
Difference between weight of air and vapour	·633 grm.	·5722 grm.
Temperature of balance case.....	8°C	11°C
Temperature of sealing.....	299°C	306°C
Capacity of globe	101·7 c.c.	94·02 c.c.
Residual air	1·7 c.c.	·6 c.c.
Calculated density of vapour	12·33	12·09

Mean 12·21.

This vapour-density is very high, and in order to make an atom of chlorophosphuret of nitrogen occupy the same space as one of water H_2O , it is necessary to triple Laurent's formula, and $P_3N_3Cl_6$ would give a vapour-density of 12·10, almost exactly that found by experiment.

Deutazophosphoric acid.—In the previous paper, the formula of this acid was deduced inferentially rather than from the analyses of the deutazophosphates of barium and ammonium, which alone were examined quantitatively; but we thought it desirable to prepare some salt of this acid, if possible, and analyse it. Many attempts were made, but the only success was with the silver-salt prepared in the following manner:—Chlorophosphuret of nitrogen was decomposed by alcohol and ammonia, and from the neutral solution the mixed chloride and deutazophosphate of silver were precipitated by nitrate of silver in the cold, then collected, and washed with as little cold water as possible, as the deutazophosphate :

slightly soluble. It was dried in vacuo, and a weighed portion boiled with dilute nitric acid, which dissolved the deutazophosphate and left the chloride; this of course had to be subtracted from the original weight; from the solution hydrochloric acid separates the silver, and after boiling for some hours converts the acid into ammonia and tribasic phosphoric acid.

- I.—1·203 grm. of mixed silver salts yielded ·8345 grm. original AgCl, ·264 grm. precipitated AgCl, and ·210 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.
 II.—·302 grm. deutazophosphate gave ·218 grm. AgCl, and ·170 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.
 III.—·2666 grm. gave ·300 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.
 IV.—·335 grm. gave ·241 AgCl, and ·187 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.
 V.—·3132 grm. gave ·3435 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.
 VI.—·464 grm. ignited per se, the water collected by means of sticks of potash, and the ammonia by hydrochloric acid, yielded ·007 grm. H_2O and ·2545 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.

The silver-salt of this acid prepared from oxychloride of phosphorus gave as follows:—

- VII.—·543 grm. yielded ·404 grm. AgCl, and ·266 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.
 VIII.—·3405 grm. gave ·2475 grm. AgCl, and ·417 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.

The following are the percentage results, and they agree sufficiently well with the formula $\text{Ag}_2\text{P}_2\text{N}_2\text{H}_4\text{O}_5$:—

	Calculated.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ag ₂	216 55·38	53·94	54·33	—	54·12	—	—	55·98	54·7
P ₂	62 15·89	15·91	15·72	—	15·59	—	—	15·50	—
N ₂	28 7·18	—	—	7·05	—	6·87	—	—	7·67
H ₄	4 1·03	—	—	—	—	—	·91	—	—
O ₅	80 20·52	—	—	—	—	—	—	—	—
	390 100·00								

In experiment VI. the ·2545 grm. of platinum-salt obtained is equivalent to 3·51 per cent. of nitrogen, and shows that when this salt was heated per se, only one-half of its nitrogen was evolved as ammonia.

The silver-salt obtained from anhydrous phosphoric acid treated

with ammonia, gave too little nitrogen, and was in fact more or less metaphosphate of silver. Schiff may have been more fortunate in obtaining pure deutazophosphates, or phosphamates, but there is no proof of this in his analyses; for he only determined the metal and the phosphorus, and these are almost the same in percentage amount in a metaphosphate and a "phosphamate." Thus in the barium-salt:—

	Phosphamate.	Schiff's analysis.	Metaphosphate.
Barium	46·6	47·1	46·4
Phosphorus	21·3	21·2	21·2

The oxychloride of phosphorus afforded the means of preparing other deutazophosphates.

Zinc-salt.—This is a gelatinous precipitate, readily soluble in acids, and to some extent in ammoniacal salts; when dry it forms a white powder.

I.—·456 grm. fused with carbonates of potassium and sodium and a little nitre, yielded ·153 grm. Zn_2O , and ·415 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.

II.—·441 grm. gave ·828 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.

These are equivalent to the following percentages; agreeing with the formula $\text{Zn}_2\text{P}_2\text{N}_2\text{H}_4\text{O}_5$:—

	Calculated.		I.	II.
Zn_2	65	27·20	26·84	—
P_2	62	25·94	25·41	—
N_2	28	11·72	—	11·77
H_4	4	1·67	—	—
O_5	80	33·47	—	—
	239	100·00		

Barium-salt.—This also was a gelatinous precipitate which dried to a white earthy powder.

I.—·3995 grm. gave ·2975 grm. Ba_2SO_4 and ·57 grm. $\text{PtCl}_2\text{NH}_4\text{Cl}$.

II.—·4395 grm. gave ·329 grm. Ba_2SO_4 and ·298 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.

These determinations agree with the formula $\text{Ba}_2\text{P}_2\text{N}_2\text{H}_4\text{O}_5$.

	Calculated.		I.	II.
Ba ₂	137·2	44·08	43·81	44·04
P ₂	62·0	19·91	—	18·94
N ₂	28·0	9·00	8·94	—
H ₄	4·0	1·27	—	—
O ₅	80·0	25·74	—	—
	311·2	100·00		

Azophosphoric Acid.—There is less difficulty in the preparation of pure azophosphates, for some of the metallic salts form in an acid solution, and are very stable.

The analyses formerly recorded gave results which differed little from those required by Laurent's formula, unless perhaps in the amount of hydrogen, but it was considered desirable to obtain additional determinations by a method similar to that which had been found so successful in the analysis of the compounds already described.

Ferric-salt.—This salt was dried at 100° C., but it was found to be difficult to obtain it perfectly dry at that temperature, and it was very hygroscopic. The ferric oxide was separated by a solution of caustic soda, the washed precipitate redissolved in acid, and precipitated again by ammonia, while the soda solution was treated with a large excess of hydrochloric acid, and boiled to convert the azophosphoric acid into phosphoric acid and ammonia. The hydrogen was found to be capable of estimation by the usual process of organic combustion.

I.—·242 gram. azophosphate, prepared from chlorophosphuret of nitrogen, gave ·075 gram. Fe₄O₃ and ·2085 gram. Mg₄P₂O₇.

II.—·243 gram. gave ·076 gram. Fe₄O₃. The solution containing azophosphoric acid was boiled with caustic soda, and the ammonia condensed in hydrochloric acid produced ·2005 gram. PtCl₂NH₄Cl; from the residue ·2078 gram. Mg₄P₂O₇ was obtained.

III.—·400 gram. gave ·066 gram. H₂O.

IV.—·575 gram. gave ·0995 gram. H₂O.

V.—·4515 gram., prepared from anhydrous phosphoric acid, gave ·1425 gram. Fe₄O₃.

VI.—·4035 gram. of the same gave ·3625 gram. PtCl₂NH₄Cl.

VII.—·2375 gram., prepared from oxychloride of phosphorus, gave ·2045 gram. PtCl₂NH₄Cl.

VIII.—450 grm. of the same gave 1435 grm. Fe_4O_3 . and 41 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.

The following are the percentages deduced from these numbers, showing that the salt is of the same composition from whichever compound of phosphorus it was originally prepared, and that the ratio of the iron, phosphorus, and nitrogen was correctly determined before. The formula $\text{Fe}_2'''\text{P}_2\text{NH}_2\text{O}_6\cdot\text{H}_2\text{O}$ is sufficiently accordant with the results, if we suppose that the last traces of water were not always removed at 100°C :—

Calculated.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Mean of former experiments.
Fe_2 56 22.58	21.60	21.96	—	—	22.09	—	—	22.32	23.83
P_2 62 25.00	23.96	23.98	—	—	—	—	—	25.44	25.30
N 14 5.65	—	5.16	—	—	—	5.63	5.40	—	5.45
H_4 4 1.61	—	—	1.83	1.91	—	—	—	—	1.87
O_7 112 45.16	—	—	—	—	—	—	—	—	—
248 100.00									

Schiff analysed an iron-salt which was unquestionably this one, though he viewed it as the phosphamate (deutazophosphate) of ferrous oxide. The mean of his determinations comes remarkably close to the calculated numbers, viz.:—

Iron	22.51
Phosphorus	24.95
Hydrogen	1.63

He does not give his determinations of nitrogen, but says, in reference apparently to all the salts analysed by him, that they were considerably too low. His formula in fact requires 11 per cent. His determinations were doubtless more correct than he imagined.

Copper-salt.—The copper salt was originally prepared in the same way as the ferric salt, and the former analyses, though not made by our present improved method, are sufficiently accordant with the rectified formula, $\text{Cu}_3\text{P}_2\text{NH}_2\text{O}_6\cdot\text{H}_2\text{O}$.

	Calculated.	Mean of former experiments.
Cu_3	94.8 33.05	33.85
P_2	62.0 21.62	—
N	14.0 4.88	4.72
H_4	4.0 1.40	1.94
O_7	112.0 39.05	—
	286.8 100.00	

Zinc-salt.—When the filtrate from the precipitate of deutazophosphate of zinc, containing the deutazophosphate dissolved by the ammoniacal salts and excess of chloride of zinc, is boiled, it becomes turbid and deposits a white granular powder, which was found to be anhydrous azophosphate of zinc.

I.—·455 grm. gave ·202 grm. Zn_2O , and ·363 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.

II.—·4556 grm. gave ·473 grm. $\text{PtCl}_2\cdot\text{NH}_4\text{Cl}$.

These numbers give the following percentages, agreeing with the formula $\text{Zn}_3\text{P}_2\text{NH}_2\text{O}_6$:—

	Calculated.		I.	II.
Zn_3	97·5	35·91	35·63	—
P_2	62·0	22·83	22·28	—
N	14·0	5·16	—	5·12
H_2	2·0	0·74	—	—
O_6	96·0	35·36	—	—
	271·5	100·00		

Barium-salt.—This salt is formed under exactly the same circumstances as the zinc-salt, the deutazophosphate of barium in solution being decomposed at a high temperature by the excess of barium-salt.

It falls as a white granular precipitate readily soluble in hydrochloric or nitric acid, but insoluble in acetic acid. The following analyses show that it is anhydrous, and agree with the formula $\text{Ba}_3\text{P}_2\text{NH}_2\text{O}_6$:—

I.—·2388 grm. gave ·2185 grm. Ba_2SO_4 .

II.—·345 grm. gave ·316 grm. Ba_2SO_4 .

III.—·415 grm. gave ·3815 grm. Ba_2SO_4 , and ·2435 grm. $\text{Mg}_4\text{P}_2\text{O}_7$.

IV.—·739 grm. gave ·675 grm. Ba_2SO_4 , and ·429 grm. $\text{PtCl}_2\cdot\text{NH}_4\text{Cl}$.

These numbers yield the following percentages:—

	Calculated.		I.	II.	III.	IV.
Ba_3	205·8	54·21	53·85	53·95	54·08	53·74
P_2	62·0	16·32	—	—	16·38	—
N	14·0	3·68	—	—	—	3·64
H_2	2·0	0·53	—	—	—	—
O_6	96·0	25·26	—	—	—	—
	379·8	100·00				

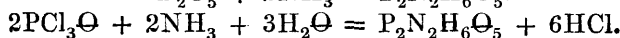
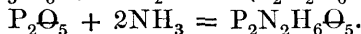
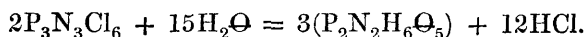
The salts of barium and silver formerly analysed do not give good results, but this is easily accounted for by their mode of preparation. The iron-salt was decomposed by potash, and from this solution they were prepared by double decomposition; now when a caustic alkali is added to the ferric salt, there seems to be always a slight odour of ammonia produced, showing a partial decomposition of the acid, and a consequent formation of phosphoric acid, which will cause an admixture of more or less phosphate with the azophosphate examined. The same remark applies to the potassium-salt formerly analysed.

Hitherto we have concerned ourselves simply with the ultimate composition of the bodies analysed, and have called them by the names originally given; but we must add a few words on their probable rational composition, though we hope some experiments now in progress will throw additional light on this subject.

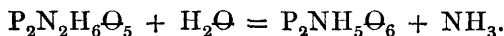
No formula can yet be assigned for the formation of chlorophosphuret of nitrogen by the action of ammonia, or its compounds, on pentachloride of phosphorus. It seems to be in all cases a secondary product. It would be idle to speculate as yet on how the compound molecule $P_3N_3Cl_6$ is built up, and its old name, chlorophosphuret of nitrogen, may be as good as any other.

The names azophosphoric and deutazophosphoric acid have this significance, that the one acid contains a portion of nitrogen as well as phosphorus and oxygen, and the other a second portion, but it seems preferable to adopt the names given by Laurent, who first divined their true composition. These are *pyrophosphamic* and *pyrophosphodiamic acids*.

The reactions by which pyrophosphodiamic acid is produced according to the methods above described, are as follows:—



and the reaction by which pyrophosphamic acid may be derived from it, will be as follows:—



or in actual experiment—

