seen. In one instance an aluminico-tungstate (1 : 12 or 2 : 24) was noticed together with the usual 2 : 18-compound. Its quantity was never very great.

The ferrico-, chromico- and cobaltico-tungstates are being investigated.

In conclusion, the writers would here acknowledge their indebtedness and extend thanks to Dr. H. S. Miner, of the Welsbach Lighting Co., for the generous gift of rare earth salts, and to Messrs. Dox, Masland and Poole, for valuable and patient assistance in the analytical work connected with this study.

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AN INVESTIGATION OF SODAMIDE AND OF CERTAIN OF ITS REACTION-PRODUCTS.[1]

BY W. PHILLIPS WINTER.
Received June 10, 1904.

THE history of the preparation of sodamide dates from 1809, when Sir Humphry Davy,[2] in England, and Gay-Lussac and Thénard,[3] in France, almost simultaneously discovered the amides of sodium and of potassium. They were carrying on investigations to determine the composition of ammonia and they led a strong current of the latter gas, for several hours, over the pure metal heated in a glass retort to about 300°. The glass of the retort was considerably etched, and the semicrystalline mass of sodamide obtained was olive-green in color.

They investigated and sought to analyze it. Davy plunged pieces of sodamide under the mouths of jars filled with water, transferred the unabsorbed gas to a eudiometer and determined that hydrogen was formed in the decomposition of sodamide by water. Gay-Lussac and Thénard, by strongly heating the substance, obtained two-fifths of the ammonia that had disappeared in the reaction; at a higher temperature nitrogen and hydrogen gases were formed in the ratio of 2.5 of the former to 1 of the latter in quantities to account for one-fifth more of the ammonia. Decomposition of the residue by water yielded the remaining portions of ammonia.

These investigators are also responsible for a method, published by them, for the preparation of sodium nitride. They stated that when sodamide is strongly heated it decomposes in accordance with the equation
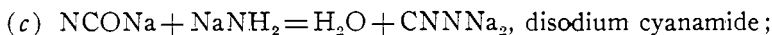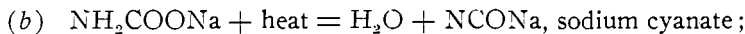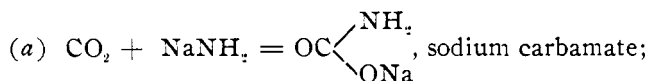
$$3NaNH_2 = Na_3N + 2NH_3.$$
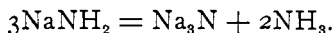
They described the nitride as a dark brown powder. Titherly,[1] in 1894, carefully repeated these experiments, employing a pure quality of sodamide, and he found that strong heat completely dissociates it. He concluded that the so-called nitride was to be ascribed to impurities in the sodium employed and to contamination by the constituents of the glass of the retorts.

Beilstein and Geuther,[2] in 1858, prepared sodamide in the same way as the discoverers did. They analyzed it by determining the amounts of sodium and of ammonium chlorides formed when it was decomposed by hydrochloric acid, and they further investigated its reaction products when currents of dry carbon monoxide. carbon dioxide and carbon disulphide were led over the heated sodamide. The reactions are.

$$NaNH_2 + CO = NaCN + H_2O,$$
$$2NaNH_2 + CO_2 = CNNNa_2 + 2H_2O,$$
$$NaNH_2 + CS_2 = NaCNS + H_2S.$$
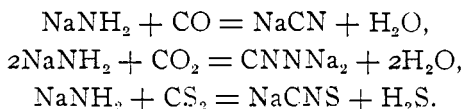
The presence of water produced secondary reactions with sodamide not included in the equations.

Drechsel[3] showed that the reaction with carbon dioxide was not analogous with the one given for carbon disulphide and he proved that the nature of the reaction with carbon dioxide was better expressed in consecutive stages, thus:

(a) $CO_2 + NaNH_2 = OC{<}^{NH_2}_{ONa}$, sodium carbamate;

(b) $NH_2COONa + heat = H_2O + NCONa$, sodium cyanate;

(c) $NCONa + NaNH_2 = H_2O + CNNNa_2$, disodium cyanamide;

the reaction evidently proceeding one step farther than in the case of carbon disulphide.

[1] *J. Chem. Soc.* (London), **65.** 504. and **71.** 460.
[2] *Ann. Chem.* (Liebig). **108.** 88.
[3] *J. prakt. Chem.* (2), **11.** 308 ; and **16.** 203.

Wislicenus[1] heated sodamide in a stream of dry nitrous oxide. It affords a simple and effective means for the synthesis of sodium triazoate,

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$
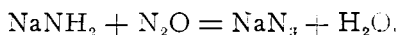
This method has been recently considerably improved by Dennis and Browne.[2]

Titherly[3] carried on an extensive investigation of sodamide. He made the discovery that it can be made in vessels of pure metal, such as silver or iron, in considerable quantity and free from the contaminations that glass always imparts to it. Sodamide thus made is of a pure white color. Titherly employed two different synthetical methods for the analysis of his product, the results of which confirmed each other and pointed conclusively to the hitherto accepted formula for sodamide. He further showed that disodimide and sodium nitride could not be formed by continued substitution of ammonia hydrogen by sodium, but that certain organic residues have the power to substitute one or both of the hydrogen atoms of sodamide.

The preparation of sodamide presents no especial difficulties. Fig. 1 represents the apparatus as used. *A* is a flask in which concentrated ammonia water is heated with a low flame. *B* is an empty gas-washing bottle, kept cool to condense excess of moisture. 1, 2, 3 and 4 are drying towers, filled with soda-lime. *C* is a tube filled with pieces of sodium. It may conveniently be about 40 cm. long. *D* is a wrought iron retort, made in two parts, which fit together at the flange in the center. It is capable of holding about 200 grams of sodium when filled nearly to the flange. Before heating the sodium, ammonia is passed for a long time through the apparatus, and at the conclusion of the experiment the sodamide is allowed to cool in the current of ammonia. Precautions are taken to have a *continuous* supply of ammonia.

The writer has found, by careful tests, that a silver-plated crucible is rapidly attacked, but that a pure wrought iron crucible can be used repeatedly, the sodamide formed in it showing no trace of iron when its solution in water was acidified and treated with potassium ferrocyanide. The crucible was heated for about

[1] *Ber. d. chem. Ges.,* **25**, 2084.

[2] This Journal, **26**, 577.
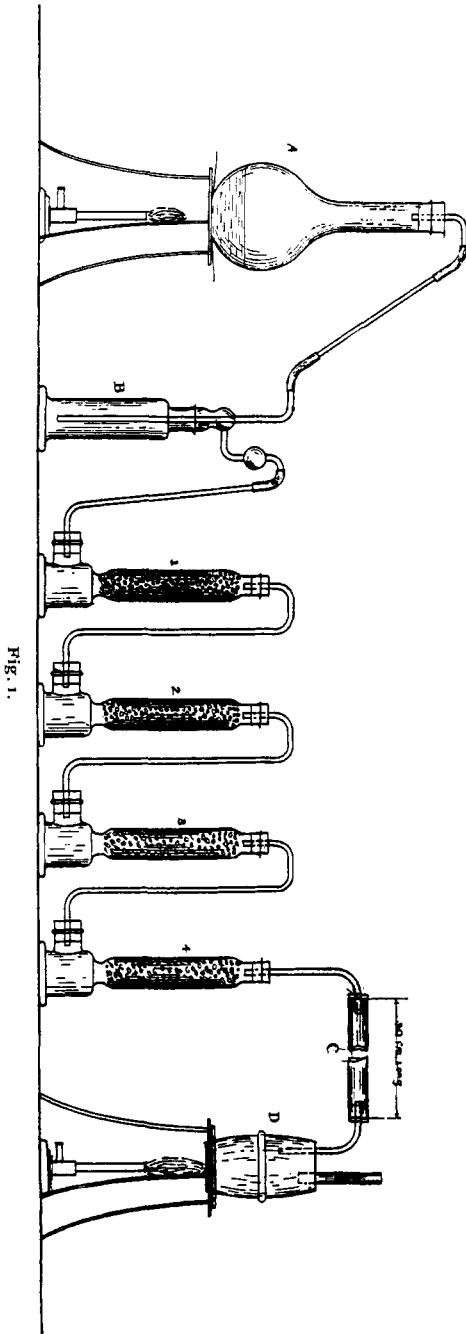
[3] *Loc. cit.*

Fig. 1.

five hours with a single Bunsen burner, so regulated as to prevent the distillation of the sodamide into the air. More elaborate apparatus has been described for the preparation of sodamide, but the chief merit of the apparatus here described is that it can be quickly put together from apparatus to be found in almost any laboratory and with it sodamide of excellent quality has been repeatedly made.

Omitting the discussion of the better known properties of sodamide, we have noted that under certain circumstances, not fully understood as yet, sodamide kept in dry, glass-stoppered bottles slowly undergoes a peculiar color change from white to yellowish brown. The change is more rapid if the sodamide is powdered. Light or its absence was not responsible for the change. It does not necessarily depend on the method of its manufacture for samples of the same sodamide were powdered and kept side by side in different vessels for some weeks. The change had taken place in part of the samples only. The change is, in some way, dependent on the amount of dry air which comes in contact with the sodamide and upon the duration of exposure to it, for it was observed that: (1) The sodamide which had been kept longest had undergone the greatest change when conditions otherwise were the same; (2) small bottles with *accurately fitting* stoppers, not opened repeatedly, as many of the samples were, underwent little or no change in their contents; (3) the powdering of sodamide brings the air more completely into contact with the sodamide.

When sodamide is thrown into water the behavior is quite similar to that of sodium, forming a globule which floats about on the water and at last explodes. The globule formed by sodamide that has undergone the color change often changes to a brown or black color and explodes with increased violence. If the water is warm, these phenomena are more noticeable. It was the peculiar sharp explosion that first suggested the possibility of the presence of traces of a triazoate or some such compound as a working hypothesis.

Sodamide is rapidly decomposed by absolute alcohol with evolution of ammonia and formation of sodium ethylate. The alcohol is heated to boiling, if the sodamide is added rapidly, but since it does not float on the alcohol there is no final explosion. While the white sodamide imparts no color to the alcohol until after long

standing, the yellow variety colors it a deep brown, out of all proportion to the color in the sodamide used. With the yellow variety there is usually formed also an insoluble residue.

Examination of the Insoluble Gases Formed on Decomposing Sodamide with Water.—It has long been known that water breaks down sodamide into sodium hydroxide. setting free ammonia; and Davy also noted the formation of hydrogen. In all the sodamide examined by the writer there was found also traces of nitrogen, the ratio between hydrogen and nitrogen depending not only on the way in which the sodamide was prepared, but also on
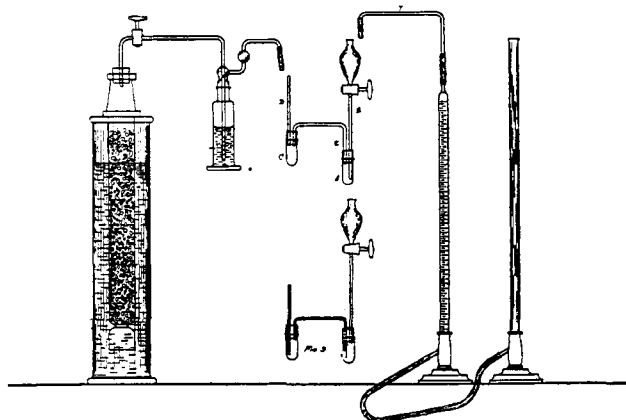

Fig. 2.

the length of time and manner in which it was kept previous to analysis. The apparatus in which these experiments were carried on is represented in Figs. 2 and 3. Carbon dioxide, dried by sulphuric acid, was first conducted through the apparatus (Fig. 2), the gas entering at *D* and escaping at *B*. The weighed substance (finely powdered) was then introduced into *A* and the current of carbon dioxide continued until the gas, issuing from *B*, was *completely* absorbed by a strong solution of caustic soda. Without removal of the stoppers the tubes were shifted into the position shown in Fig. 3, the stop-cock of *B* closed and the funnel filled with distilled water. The tube *D* was connected to the capillary of a Hempel's burette, *F*, completely filled with a 10 per cent. solution of caustic soda. In some experiments it was found necessary to introduce into the burette measured portions of pure oxygen. Water was slowly dropped from the funnel into the

sodamide, diminished pressure being produced in the burette. At the end, water was admitted to drive over every trace of gas, and the carbon dioxide and ammonia were completely absorbed.

Hydrogen was determined by explosion in a eudiometer, the nitrogen being estimated by difference. The identity of nitrogen was established beyond question by sparking known volumes of it in the presence of excess of oxygen and traces of caustic potash for several hours with a high voltage current. The gas remaining was then completely absorbed by phosphorus.

In the experiments there was employed: (1) Sodamide which had been insufficiently heated, all visible excess of sodium having been mechanically removed: (2) sodamide which had been properly made; (3) sodamide which had been kept until it had undergone the color change referred to.

From a large number of results. which are quite concordant. the following summary is drawn: (1) The relative proportion of nitrogen to hydrogen is low in sodamide that has been insufficiently heated, but high in sodamide properly prepared; (2) the ratio of nitrogen to the total insoluble gases formed increases both relatively to the hydrogen and absolutely after sodamide has been kept for some time; (3) free nitrogen is always given off in small amounts when sodamide is decomposed by water.

Approximately 0.6 gram of freshly prepared sodamide, insufficiently heated. yielded 17 cc. of insoluble gases, of which 16 per cent. was nitrogen. Six weeks later 0.4 gram of the same sample yielded 13.7 cc. of gases, of which 65.8 per cent. was nitrogen. 0.85 gram of sodamide, properly prepared, yielded 5 cc. of gases of which 72.5 per cent. was nitrogen; 14 weeks later 0.92 gram of the same sample yielded 6.65 cc. of gases, of which 92 per cent. was nitrogen. Since the amount of gas obtained from a sample of sodamide that has been heated a sufficiently long time is so much less and the ratio of nitrogen so much higher, we can not escape the conclusion that the hydrogen is due to minute particles of sodium, invisible to the unaided eye, and that these are gradually converted into sodamide at the *ordinary* temperature by the atmosphere of ammonia always present over sodamide. The source of nitrogen has not been satisfactorily explained as yet, and it is still under investigation. A provisional theory, which has every indication of probability, will be referred to in connection with the next phase of the investigation.

If the water solution of the yellow sodamide is acidified, nitric oxide is given off; none is obtained when freshly made sodamide is similarly treated. The water solution of yellow sodamide was placed in an apparatus similar to the one described under Fig. 2, and the air was displaced in the same way. Sulphuric acid was admitted from the funnel and the gases evolved were collected in a Hempel burette. The amount of nitric oxide present after absorption of the carbon dioxide was determined both by absorption in ferrous sulphate solution and by admitting measured portions of oxygen and noting carefully the diminution in volume. The mean of several experiments indicated that somewhat more than half of the gas thus obtained was nitric oxide, while the remainder was nitrogen. We thus have nitrogen occurring as a product when sodamide is decomposed by water, and again when the water solution of yellow sodamide is treated with acids. The nitrogen source cannot be the same in both cases. Qualitative tests of the water solution for nitrous and hyponitrous acids were made, a considerable amount of the former, but only traces of the latter, being indicated.

To account for the presence in sodamide of these bodies capable of yielding nitrogen and its oxides, recourse must be had to the well-known slow oxidation which ammonia can undergo; thus,

$$2NH_3 + 4O \rightarrowtail 2NH(OH)_2 \rightarrowtail HON : NOH + 2H_2O.$$
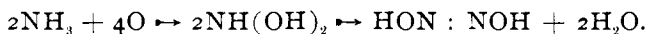
The first product is unknown, the second is hyponitrous acid. If oxidation stops at this stage, the unstable hyponitrous acid breaks down into nitrous oxide and water, and the formation of nascent nitrous oxide lends some probability to the suggested explanation that a compound is formed by it with sodamide analogous to, if not identical with, sodium triazoate. It can not be denied that a reaction which proceeds rapidly at a definite elevated temperature may also proceed with greatly reduced velocity at ordinary temperatures. Since the decomposition of sodamide by water in the apparatus described above, takes place with extreme violence and with sudden rise of temperature, the presence of traces of such triazoate will readily account for the small amount of nitrogen obtained from freshly prepared sodamide and for larger amounts in that which has stood for some time in contact with dry air.

But continued action of oxygen upon ammonia yields nitrous and finally nitric acids, and the undoubted presence of nitrous

acid in appreciable quantity, along with traces of hyponitrous acid, serves to confirm the theory. The decomposition of nitrous acid by mineral acids readily accounts for the nitric oxide, but not for the nitrogen.

Hyponitrous acid may break down in either of two ways, yielding, according to the one, which is the more common method, nitrous oxide and water; but when suddenly or violently decomposed the products are water, nitrogen and oxygen. The oxygen would be removed by the excess of nitric oxide, thus accounting for the brown fumes always noted for a short time in the apparatus, despite the utmost care to exclude all traces of air.

Sodium Cyanamide from Sodamide.—Beilstein and Geuther[1] have already shown that when dry carbon dioxide is passed in a slow stream over heated sodamide sodium cyanamide, $CNNNa_2$. is formed. In the course of certain experiments by the writer it was noted that when a cylinder containing a small amount of water, heated almost to boiling, was connected to the carbon dioxide generator, so that there might be a continued supply of the gas, a shower of brilliant sparks occurred when sodamide, finely powdered, was sifted into the cylinder. The reaction was most complete when the temperature of the water was between 60° and 100°, and when the gas in the cylinder was not too much diluted with hydrogen, nitrogen or air.

Examination of the water solution at the end of the experiment showed the presence of cyanamide, the most satisfactory yield being found in those experiments in which there had been the greatest production of sparks. A quantitative analysis was made of the silver cyanamide produced by addition of ammoniacal silver nitrate solution to a solution of cyanamide or any of its salts. After drying the amorphous, brilliant yellow silver cyanamide at 130° for a sufficient time, the analysis was carried on as follows:

(1) For silver, gravimetrically as silver chloride. 0.3576 gram gave 0.3930 gram AgCl, equivalent to 0.2958 gram Ag, or 82.71 per cent. The theory calls for 84.34 per cent.

Beilstein and Geuther obtained $\begin{cases} 81.34 \text{ per cent.} \\ 81.68 \text{ per cent.} \end{cases}$

Drechsel obtained $\begin{cases} 80.6 \text{ per cent.} \\ 81.6 \text{ per cent.} \end{cases}$

Mulder obtained 82.9 per cent.

[1] *Loc. cit.*

It was pointed out by Mulder that the explanation for these uniformly low results was probably to be found in the presence of silver dicyandiamide, $C_2N_4H_3Ag$, in small quantity, formed through the tendency to polymerize, so frequently displayed by cyanogen compounds.

(2) For nitrogen, volumetrically by Dumas' method, giving 11.37 per cent.; calculated, 10.97 per cent.

(3) For carbon and hydrogen by combustion with copper oxide in presence of a copper spiral, which gave, C, 5.47; H, 0.35; calculated, C, 4.68 per cent.

These results for nitrogen and carbon serve to confirm the presence of a polymer of cyanamide for, while a portion of the water obtained may not unlikely be attributed to traces of moisture absorbed by the apparatus and reagents or imperfectly removed from the oxygen, it is hardly probable that both nitrogen and carbon should be in excess of the theoretical, while at the same time silver was deficient, unless traces of a compound were present containing a higher proportion of carbon and of nitrogen and a lower one of silver, as silver dicyandiamide does.
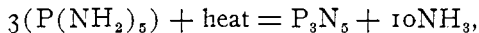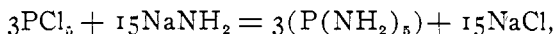
SODAMIDE AND PHOSPHORUS PENTACHLORIDE.

A number of weeks after the investigation, herein described, had been commenced, Stock and Hoffman[1] published an account of the preparation of a new nitride of phosphorus, P_3N_5, by treating phosphorus pentasulphide with liquid ammonia and heating the complex compound formed. It may also be formed by heating the pentasulphide directly in a stream of ammonia gas to 230°.

It seemed not improbable that sodamide, acting on phosphorus pentachloride, could effect a transformation such as

$$3PCl_5 + 10NaNH_2 = P_3N_5 + 5NH_4Cl + 10NaCl,$$

or

$$3PCl_5 + 15NaNH_2 = 3(P(NH_2)_5) + 15NaCl,$$

$$3(P(NH_2)_5) + heat = P_3N_5 + 10NH_3,$$

or some similar compound of phosphorus with amidogen or its residue.

The work of Joannis,[2] who obtained boron triamide by passing the vapor of boron trichloride together with hydrogen through liquid ammonia: of Hugot,[3] who worked with sodammonium,

[1] *Ber. d. chem. Ges.*, **36.** 314.
[2] *Compt. Rend.*, **135.** 1106.
[3] *Ibid.*, **121.** 206; **126.** 1719; **127.** 553.

NaNH$_2$, on phosphorus and on arsenic; of Besson,[1] who obtained as a final product phospham, PN$_2$H, from the double salt obtained by treating phosphorus pentachloride with ammonia; and of others who have used liquid ammonia and ammonia gas, points clearly to the fact that compounds containing ammonia-nitrogen have been made in considerable variety and are of unusual chemical interest.

Preparation.—When powdered sodamide and phosphorus pentachloride are brought together in *small quantities* in a dry test-tube and the mixture slightly warmed a violent reaction ensues, accompanied by flame and by the evolution of a white extremely light powder, the greater part of which settles on the sides of the tube. The bottom of the tube is usually melted out by the heat generated. The white powder, which had sublimed on the walls of the tube, was collected and thrown into water. The greater part of it dissolved readily, and this was found by qualitative tests to consist of ammonium chloride, sodium chloride, and traces of phosphorus compounds. A small portion was found to be insoluble in water.

The results attained in this rough qualitative way seemed to warrant more careful experiment, and accordingly the following apparatus was devised for the work: A large bell-jar of about 20 cm. diameter and 30 cm. in height was fitted to a ground glass plate from which had been cut a portion of sufficient width to admit the glass tube through which pure nitrogen was admitted. The nitrogen, made from molecular equivalent amounts of sodium nitrite and ammonium chloride, was stored in a gasometer, washed through three drying bottles containing strong sulphuric acid and passed over heated copper gauze to remove traces of oxygen and of oxides of nitrogen. Fitted tightly into the neck of the bell-jar was a wide glass tube, which could be raised or lowered at will. To the top of the tube was attached a funnel which served to direct the fall of the materials to be introduced into the small porcelain dish placed within the jar. A slow stream of nitrogen was conducted into the apparatus for a considerable time, the tube in the neck of the bell-jar having been drawn up its full length to facilitate the expulsion of air from the apparatus. Without interrupting the flow of gas, small, nearly equal, portions of powdered sodamide and of phosphorus pentachloride were

[1] *Compt. Rend.,* **114,** 264.

alternately dropped through the funnel tube, which had been partially lowered. The reaction usually took place at once, but if not, a warmed glass rod, inserted through the tube, was sufficient to start the reaction. The energy of the reaction in the atmosphere of nitrogen is much less than in the air, and if care is exercised in the successive addition of the two reacting materials, very little of the white product was projected into the air. Sufficient heat was generated by the union of the first portions to carry the operation on to the end. The time consumed in introducing into the apparatus about 36 grams of phosphorus pentachloride and 30 grams of sodamide was about two hours.

The addition of either reagent in excess soon interrupted ignition of the mixture, but action is at once restored with considerable vigor when change to the other reagent is made. The apparatus was allowed to cool in the stream of nitrogen and upon opening the bell-jar its sides and the bottom plate were found to be covered to a considerable depth with a deposit of a white, light powder in a state of extremely fine subdivision. In the porcelain dish was a solid core consisting largely of sodium chloride and of traces of the reagents used.

Separation and Purification of the Sublimate.—To separate the soluble from the insoluble portions was found to be an exceedingly difficult task. When the powder is thrown into water, much of it goes into solution, a small portion settles, but the water assumes and retains a milky appearance, which does not disappear after two months' standing. It has been found impossible to separate and purify the residue in this way. The pores of the paper or of the asbestos-filter quickly become clogged and the portion of the residue which comes into contact with the filter forms a gummy mass and adheres to it with such tenacity that separation of filter and precipitate is impossible after drying. The yield of insoluble powder is so small that washing by decantation results in almost complete loss of the precipitate. Washing with alcohol or other organic solvents is impracticable, owing to the quite general insolubility of the chlorides which it is desired to remove. If the powder be treated with moderately dilute hot nitric acid, an insoluble residue soon settles and the supernatant liquid becomes clear. Specimens of the powder for analysis were obtained in this way. Brown fumes of nitrogen peroxide were evolved on heating and these were ascribed at first to the action

of the hydrochloric acid formed from traces of phosphorus oxychloride, which are undoubtedly present. The results of analysis indicate that it is far more likely that the oxidation takes place in the insoluble compound itself.

Acetic acid of 25 per cent. strength can also be used to separate the soluble impurities—the powder obtained being somewhat more voluminous. If hydrochloric acid is used, there is also rapid settling of the insoluble residue, but when this is dried at 100° in an air-bath it is semi-liquid and gummy, and on further heating to 145° the mass becomes, after cooling, gray, hard tenacious and vitreous.

The above acids, if diluted further, as well as sulphuric acid or solutions of the fixed alkali hydroxides would not effect separation of the two portions. After decantation from the acid washings the powder was dried in glass vessels at 100° and separated from the glass by the aid of a piece of stiff platinum wire. The yield was about 2.5 per cent. of the weight of sublimate used.

Properties of the Insoluble Portion.—The powder thus obtained was a white, nearly tasteless, odorless compound, exceedingly inert. Boiling with the strong mineral acids did not affect it and similar treatment with aqua regia or with concentrated potassium hydroxide solution affected it, if at all, to so slight an extent as to be unnoticeable, if the action was not prolonged.

Three methods were devised which were effective in decomposing it:

(*a*) Heated with water in a sealed tube for three hours to 180° it was decomposed and the solution, on opening the tube, yielded the odor of ammonia and responded to the molybdate of ammonia test for phosphoric acid.

(*b*) Treated with an aqueous solution of hydrofluoric acid and a little sulphuric acid in a platinum crucible, the compound was broken down upon the application of gentle heat. A solution of the residue gave the test for phosphoric acid.

(*c*) Heated to dull redness for four hours in a combustion tube with a mixture of powdered hydroxide and nitrate of potassium, ammonia was evolved and a phosphate remained behind. A silver boat was used and a slow stream of dry air was forced over the heated mass.

Analysis.—The above methods were all employed in the analysis of the compound. In the practical application of the first

method it was noted that when water alone was used the tube was badly attacked and several grams of silica were separated. It was found best to employ dilute hydrochloric or sulphuric acid for the twofold purpose of diminishing the separation of silica and of fixing the ammonia in the non-volatile condition. In all determinations of phosphoric acid by this method, however, it was necessary to separate silica in the usual way before estimating the phosphorus as magnesium pyrophosphate. The second method was available for the determination of phosphoric acid only. It possessed the advantage of rendering unnecessary the previous removal of silica. The third method was not free from silica contamination, since it was impossible to prevent distillation of the contents of the silver boat on to the combustion tube.

In the first method the ammonium salt was decomposed by distillation with sodium hydroxide, the ammonia being absorbed by a standard acid, while in the third method the ammonia was received directly into the acid.

POWDER PURIFIED BY NITRIC ACID.

Weight. Gram.	Per cent. of P.	Per cent. of N.	Method of decomposition.
0.0864	33.67	19.42	Fusion with KOH and KNO_3 4 hours.
0.0739	40.31	20.58	" " " " " 5 ½ hours.
0.0810	....	21.54	" " " " " 5 ½ hours·
0.0578	40.31	....	By hydrofluoric acid.
0.0638	40.26	20.75	Sealed tube with HCl at 180°.
0.1108	....	21.50	" " " " " 180°.

Vitreous mass obtained by hydrochloric acid.

0.0630	26.56	15.11	In sealed tube, 180°.
0.1008	27.58	14.57	" " " 180°.

Analysis of portion dissolved out by nitric acid.

Weight of material.	Weight of NH_4.	Weight of Cl.	Weight of P.	Weight of Na.
3.608	0.2879	1.6998	0.2512	0.7382

Corresponding to :

	Grams.
NaCl	1.8735
NH_4Cl	0.8524
H_3PO_4	0.7944
Undetermined	0.0777
	3.608

Interpretation of Results.—Whatever the composition of the compound represented by the above analyses may prove to be,

it is clear that the phosphorus and the nitrogen stand in the ratio of $1:1$. The results of the analysis of the compound, purified by hydrochloric acid, show that it was, to a considerable extent, broken down and they are, therefore, not considered. The analyses correspond to the formula PO_2N or to some polymer of it. Such a formula requires 40.24 per cent. phosphorus, 41.53 per cent. oxygen, 18.22 per cent. nitrogen. There was found 40.28 per cent. phosphorus, 20.35 per cent. nitrogen. The excess of nitrogen is not surprising when the method of preparation of the material for analysis is considered.

The phosphamic acid described by Schiff,[1] the identity of which was called in question by Gladstone and Holmes,[2] agrees quite well in analysis and in all properties save one, that of its solubility in water, with the compound we have obtained. A series of metaphosphimic acids. $PONHOH$, empirically isomeric with Schiff's compound has been described by Stokes[3] and he has suggested that in this instance there may possibly occur a complex polymer of metaphosphimic acid. $(PONHOH)_x$. But since nitric acid undoubtedly oxidizes the original product of the reaction and since water probably hydrolyzes it, the analysis, as given, throws little light on the original product of the energetic reaction between phosphorus pentachloride and sodamide.

SODAMIDE AND YELLOW PHOSPHORUS.

Sodamide and phosphorus exhibit an energetic reaction when brought together in a test-tube and slightly warmed. In an endeavor to control this reaction the above reagents were heated together in benzene, xylene, aniline, and paraffin oil successively to the respective boiling-points of these liquids, but there was no direct combination between the sodamide and phosphorus. But when the reaction occurs in glass vessels of any kind the glass is invariably broken by the sudden heating, thus preventing the preparation of any considerable amount of the material. The products of the reaction were found to consist of some red phosphorus and of particles of a black compound which, when thrown into water, produced inflammable phosphine. Red phosphorus and sodamide heated together rather more strongly produced a similar compound.

[1] *Ann. Chem.* (Liebig). **103.** 168.
[2] *J. Chem. Soc.* (London), **17.** 126.
[3] *Am. Chem. J.*, **15.** 198, and **18.** 630.

Porcelain vessels could be used without fear of breakage and the experiment whereby about 12 grams could be prepared at one time was carried out as follows: The bottom of a wide-mouthed bottle of about 3 liters capacity was covered with glass beads to a sufficient depth to hold in place a large porcelain crucible about 30 x 30 mm. The bottom of the crucible was kept from direct contact with the bottom of the bottle that the latter might not be cracked by local heating. Through the neck of the bottle was passed a gas delivery tube, reaching to the bottom of the bottle, and a wide glass tube, about 30 mm. in diameter, which could be raised before beginning the experiment to assist in driving out air, but lowered almost to the mouth of the crucible when the re-agents are to be dropped in. A gas tube was passed into this wide tube and connected by a Y with the same nitrogen apparatus described in the reaction with sodamide and phosphorus penta-chloride. By means of pinch-cocks nitrogen could be delivered into the bottom of the bottle, into the vicinity of the reacting sub-stances, or simultaneously through both tubes at will. The stream of nitrogen was not discontinued at the end of the experiment until the apparatus was quite cool. The reaction proceeded with far less vigor in an atmosphere of nitrogen than in air. The heat of a warmed glass rod was sufficient to start the reaction. Precautions had to be employed to prevent too great a rise in temperature, for with such rise much of the phosphorus was con-verted into the red modification. It has not been found possible to prevent entirely this formation of red phosphorus, but under favorable conditions not much in excess of 1 per cent. of the com-pound consists of it.

When the air had been displaced, the finely powdered sodamide and the phosphorus in small pieces were dropped through the long tube into the crucible in small successive portions. The phos-phorus was dried as thoroughly as possible by absorbent paper or, better, by benzene. The material could not be removed from the atmosphere of nitrogen before it had become cool nor subjected to any friction without danger of spontaneously inflaming. It was, therefore, moistened with carbon disulphide when cool, re-moved to a mortar, pulverized under the same liquid and freed from excess of phosphorus by repeated washing in carbon disul-phide, which had been dried over calcium chloride.

The attempt was made to remove any excess of sodamide which it might contain by washing with absolute alcohol, but it was found that the entire compound was broken down with evolution of phosphine. In fact, even the treatment with carbon disulphide was observed to set free appreciable amounts of ammonia and of phosphine, and this was taken as a significant indication of the presence of certain unstable components of the reaction. The purified powder was dried at the ordinary temperature in an atmosphere of nitrogen, transferred to tightly stoppered containers and placed in a phosphorus pentoxide desiccator.

Properties.—The chocolate-red powder thus obtained is sensitive to traces of moisture and gives off continually a disagreeable odor suggestive of garlic. In the air it rapidly deliquesces and becomes lighter in color. When heated in air it gives off ammonia and phosphine, while the sodium salts of hypophosphorous and phosphorous acids remain. Heated in a supply of dry carbon dioxide gas it gives off the two gases above and there remain sodium carbonate, hypophosphite and phosphite. Water, dilute acids and alcohol break it down in the same way, but if alcohol is used, the phosphine is not inflammable. Hydrogen is also evolved in considerable quantity by decomposition with water or acids. Absolute ether, chloroform or benzene are without apparent action on the compound.

Historical.—Before entering upon the analysis or constitution of this compound brief reference must be made to work which has been done along similar lines. Gay-Lussac and Thénard, and also Davy supposed that phosphides of the alkali metals could be formed by heating the elements together in nitrogen.

In 1829, Magnus[1] devised a method for the preparation of potassium phosphide, K_3P, which was later used by Vigier[2] in preparing the similar sodium phosphide. Phosphorus was melted under petroleum (boiling-point $120°$) and bits of potassium were added from time to time. The oil was distilled off, the excess of phosphorus removed by carbon disulphide and the residue dried at a low temperature in a current of dry carbon dioxide. He stated that the compound separated carbon as well as phosphine when treated with water or dilute acids, and that he was not able to get the phosphide in a state of purity. Vigier's sodium

[1] Pogg. *Ann.*, **17**, 527.
[2] *Chem. News*, 1861, p. 273.

phosphide was described as a black compound. In the course of this work his experiments were repeated, resulting in the verification of his method and description, and, in addition, a partial analysis was made. Vigier used his phosphide in an organic research and he made no attempt to analyze it. Magnus gives nothing but the formula for his potassium phosphide, making no statement as to any analyses upon which he based his conclusions. Rose[1] caused potassium and phosphorus to combine in a flask in the presence of hydrogen. At the end of the experiment the excess of phosphorus was distilled off. He obtained a crystalline mass of the color of "japanned copper."

Bunsen[2] showed that sodium phosphide was formed by heating sodium and sodium phosphate together in a tube and he recommended this as a qualitative method in testing for the presence of phosphorus. Sodammonium, $NaNH_3$, and potassammonium, RNH_3, have, in the hands of Hugot and Joannis, working independently, been of considerable importance. Sodammonium in excess, red phosphorus and sodium, left in contact for several days, formed $P_2H_3Na_3$ ($Na_3P.PH_3$), sodamide and ammonia. The phosphide is described as a yellow crystalline body yielding phosphine in the presence of moisture.[3] The authors claim that if the red phosphorus is in excess $P_5K.3NH_3$ is formed, which loses its ammonia at 180°. It is always more or less contaminated with potassamide. With sodium $P_3Na.3NH_3$ is formed, becoming P_3Na at 180°.[4] If no sodium (or potassium) is used, or if phosphine be led into sodammonium or potassammonium, the substituted phosphines $NaPH_2$ and KPH_2 are formed.[5]

The chemistry of the phosphides of hydrogen is also closely interwoven with this work, because the phosphine produced was relied upon as a measure of the amount of sodium phosphide in the compounds analyzed. It was Thénard[6] and, later, Gatterman.[7] who first separated and determined the constitution and properties of gaseous, liquid and solid phosphines. The former also noted the presence of free hydrogen in ordinary phosphine.

[1] Pogg. *Ann.*, **12.** 547.
[2] *Ann. Chem.* (Liebig). **138.** 292.
[3] *Compt. Rend.*, **127.** 553. and **126.** 1719.
[4] *Ibid.*, **121.** 206.
[5] *Ibid.*, **119.** 557.
[6] *Ann. Chem.* (Liebig). **55.** 27.
[7] *Ber. d. chem. Ges.*, **23.** 1174.

Hoffman[1] showed that in all the common methods of producing phosphine the gas was diluted with from 6 to 80 per cent. of hydrogen (volumetric). When phosphine was made in the ordinary way. by heating an aqueous solution of potassium hydroxide with yellow phosphorus, only from 10 per cent. to 40 per cent. of the gas obtained was phosphine. Alcoholic potash gave about 45 per cent. phosphine. If calcium phosphide was used. the yield of phosphine was better, but was far from pure. The amount of hydrogen formed was very changeable. Even the decomposition by heat of pure phosphoric acid yielded a phosphine which contained at least 6 per cent. of hydrogen. The decomposition of pure phosphonium iodide, PH_4I, is the only method of obtaining pure phosphine. He also showed that fuming nitric acid. as well as the vapor of chlorine and bromine. render non-inflammable phosphine self-inflammable.

Bodroux[2] pointed out that temperature had something to do with the amount of hydrogen produced; in the case, at least, of the decomposition of certain phosphides. When aluminum or magnesium phosphides are decomposed with water they yield phosphine slowly. If the water be above 50° or if acids are used. much hydrogen is developed; if ice-water is used, no hydrogen is formed.

Analysis. Volumetric Gas Determination.—The powdered compound was decomposed by water or by acids in the apparatus described for the examination of sodamide (see Figs. 2 and 3) in an exactly similar way. The atmosphere of carbon dioxide prevented the phosphine from inflaming, although the reaction was violent and a great amount of heat was liberated. The solution remaining in the generator A was strongly alkaline, responded to the tests for hypophosphorous acid and contained a small amount of red phosphorus.

The volume of the gases remaining in the burette after the absorption of the ammonia and the carbon dioxide was noted and they were then passed into a Bunsen gas pipette filled with a freshly prepared solution of cuprous chloride in concentrated hydrochloric acid to absorb the phosphine. Measured portions of the unabsorbed gas remaining were then transferred to a eudiometer and exploded over mercury with electrolytic oxygen.

[1] *Ber. d. chem. Ges.*, **4**, 206.
[2] *Bull. Soc. Chim.* (3), **27**, 568.

Portions made at different times showed a variation in composition, and analyses of the same material at widely different periods further showed deterioration to be continuous. In the preparation of the first portion sodamide was used in excess, which was known to yield considerable nitrogen when decomposed by water. In the other two portions excess of phosphorus was used. Only a few representative data are given:

Portion 1.—

0.8664 gram of the material yielded 23.7 cc. of gases, of which 47 per cent. was phosphine, 45.7 per cent. hydrogen, and 7.2 per cent. nitrogen.

1.1614 grams (analyzed later) yielded 35.9 cc. of gases, of which 46.8 per cent. was phosphine, 46.1 per cent. hydrogen, and 7.1 per cent. nitrogen.

0.6109 gram yielded 19.5 cc. of gases, of which 46.8 per cent. was phosphine, 44.4 per cent. hydrogen, and 8.7 per cent. nitrogen.

Portion 2.—

0.9043 gram yielded 69 cc. of gases, of which 28.1 per cent. was phosphine, 71.8 per cent. hydrogen, and no nitrogen.

0.6764 gram (analyzed later) yielded 59.9 cc. of gases, of which 19.9 per cent. was phosphine, 80.1 per cent. hydrogen, and no nitrogen.

Portion 3.—

0.4126 gram yielded 57 cc. of gases, of which 16.15 per cent. was phosphine, 83.8 per cent. hydrogen, and no nitrogen.

0.4765 gram (analyzed later) gave 67.3 cc. of gases, of which 14.8 per cent. was phosphine, 85.1 per cent. hydrogen, and no nitrogen.

Although Bodroux[1] had shown temperature to be a controlling factor in the amount of hydrogen obtained from aluminum and magnesium phosphides, it was found in similar experiments with the sodium phosphide, made by the method of Vigier, that only a slight change could be detected.

0.2987 gram, decomposed by water at 20°, yielded 39.01 per cent. phosphine, the remaining percentage being hydrogen.

0.3467 gram, decomposed by water at 0°, the generator being immersed in ice-water, yielded 40.84 per cent. phosphine. It will be remembered that Bodroux obtained no hydrogen when he used ice-water.

[1] *Loc. cit.*

Ammonia was determined by two methods:

(1) A weighed portion of the compound was placed in a small weighing bottle and lowered into a pressure bottle containing some six-normal hydrochloric acid. The top was adjusted and the apparatus was set away for twenty-four hours for the vapor of the acid to slowly attack the compound. At the end of that time substance and acid could be intimately mingled without development of dangerous pressures. The contents of the bottle were then distilled with excess of sodium hydroxide into a standard acid and the liberated ammonia determined in the usual way by means of titration.

0.2418 gram of the compound gave 22.49 per cent. of ammonia.

(2) A second weighed portion was placed in a small U-tube and hydrochloric acid gas was forced or drawn over it and then through two U-tubes containing dilute sulphuric acid. The dilute acid itself was finally brought into contact with the substance by rapidly boiling the hydrochloric acid. The contents of the three U-tubes were then proceeded with as above.

0.4434 gram of the compound gave 22.8 per cent. of ammonia.

Gravimetric Determinations.—Sodium was determined gravimetrically as sulphate. The phosphorus was removed by oxidation with nitric acid, precipitation by lead acetate and lead carbonate. and after filtration from the phosphates, excess of lead was removed by hydrogen sulphide.

0.4627 gram of compound gave 0.6313 gram of sulphate, equal to 44.22 per cent. Na.

0.1559 gram of compound gave 0.2098 gram of sulphate, equal to 43.63 per cent. Na.

The determination of phosphorus was made in a pressure bottle with fuming nitric acid, the preliminary details being after the manner described for the absorption of ammonia. Fuming acid was used because it was certain that it would oxidize every trace of phosphine and complete the oxidation to phosphate of any lower oxygen compounds of phosphorus. The action within the pressure bottle was usually violent. In from one to two hours after closing the bottle an explosion with flame, of sufficient force to shatter the weighing glass within which was contained the substance, usually occurred within the bottle. After the lapse of several hours the bottle was gently heated in a water-bath without removal of the stopper, to complete the oxidation of all traces of

volatile phosphorus compounds. The bottle was then opened and its contents evaporated on the water-bath almost to dryness. The phosphorus was determined as magnesium pyrophosphate. The determination was verified by first precipitating a second portion to be analyzed with ammonium molybdate and then with magnesia mixture.

In the third determination, to show that there was no conversion of the phosphates into metaphosphates, the solution was boiled with a large excess of water for thirty hours, the water lost by evaporation being restored from time to time. The results reached in all these methods agreed well within the limits of experimental error.

0.2496 gram of compound gave 0.1476 gram magnesium pyrophosphate, or 16.46 per cent. phosphorus.

0.1637 gram of compound gave 0.0968 gram magnesium pyrophosphate, or 16.45 per cent. phosphorus.

0.1750 gram of compound gave 0.1064 gram magnesium pyrophosphate, or 16.91 per cent. phosphorus.

Reactions and Composition.—(1) It has been shown by analytical results that successive preparations do not possess the same composition.

(2) The products of its decomposition by water or acids are numerous. Phosphine, hydrogen, ammonia, sodium hypophosphite, sodium hydroxide. and red phosphorus have been detected and there is much reason for believing that salts of phosphorous and of phosphoric acids are also formed. There is no one salt of definite composition which can be conceived to be formed by these two reagents capable of yielding all these products simultaneously in the proportions found.

(3) It has been shown that the instability of the compound in the presence of air, heat, and the common solvents is very great, while, on the other hand, the common organic solvents, alcohol excepted, are, if dry, without action upon any of its constituents. Owing to these facts the attempt to purify the compound or to isolate any of its constituents has met with no success.

(4) Sodamide may break down in the presence of substances capable of uniting with it in either one of two ways. Thus, as in the union with water, the point of rupture in the sodamide is between the sodium and the amido group. On the other hand,

as Titherly[1] has shown, when sodamide reacts with many organic compounds, especially the organic amides, an amido hydrogen atom is substituted by the organic residue.

(5) The behavior of phosphorus is even more anomalous. The long list of phosphorus compounds, prepared by chemists from the time of Magnus and Rose to the present, show clearly that the distribution of the valencies of phosphorus toward groups with which it is capable of uniting lead to no certain generalizations. To a certain extent, but in a less degree, phosphorus resembles carbon in the formation of the complex chains. Vigier's compound has had ascribed to it the formula Na_3P. but it certainly contains a considerable portion of Na_4P_2, for its phosphine is very inflammable.

In view of all these facts the reaction between phosphorus and sodamide in the presence of an inert gas may be supposed to take place in any of the following ways:

(1) Assuming sodamide to break down into sodium and amidogen,

(a) $2P + 6NaNH_2 = 2Na_3P + 4NH_3 + N_2.$
(b) $2P + 3NaNH_2 = Na_3P + (NH_2)_3P.$
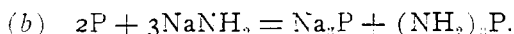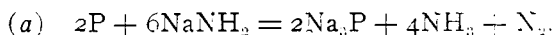
(2) Assuming sodamide to substitute phosphorus for hydrogen in the amide group,

(c) $P + 3NaNH_2 = (NaNH)_3P + 3H.$
(d) $2P + 3NaNH_2 = (NaN)_3P_2 + 6H.$
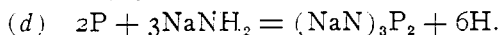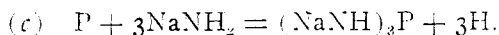
Two methods were employed in the attempt to determine which of these reactions occur:

(1) Analysis of the products of decomposition.

(2) To conduct the synthesis of the compound in such a manner that the evolved gases, if any, may be collected and their nature and amount determined. The solution of this problem would be relatively easy, if the compound were not a mixture of such great instability.

In the prosecution of the first method it was ascertained that the compound contains sodium hypophosphite through the action of the sodium hydroxide, always found in sodamide in amounts varying from 1 to 10 per cent. upon the excess of phosphorus.

The reaction is

[1] *J. Chem. Soc.* (London), **71**, 460.

$$6NaOH + 4P = 3NaH_2PO_2 + Na_3P.$$
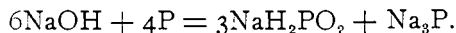
Red phosphorus is also always formed in amounts varying from 0.25 to 1.5 per cent., according to the temperature of the reacting mass and the proportion of the constituents. Inability to exclude air and moisture completely also insures the presence of other oxygen acids of phosphorus.

The analysis to determine the products of decomposition was carried on in three ways:

(1) Volumetrically, as already described, whereby the proportion of phosphine and of hydrogen was determined.

(2) Qualitatively, to show the presence of sodium hydroxide and of the salts of the acids of phosphorus.

As is well known, the recognition of hypophosphorous, phosphorous and phosphoric acids when all three are present in the same solution is a difficult matter. The presence of hypophosphorous acid could be assumed in view of the reaction between sodium hydroxide and phosphorus given above. The fresh solution also reduces potassium permanganate immediately, as do hypophosphites. The decomposition of sodium phosphide by water also yields sodium hypophosphite, as was proven by examination of the solution obtained by decomposing Vigier's sodium phosphide with water. But that phosphorous or phosphoric acids, or both. are also present is shown by the fact that after neutralization of the sodium hydroxide with acetic acid the addition of lead acetate solution gives a white precipitate, whereas lead hypophosphite is soluble in acetic acid. When ammonium molybdate is added to the solution, freshly obtained by decomposing the compound with water, a blue coloration was observed which, on standing or gentle warming. became colorless, and with the addition of a drop or two of nitric acid, well diluted, and gentle heat, the usual ammonium phosphomolybdate precipitate, indicative of phosphoric acid, was obtained.

Knowing the energetic reducing properties of hypophosphorous acid, it was at first thought that the blue color was due to reduction of the molybdic anhydride to the sesquioxide by the hypophosphorous acid, and that this could advantageously be used as a qualitative test for the presence of this acid. But when pure hypophosphorous acid was prepared free from traces of phosphine no such reduction occurred. When it is recalled that phosphine

is even more energetic as a reducing agent than hypophosphorous acid. and that phosphine is, to some extent, soluble in water and more so in a strong solution of sodium hydroxide, the reduction of the molybdic anhydride must be ascribed to the presence of phosphine. To confirm this observation it is known that phosphorous acid, reduced with nascent hydrogen, yields phosphine and hypophosphorous acid, and when ammonium molybdate solution is added to this reduction product of phosphorous acid the blue coloration is observed.

(3) Quantitatively, to determine how much of the phosphorus in the original compound went to the formation of phosphine and how much to the formation of oxygen or other compounds of phosphorus. The compound was decomposed by alcohol to prevent ignition of phosphine, the oxidation products of which would be dissolved in the liquid and vitiate the results. The solution was boiled to expel the phosphine, oxidized with nitric acid and the phosphorus precipitated with magnesia mixture.

0.1418 gram of compound gave 0.042 gram magnesium pyrophosphate, corresponding to 8.24 per cent. phosphorus.

As the total phosphorus obtained from the compound was 16.68 per cent., it is seen that the result of this experiment indicates that half of the phosphorus of the compound disappears as phosphine, and the other half remains in solution as a salt of one or more of the acids of phosphorus.

The synthesis of the compound was carried on by the aid of the apparatus described in Fig. 2. In the bottom of the generator, A, was placed a small cup of sheet aluminum to protect the apparatus from breaking in the heat generated by the reaction. After filling the apparatus with dry carbon dioxide, about 0.4 gram of phosphorus dried by benzene and approximately 0.7 gram of powdered sodamide were dropped into the cup and carbon dioxide was again passed through for some time. No combination took place in the presence of this inert gas at ordinary temperatures. The Hempel's burette, filled with sodium hydroxide solution, was attached after introducing into it a measured small portion of oxygen to act as a gas cushion. On gentle heating under diminished pressure. a quantity of gas was forced over, most of which was absorbable. After the generator had cooled to the normal temperature dry benzene (which does not decompose the compound) was admitted through the funnel and all the gas driven

into the burette. After thorough shaking the gas volume was read. Deducting for the oxygen there was a remainder of 7.58 cc. This gas was transferred to a eudiometer, exploded over mercury with a known excess of oxygen, the oxygen remaining absorbed by potassium pyrogallate solution and the remainder calculated as nitrogen. The results which, of course, are merely approximate, show that both nitrogen and hydrogen are liberated in the reaction, the latter being in slight excess. Since ammonia is also formed, the two equations which best accord with these conditions are (a) and (c), page 1506. Thermometric measurements of the temperature at which combination of phosphorus and sodamide takes place are of little value. The heat evolved is sudden and ephemeral. Reaction began at 150°, or about the melting-point of sodamide and in a few seconds rose to nearly 250° (uncorrected).

The invariable presence of hydrogen among the gases formed calls for explanation and in regard to the formation of this no information could be obtained from the published work of those who had investigated the compounds of phosphorus and hydrogen.
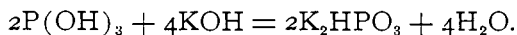
For the formation of phosphine in the usual way from phosphorus and potassium or sodium hydroxide, heated together, the following equation is usually given:

$$4P + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2.$$
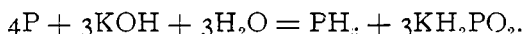
Without doubt the reaction is far more complicated, and for the sake of clearness may be assumed to take place in the following stages:

(a) $4P + 6KOH = 2K_3P + 2P(OH)_3.$

(b) $2K_3P + 7H_2O = PH_3 + KH_2PO_2 + 5KOH + 4H.$
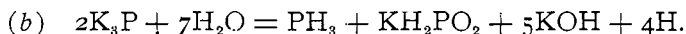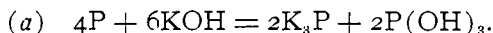
(c) with excess of KOH, as is always the case,

$$2P(OH)_3 + 4KOH = 2K_2HPO_3 + 4H_2O.$$

Whence by combination of these three and reduction to simplest terms there remains the completed equation:

(d) $4P + 5KOH + 3H_2O =$
$$PH_3 + KH_2PO_2 + 2K_2HPO_3 + 4H.$$
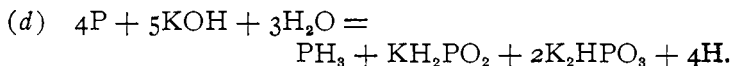
The presence of a higher oxidation product than hypophosphorous acid can be shown by the method already given. In a

similar way while we might expect a compound of the formula Na_3P to unite with water thus:

$$Na_3P + 3H_2O = PH_3 + 3NaOH.$$
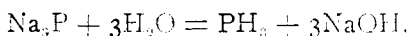
the analyses show that more complex changes occur, probably represented by

$$4Na_3P + 14H_2O = 2PH_3 + NaH_2PO_2 +$$
$$Na_2HPO_3 + 9NaOH + 10H:$$
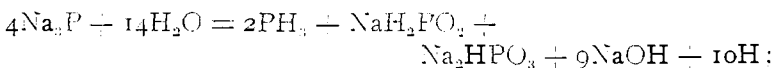
and to account for the inflammable phosphine, traces of the sodium salt of which are undoubtedly present.

$$2Na_4P_2 + 10H_2O = P_2H_4 + NaH_2PO_2 +$$
$$Na_2HPO_3 + 5NaOH + 8H.$$
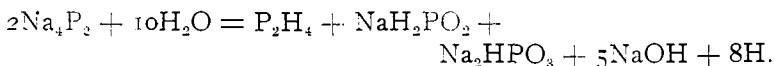
Reference should be made here to the occurrence of ammonia-nitrogen in the compound. Analysis yields 22.64 per cent. NH_3, equivalent to 21.3 per cent. NH_2. That this is not present as unchanged sodamide is definitely known from:

(1) The appearance of the compound before pulverizing it—its uniform color showing it to be quite homogeneous.

(2) This amount of NH_2 would demand over 51 per cent. of the compound to be sodamide, of which 30.58 per cent. would be sodium. The absence of free nitrogen from the gases obtained by decomposition is, of itself, proof of the absence of sodamide. But further, if, as has been shown by analyses, the amount of phosphorus in phosphine represents one-half of the phosphorus present in the form of sodium phosphide there would, on this basis, be 19.29 per cent. sodium phosphide. Of this, 13.32 per cent. would be sodium, and thus to assume sodamide present in the per cent. mentioned would, for these two compounds, require all of the sodium and all of the ammonia-nitrogen, leaving 13.7 per cent. of phosphorus unprovided for. It is justifiable, therefore, to assume some substituted amide of phosphorus to be present analogous to the substituted amides of organic compounds, described by Titherly. It could hardly be surmised that any ammonium compounds were formed. In the presence of other constituents of this compound it is impossible to say how such compounds would break down.

Sodamide as a Reagent.—Sodamide lends itself very readily to synthetical operations, and the only drawback to its use is the difficulty of obtaining it in the pure condition. Its use is also

further hampered by the difficulty of separating the by-products from the end-products desired. This is well illustrated by the present work. Sodamide affords a quick method for the preparation of impure phosphine and a number of its by-products have led into interesting theoretical discussions. Much work remains to be done with sodamide in the field of inorganic chemistry. While in the present instance the reaction is not a clean-cut one, it would be unfair to assume that with elements not so closely related, according to our present views of the periodic system, as are phosphorus and nitrogen, results of a far more satisfactory character will not be gained.

FINAL SUMMARY.

Sodamide.—

(1) Yields hydrogen and nitrogen in varying amounts when decomposed by water.

(2) Hydrogen can be almost completely eliminated
    (*a*) By prolonged heating at high temperatures with excess of NH_3.
    (*b*) By long standing in closed bottles.

(3) Nitrogen is always present and is very probably due to sodium triazoate or some analogous compound, the formation of which in sodamide is due to partial oxidation of ammonia, as pointed out
    (*a*) In process of manufacture of sodamide.
    (*b*) By long standing in presence of dry air.

(4) Occurrence of nitrous and hyponitrous acids in sodamide that has become yellow through exposure to dry air.

(5) Formation of disodium cyanamide in the wet way.

Sodamide and Phosphorus Pentachloride.—

(1) Formation of an insoluble compound which cannot be isolated from the products formed along with it without undergoing change.

(2) When thus separated by nitric or acetic acids and analyzed it is found to correspond to the formula PO_2N, or $PONHOH$.

Sodamide and Yellow Phosphorus.—

(1) Forms a complex compound containing sodium phosphide along with other products (probably an amide of phosphorus), oxygen acids of phosphorus, etc.

(2) Pressure bottle method of decomposition and analysis for explosive or volatile compounds capable of decomposition at temperatures below the boiling-point.

(3) Elaboration of methods for simultaneous recognition of hypophosphorous, phosphorous and phosphoric acids.

(4) Discussion of the source of hydrogen in the preparation of phosphine.

(5) Qualitative test for phosphine by ammonium molybdate.

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VOLATILIZATION OF PLATINUM.

By G. A. HULETT AND H. W. BERGER.

IN DETERMINING the effect of heat on barium sulphate[1] we observed a decrease in the weight of the platinum dish used. Heated to 1125° C. for four hours in an electric furnace there was a loss of 1.4 mg. and a platinum mirror was deposited on the cover of the furnace.

In 1852, Deville observed that noticeable amounts of platinum collected on the cover of the furnace in which he melted his platinum. Deville suggested that this might be due to volatilization. Aitken,[2] in 1879, in studying the formation of fog, observed that a platinum spiral glowed by an electric current gave off particles which produced a fog in an otherwise dust-free but moist atmosphere. The so-called "Zerstäubung" of electrically glowed platinum wires and points has been frequently observed, also that a metallic mirror is deposited on colder objects in the vicinity of the glowing wire. R. Nahrwold[3] paid particular attention to this phenomenon and was able to show that no "Zerstäubung" took place in an atmosphere of hydrogen or in a vacuum. It was necessary for oxygen to be present in order that the platinum wire lose weight when glowed by an electric current. Further evidence of the same nature has been obtained by W. Stewart,[4] and more particularly Holborn and Henning.[5] and Hol-

[1] Ztschr. anorg. Chem., **40.** 209 (1904).
[2] Nature, **31.** 268.
[3] Wied. Ann., **35.** 116 (1888).
[4] Ibid., **66.** 88 (1898).
[5] Sitzungsber. Berl. Akad., 1902, p. 936.