

(9) It is shown that the point of minimum dilatation is displaced upwards when triphenylmethane is dissolved in the sulphur. The displacement averages 2.8° for 1 per cent. of this foreign body.

(10) An experiment is described in which the separation of the two phases, yellow and brown liquid sulphur, may be observed.

(11) It is thus shown conclusively that there are two liquid states of sulphur which are partially, but only partially, miscible. These are S_λ , which predominates from the melting-point to 160° , and S_μ , which prevails above 160° . As the temperature ascends, saturation of the former with the latter determines the separation of the new phase, and conversely when the temperature falls.

REACTIONS IN LIQUID AMMONIA.¹

BY EDWARD CURTIS FRANKLIN.

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INTRODUCTION.

THE striking parallelism between the general properties of liquid ammonia and water has been emphasized by the writer and his co-workers in previous papers.² Water, among solvents, is characterized by its high boiling-point, its high specific heat, its high heat of volatilization and heat of fusion, its high critical temperature and pressure, its high association in the liquid condition, its high dielectric constant, by its low boiling-point elevation constant, by its power to unite with salts as water of crystallization, by its wide solvent power, and by the fact that, with the possible exception of hydrocyanic acid, it is the most powerful ionizing solvent known. Aqueous solutions of salts are also, generally excellent conductors of electricity.

Of all well-known solvents ammonia most closely approaches water in all those properties, which give to the latter its unique position among solvents. While the boiling-point of liquid ammonia is 33.6° below zero, it still appears abnormally high when compared with the boiling-points of such substances as methane, ethylene, hydrogen sulphide, phosphine, arsine, hydrochloric acid,

¹ Presented in abstract at the Philadelphia Meeting of the American Chemical Society.

² Franklin and Kraus: *Am. Chem. J.*, **20**, 820 and 836 (1898); **21**, 8 (1899); **23**, 277 (1900); Franklin and Stafford: *Ibid.*, **28**, 83 (1902).

etc.¹ The specific heat of liquid ammonia and the heat of fusion of the solid are greater than the corresponding constants for water, while its heat of volatilization, with the one exception of water, is the highest of any known liquid. Its critical temperature is abnormally high, while its critical pressure, the more characteristic constant, is higher than that of any other liquid, excepting water. Ammonia is an associated liquid, and its dielectric constant, while much below that of water, is still high. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3.4, as compared with 5.2 for water, and it quite equals, or even exceeds, water in its power to unite with salts as ammonia of crystallization. As a solvent for salts it is inferior to water, though some salts, for example, silver iodide, dissolve much more abundantly in ammonia than they do in water, and it far surpasses the latter solvent in its power to dissolve the compounds of carbon. Finally, it exhibits very marked power as an ionizing solvent, the more dilute ammonia solutions being even better conductors of electricity than aqueous solutions of the same concentration.

It is perhaps well to add that, contrary to the behavior of water, liquid ammonia does not show a maximum density above its freezing-point.

METATHETIC REACTIONS BETWEEN ORDINARY SALTS, ACIDS AND BASES IN LIQUID AMMONIA.

Reactions between Salts.—The general resemblance between ammonia and water, outlined above, led Franklin and Kraus to inquire whether the ordinary metathetic reactions take place in the former solvent as they do in the latter. This was found to be the case,² with the interesting difference that, as a result of variations in the order of solubilities in ammonia as compared with water, many reactions take place in the former solvent, which do not occur in the latter, or they may even proceed in opposite directions in the

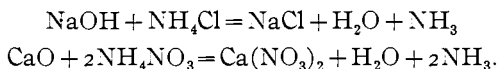
¹ The abnormally high boiling-point of liquid hydrofluoric acid, its evident association, even in the gaseous state, its power of uniting with fluorides, and the fact that Moissan has found a hydrofluoric acid solution of potassium fluoride to be a good conductor of electricity, are considerations which have led the writer to suspect that hydrofluoric acid is to be classed with water and liquid ammonia as an excellent electrolytic solvent.

Some preliminary experiments on hydrofluoric acid have shown it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, sodium nitrate, sodium chlorate, potassium bromate, acetamide, urea, and potassium sulphate are abundantly soluble; silver cyanide, barium fluoride, and copper chloride appear to dissolve to some extent, while calcium fluoride, copper sulphate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride, and metallic magnesium are insoluble.

² *Am. Chem. J.*, 21, 1 (1899).

two solvents. As examples, may be mentioned the separation of the sulphides of the alkaline earth metals as white precipitates, when solutions of soluble salts of these metals and ammonium sulphide are brought together, and the precipitation of calcium chloride when solutions of sodium chloride and calcium nitrate are mixed.

Reactions between Bases and Acids.—So far as such compounds have been tested, no metallic oxides or hydroxides are soluble in liquid ammonia. On the other hand, many acids, both oxygen acids and halogen acids, as a matter of course in the form of their ammonium salts,¹ dissolve freely in ammonia to form solutions which exhibit certain truly acid properties, as follows: First, they discharge the color of an ammonia solution of phenolphthalein, which has been rendered alkaline² by the addition of a small quantity of a base. Second, solutions of ammonium salts in ammonia dissolve sodium, potassium, calcium and magnesium with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation, $M + NH_4X = MX + NH_3 + H$. Third, many metallic oxides and certain basic salts, all the members of both classes of compounds being insoluble in ammonia, dissolve in solutions of ammonium salts. For example, Divers found sodium hydroxide, potassium hydroxide, and the oxides of cobalt, copper, lead, magnesium, mercury, cadmium, and zinc to be soluble in ammonia solutions of ammonium nitrate, while the writer has confirmed these results, and has also observed the solubility of potassium hydroxide in solutions of ammonium salts other than the nitrate. It therefore, appears, that bases dissolve in ammonia solutions of ammonium salts in a manner analogous to the solution of insoluble bases in aqueous acid solutions as indicated by the equations:



Even in water solutions what may be called the acid properties of ammonium salts are sometimes in evidence, as, for example, in

¹ Note: The acid properties of ammonia solutions of ammonium salts suggest that, analogously, in water solutions, the hydrogen ion may be associated with water as $\overset{+}{OH}_3$.

² It seems hardly necessary to emphasize the fact that the compound ammonia is not a base, and that, consequently, it is not surprising that the dry liquid has no effect upon phenolphthalein other than to dissolve it.

the solution of magnesium hydroxide and the mercuri-ammonium compounds in aqueous solutions of ammonium salts.

REACTIONS IN LIQUID AMMONIA BETWEEN COMPOUNDS RELATED TO AMMONIA AS THE ORDINARY OXYGEN SALTS, ACIDS, AND BASES ARE RELATED TO WATER.

Nomenclature.—In order to distinguish by name between the oxygen salts, acids and bases on the one hand, and those compounds which bear to ammonia relations analogous to those which salts, acids and bases bear to water on the other, the writer ventures to refer to the water derivatives as hydro-salts, hydro-acids and hydro-bases, and to offer for general use the names, ammono-salts, ammono-acids and ammono-bases, for the corresponding ammonia derivatives.

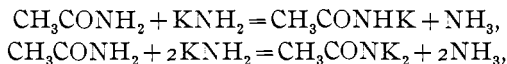
Potassium nitrate, calcium sulphate and sodium acetate are accordingly hydro-salts; potassium hydroxide and calcium oxide, hydro-bases; and acetic acid and sulphuric acid, hydro-acids; while potassium acetamide, sodium succinimide, sulphamide and mercury urea are ammono-salts; sodium amide, lead imide and mercuric nitride are ammono-bases; and acetamide, carbamide, succinimide and picramide are ammono-acids.

The relations of the halogen acids and salts and of the sulpho-acids and sulpho-salts to ammonia are quite the same as their relations to water, with the exception, of course, that the acids in solution in ammonia are present as the ammonium salts.

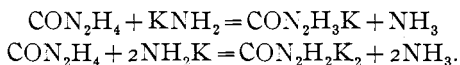
Ammono Salts.—The obvious parallelism between water and its derivatives, the bases, acids and salts on the one hand, and ammonia with its family of derivatives, the metallic amides, the acid amides, and the ammono-salts on the other, led the writer, collaborating with Mr. O. F. Stafford, to study in some detail the reactions between the acid and basic amides in ammonia solutions.¹ The result of this work was to show that the acid amides, which discharge the red color of an alkaline solution of phenolphthalein in liquid ammonia, react with the soluble metallic amides, which give the characteristic red color with the same indicator, to form metallic derivatives of the acid amides in a manner analogous to the familiar reaction between acids and bases in water solutions.

¹ *Am. Chem. J.*, 28, 83 (1902).

For example, acetamide, an ammonio-acid and potassium amide, an ammonio-base, react with each other in ammonia solutions to form potassium acetamide, an ammonio-salt, as follows:



and urea, the ammonia analogue of carbonic acid reacts with potassium amide to form potassium carbamide.



Such of these ammonio-salts as are soluble should, if the analogy between these compounds and the hydro-salts is to hold, give solutions which are good conductors of electricity. Only one such compound has so far been tested in this respect. Franklin and Kraus have found the solution of mercury succinimide to be an excellent conductor.¹

Ammonio-Salts Analogous to the Plumbates, Aluminates, Etc.—Certain metallic derivatives of ammonia, the silver, aluminum, copper and lead compounds, for example, dissolve in excess of potassium amide just as many metallic hydroxides and oxides dissolve in aqueous solutions of potassium hydroxide. The compounds formed are presumably related to ammonia as potassium aluminate, for example, is related to water. Up to the present, attempts have been made to isolate but one of these compounds. An analysis of an impure specimen of the lead derivative gave results roughly approximating the formula $\text{PbNK} \cdot \text{NH}_3$ or PbNH_2NHK .²

Other compounds belonging to the class of ammonio-salts are probably to be prepared by the action of metallic potassium or of potassium amide upon the non-metallic³ anides and imides, and perhaps even by the action of potassium amide upon the nitrides. A study of this class of reactions is now in progress in this laboratory.

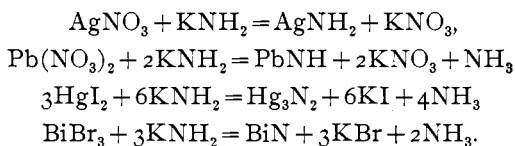
Ammonio-Bases (Metallic Amides, Imides and Nitrides).—As among the hydro-bases, the hydroxides of the alkali metals only are soluble to any considerable extent in water, so with the ammonio-

¹ This Journal, 27, 191 (1905).

² See p. 843.

³ See p. 826.

bases, it is the amides of the alkali metals which are soluble in ammonia. Indeed, potassium amide only (perhaps also rubidium and caesium amides) among the ammonio-bases is abundantly soluble in ammonia. Taking advantage of the solubility of potassium amide the writer has been able to prepare a number of insoluble metallic derivatives of ammonia by bringing soluble metallic salts and potassium amide together in ammonia solution. The new substances are thus obtained as precipitates which may be purified and analyzed, and their identity thereby established. For example, potassium amide reacts with silver nitrate to form silver amide, with lead nitrate or iodide to form lead imide, and with mercuric iodide and bismuth iodide to form mercuric nitride and bismuth nitride respectively. These reactions are represented by the following equations, which are seen to be entirely analogous to the equations representing the formation of the insoluble hydroxides and oxides from aqueous solutions:



The new bases thus obtained are insoluble in ammonia, but dissolve readily in ammonia solutions of ammonium salts, and are decomposed by the action of water with evolution of ammonia. The four above enumerated are very explosive.

The soluble members of the group of metallic amides form solutions which are good conductors of electricity and which produce color changes in ammonia solutions of various indicators in a manner analogous to the action of bases in aqueous solution.

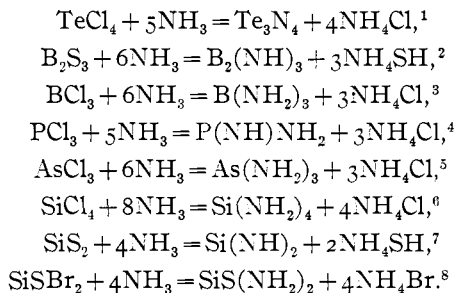
Ammono-Acids (Acid Amides, Imides and Nitrides).—The acid amides and imides derived from the organic acids constitute a very well-known group of compounds, practically every known carboxylic and sulphonic acid furnishing such a derivative. The amides of the inorganic acids are not so well known, although in recent years several such compounds have been prepared and studied,¹ among others, especially the amides of sulphuric and nitric acids. The members of the large group of ammonio-acids,

¹ Traube: *Ber. chem. Ges.*, **25**, 2472 (1892); **26**, 610 (1893); Hantzsch and Holl: *Ibid.*, **34**, 3435 (1901); Ruff: *Ibid.*, **36**, 2900 (1903); Thiele and Lachman: *Ann. Chem. (Liebig)*, **288**, 267 (1895); Franklin and Stafford: *Am. Chem. J.*, **28**, 95 (1902); Franklin and Kraus: *This Journal*, **27**, 191 (1905).

in so far at least as they are soluble, give solutions in liquid ammonia which discharge the color of alkaline solutions of phenolphthalein, which conduct the electric current—though some of them, it must be remembered, are very poor conductors—and which react with metallic amides to give representatives of the class of ammono-salts.

A further class of compounds which are properly included among the ammono-acids are the amides, imides and nitriles of the non-metallic elements. Just as the halogen derivatives of the strongly electro-negative elements, such as arsenic, phosphorus, boron, silicon, etc., are completely hydrolyzed by the action of water, so one would expect the same compounds to undergo complete decomposition in liquid ammonia, with the formation of compounds bearing relations to this solvent analogous to those which the hydrolytic products bear to water.

The following equations giving the results of recent work show that such action takes place:



Another class of ammono-acids is represented by picramide,⁹ trinitraniline, a compound related to ammonia as picric acid is to water. Ammonia solutions of picramide are excellent conductors of electricity.

Ammono-Basic Salts (Ammonolysis).—The above-cited reactions in their relation to ammonia are strictly analogous to the

¹ Metzner: *Compt. Rend.*, **124**, 32 (1897).

² Stock and Pappenberg: *Ber. chem. Ges.*, **34**, 399 (1901).

³ Joannis: *Compt. Rend.*, **135**, 1106 (1903).

⁴ Joannis: *Ibid.*, **139**, 364 (1904).

⁵ Hugot: *Ibid.*, **139**, 54 (1904).

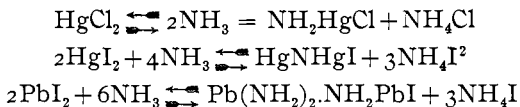
⁶ Lengfeld: *Am. Chem. J.*, **21**, 531 (1899); Vigouroux and Hugot: *Compt. Rend.*, **136**, 1670 (1903).

⁷ Blix and Wirbelauer: *Ber. chem. Ges.*, **36**, 4220 (1903).

⁸ Blix: *Ibid.*, **36**, 4219 (1903).

⁹ *Am. Chem. J.*, **28**, 102 (1902); This Journal: **27**, 197 and 215 (1905).

reactions which take place when the respective substances are treated with water. Such reactions are, therefore, appropriately designated as ammonolytic in order to recall their close relation to hydrolytic reactions. These ammonolytic reactions proceed energetically to completion just as do the corresponding reactions with water. On the other hand, as the well-known hydrolytic reactions between certain salts and water are reversible, so also many salts of mercury, lead, bismuth, and aluminum, when treated with liquid ammonia, have been found to give precipitates,¹ which are increased in amount by the addition of an ammono-base, and which are completely dissolved by the addition of an ammonium hydro- or halogen salt or of an ammono-acid. For example, when mercuric chloride, mercuric iodide, and lead iodide are treated with liquid ammonia, the following reversible equations have been found to express their respective behavior.



The ammono-basic salts NH_2HgCl , $\text{Pb}(\text{NH}_2)_2 \cdot \text{NH}_2\text{PbI}$, and Hg_2NI , appear as solid phases while the remaining components of the system constitute the liquid phase. The analogy between these reactions and the ordinary hydrolytic reactions is obvious.

THE MERCURI-AMMONIUM COMPOUNDS.

Most ammono-bases and ammono-basic salts, in the presence of water, are completely hydrolyzed into hydro-bases or hydro-basic salts and ammonia. Many mercury compounds and a few silver compounds are, however, exceptions to this rule. Especially are ammono-basic salts of mercury capable of existence in the presence of water, and as a consequence, many such compounds have been long known and are described in the literature as the mercuri-ammonium compounds.³

The action of ammonia on mercuric oxide and mercuric salts gives rise to a large group of substances upon the constitution

¹ Cf. Franklin and Cady: *This Journal*, **26**, 512 (1904).

² Francois (*Compt. Rend.*, **130**, 332 (1900)) has found the equation $\text{HgI}_2 + 4\text{NH}_3 + \text{H}_2\text{O} = \text{Hg}_2\text{NI} \cdot \text{H}_2\text{O} + 4\text{NH}_4\text{I}$ to be reversible in aqueous ammonia solution.

³ "Handb. anorg. chem." (Dammer), Vol. II, p. 896 (1894), and Vol. IV, p. 630 (1903); "Handwörterb. Chem." (Fehling), Vol. V, p. 1091 (1890); "Handwörterb. Chem." (Ladenburg), Vol. X, p. 148 (1892); "Dict. Chem." (Watts), Vol. III, p. 208 (1892).

of which the most diverse opinions have been expressed. Kane¹ showed some sixty years ago that the earlier assumption that the compounds of mercuric oxide and mercuric salts with ammonia are simple addition products, is in some cases obviously wrong, for, while certain of these compounds may be so constituted, his analyses of the infusible white precipitate showed it to have the composition HgClNH_2 . As a result of his investigations he proposed his amide theory, which for a time found considerable favor, but which was later, on the authority of A. W. Hofmann,² and especially of Rammelsberg,³ replaced by the ammonium theory, according to which these compounds are considered to be ammonium hydroxide or ammonium salts in which hydrogen is replaced by mercury. While in recent years the ammonium theory has been declared inadequate⁴ to explain the behavior of the group of compounds to which the infusible white precipitate belongs, it still finds a vigorous defender in Professor Pesci.⁵

The writer proposes to reject the ammonium theory entirely as applied to the so-called mercury ammonium compounds, and to return to the amide theory of Kane, modified to suit modern requirements, as best adapted to explain the formation and behavior of these compounds. Accordingly all the mercuri-ammonium compounds described in the literature may be classified under the three heads: first, ammono-basic salts; second, mercuric salts with ammonia of crystallization; and third, mixed hydro- and ammono-basic compounds.

I. *Ammono-Basic Salts*.—The best known representative of this class of compounds is the infusible white precipitate which

¹ *Ann. Chem.* (Liebig), 18, 135 and 288 (1836); *Pogg. Ann.*, 42, 268 (1837); *Ann. chim. phys.*, 72, 342 (1839).

Note: In the latter paper Kane makes the following remarks which are significant in the present connection:

"— "L'amidogène NH_2 peut se combiner avec les métaux; les amides métalliques ont une tendance singulière à se combiner avec les chlorures ou oxides du même métal ou d'un métal de la même famille, et à former ainsi des corps qui ressemblent aux oxichlorures, aux sulfochlorures et aux oxisulfures."

"— $\text{NH}_2 = \text{NH}_2 + \text{H}$, amidide d'hydrogène peut remplir des mêmes fonctions que l'eau, oxide d'hydrogène, soit comme une eau basique, soit comme eau de cristallisation; il peut également remplacer l'eau, à laquelle Graham a donné le nom d'eau saline, dans certaines sels."

² *Jahresber.*, 1856, p. 408.

³ *J. prakt. Chem.*, 146, 563 (1888).

⁴ Hofmann and Marburg: *Ann. Chem.* (Liebig), 305, 198 (1899); *Z. anorg. Chem.*, 23, 126 (1900).

⁵ *Z. anorg. Chem.*, 21, 361 (1899).

is found in the literature variously formulated as mercuri-ammonium chloride, $\text{Hg}:\text{NH}_2\text{-Cl}$;¹ as dimercuri-diammonium chloride, $\text{N}_2\text{H}_4\text{Hg}_2\text{Cl}_2$;¹ as a double salt of dimercuri-ammonium chloride and ammonium chloride, $\text{NHg}_2\text{Cl.NH}_4\text{Cl}$;² and as mercuric chloramide,³ $\text{NH}_2\text{.HgCl}$.

The writer's investigations show that the infusible, white precipitate and its related compounds are to be looked upon as ammono-basic salts; that is, they are compounds related to ammonia as the ordinary hydro-basic salts are to water. The infusible, white precipitate is accordingly $\text{NH}_2\text{-Hg-Cl}$, while the so-called dimercuri-ammonium salts are to be given the general formula, $\text{Hg}:\text{N-Hg-X}$, where X is any acid radical.

II. *Mercuric Salts with Ammonia of Crystallization.*—The fusible white precipitate, together with the corresponding mercuric bromide and mercuric iodide compounds, all of which are formed by the direct addition of ammonia to the respective salts, are to be included in the large class of compounds, which are properly described as salts with ammonia of crystallization. The fusible precipitate is, therefore, to be formulated as $\text{HgCl}_2\text{.}2\text{NH}_3$, and not as a double salt of dimercuri-ammonium chloride and ammonium chloride, $\text{NHg}_2\text{Cl.}3\text{NH}_4\text{Cl}$,⁴ nor yet as mercuri-diammonium chloride, $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$,⁵ although, to be sure, this latter formula may possibly represent the manner in which ammonia of crystallization is combined.

III. *Mixed Hydro- and Ammono-Basic Compounds.*—In this class are to be included all the numerous mercury ammonia compounds containing oxygen, every one of which may be formulated as compounds containing residues basic both to water and ammonia. One of the simplest members of the class is the compound 2HgO.NH_3 , which is made by the direct action of ammonia on mercuric oxide. The evidence in favor of any one of the formulas, 2HgO.NH_3 , $\text{HgO.HgNH.H}_2\text{O}$, $\text{Hg}:\text{N-Hg-OH.H}_2\text{O}$, $\text{Hg}(\text{OH})_2\text{.HgNH}$, $\text{NH}_2\text{-Hg-O-Hg-OH}$, or HO-Hg-NH-Hg-OH , which represent the substance as a mixed hydro-basic and ammono-basic compound, seems quite as good, even much better, than

¹ "Dict. Chem." (Watts), Vol. III, p. 208 (1892).

² Rammelsberg: *J. prakt. Chem.*, 146, 588 (1888); Pesci: *Loc. cit.*; Dammer's "Handbuch," *Loc. cit.*

³ Kane: *Ann. Chem.* (Liebig), 18, 135 and 288 (1836); Hofmann and Marburg: *Loc. cit.*

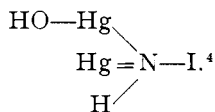
⁴ Rammelsberg: *Loc. cit.*; Pesci: *Loc. cit.*

⁵ Hofmann and Marburg: *Loc. cit.*

any the writer has been able to find in the literature in support of the formula $\text{NHg}_2\text{-OH.H}_2\text{O}$,¹ for hydrated dimercuri-ammonium hydroxide, of the formula $\text{NH}_2(\text{HgOHg})\text{-OH}$,² for oxydimercuri-ammonium hydroxide, or of the formula $(\text{NHg}_2)_2\text{O.3H}_2\text{O}$, which is included in Dammer's "Handbuch der anorganischen Chemie"³ among the dimercuri-ammonium hydroxides.

Another member of this group, which has often been the subject of investigation, is the compound $2\text{HgO.NH}_3\text{.H}_2\text{O}$, usually called Millon's base, although sometimes considered to be the hydrate of the base. There are to be found in the literature at least six different formulas for this compound, $2\text{HgO.NH}_3\text{.H}_2\text{O}$, $\text{NH}_2(\text{HgOHg})\text{OH.H}_2\text{O}$, $(\text{HOHg})_2\text{NH}_2\text{-OH}$, $(\text{NHg}_2)_2\text{O.5H}_2\text{O}$, $\text{NHg}_2\text{OH.2H}_2\text{O}$, and $\begin{matrix} \text{HgNH}_2 \\ \text{HgNH}_2 \end{matrix} \text{O.2HgO}$, in each of which, with the exception of the first, the substance is formulated as a mercuri-ammonium compound. Of the numerous possible formulas representing the compound as a mixed mercury derivative, basic both to ammonia and water, it is probably best to write simply, $2\text{HgO.NH}_3\text{.H}_2\text{O}$ or possibly, $\text{Hg}(\text{OH})_2\text{.HOHgNH}_2$ or $3\text{Hg}(\text{OH})_2\text{.Hg}(\text{NH}_2)_2$.

Another important member of this group is Nessler's precipitate, which is usually considered to be the iodide of Millon's base. The writer maintains that the formula $\text{NH}_2\text{-Hg-O-Hg-I}$, which represents the compound as a mixed ammonio-basic and hydrobasic mercuric iodide, describes the formation and behavior of Nessler's precipitate much better than does its formulation as oxydimercuri-ammonium iodide, $\text{NH}_2(\text{HgOHg})\text{I}$,⁴ or as hydrated dimercuri-ammonium iodide, $\text{NHg}_2\text{I.H}_2\text{O}$,⁴ or as hydrated tetramercuri-ammonium iodide, $\text{N}_2\text{Hg}_4\text{I}_2\text{.2H}_2\text{O}$,⁵ or yet as



EXPERIMENTAL.

The experiments described below were made to determine whether new metallic amides, imides or nitrides might be made by metathetic reactions between a soluble basic amide, potassium

¹ "Dict. Chem." (Watts), Vol. III, p. 209 (1892).

² "Handwörterb. Chem." (Ladenburg): Vol. X, p. 155 (1892).

³ Vol. II 2, p. 897 (1894).

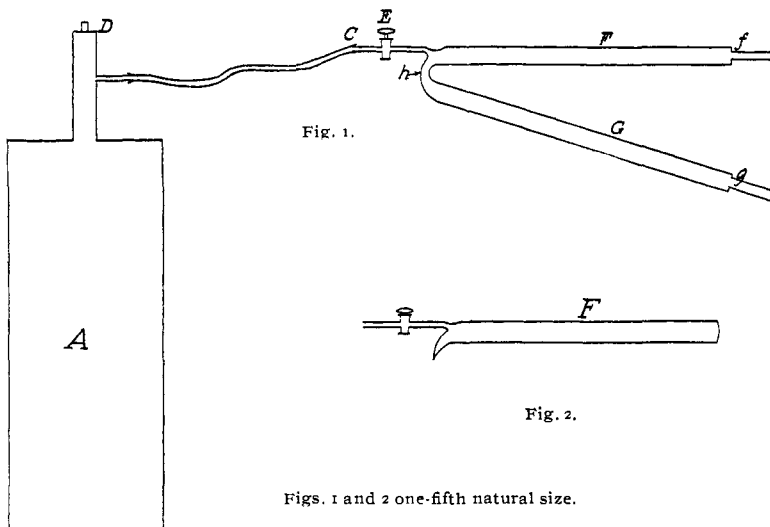
⁴ "Dictionaries of Chem."

amide, and salts of other metals in solution in liquid ammonia.

Preparation of Potassium Amide.—The potassium and sodium amides used in the previous work of the writer and his collaborators were made by the action of pure liquid ammonia on the metals,¹ the blue solution of the metals thus formed changing gradually in the course of hours, days, or even months, into solutions of the metallic amides in accordance with the equation $M + NH_3 = MNH_2 + H$.

During the earlier stages of the work described in these pages it was noticed that in certain tubes containing bits of asbestos fiber, from the filters introduced into the tubes, that the time-consuming operation of preparing the potassium amide was very markedly shortened in a number of cases. This suggested the use of some catalyzing agent to accelerate the reaction, which was soon found in spongy platinum and oxide of iron.²

Method of Manipulation.—The nature of the solvent and of the metallic amides rendered necessary the adaptation of special methods of procedure which are herewith described.



Figs. 1 and 2 one-fifth natural size.

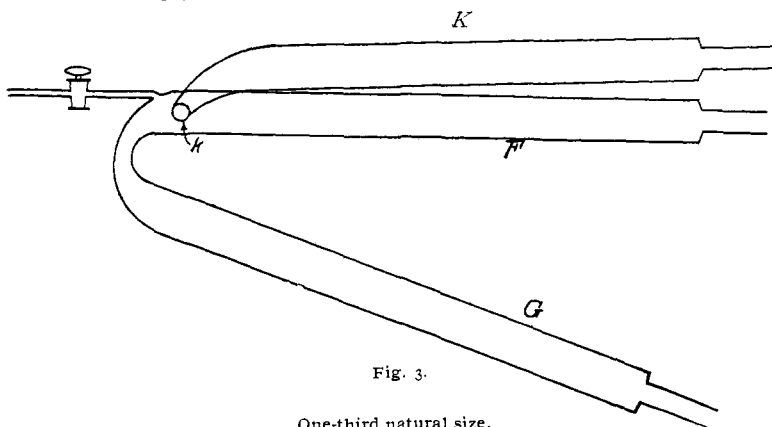
¹ Joannis: *Compt. Rend.*, 112, 392 (1891); Franklin and Stafford: *Am. Chem. J.*, 28, 83 (1902).

² It had been a matter of surprise to Franklin and Kraus during their attempts to measure the conductivity of sodium and potassium solutions to find the metal disappear so rapidly from their solutions. They also noticed that large quantities of metallic sodium introduced into the steel supply cylinders were completely transformed into sodium amide in a short space of time. The presence of platinum black on the electrodes and of ferric oxide in the cylinder account for the rapid action. *Am. Chem. J.*, 23, 306 (1900); *Ibid.*, 24, 91 (1900).

A is a steel cylinder containing purified ammonia, perfectly dried by the introduction of metallic sodium into the cylinder.¹ *FG* is the reaction tube which is attached to the exit of the ammonia container by means of small lead tubing and elastic sealing-wax, as first used by Joannis. After connection has thus been made, a slow current of ammonia is allowed to pass through the legs *F* and *G*, which are kept hot by means of a Bunsen flame, until the reaction apparatus is completely dried. With *j* closed by means of a stopper, and a current of ammonia gas escaping at *g*, a quantity of clean, unoxidized potassium is introduced into *G*, together with a few milligrams of spongy platinum. The leg *G* is then sealed off at *g*, the end blown out symmetrically and annealed to lessen the danger of explosion from the pressure, which is later developed within the tube. The shaping of the closed end of the tube is accomplished by closing momentarily the opening *j* by means of the finger. The salt is then introduced into the leg *F*, heated in a current of ammonia if necessary to insure perfect drying, and the opening *j* is closed, as has just been described, the pressure necessary for "blowing" the end *j* being obtained by removing the plug from the stop-cock *E* and closing the opening with thumb and finger. The leg *G* is now placed in ice-water and the stop-cock *E* and valve *D* are opened until the leg is about one-fourth filled with liquid, which distils over rapidly from the stock cylinder. The presence of the spongy platinum so greatly accelerates the action of the metal on the ammonia that as much as a gram of potassium will be converted into potassium amide in the course of some fifteen minutes. When the reaction is completed and the hydrogen has been allowed to escape through *E* the valve *D* is again opened and ammonia, sufficient to nearly half fill both legs, is distilled into the apparatus. The lead tube is then disconnected at *C*. When the salt in *F* is dissolved and the two solutions are homogeneous, potassium amide solution is poured from *G* into the salt solution in *F*. The precipitate, after thorough mixing with the solvent, is allowed to settle, after which the solution is poured from the precipitate into the arm *G*. The ammonia is then distilled completely from *G* into *F* by immersing *G* in luke-warm water and *F* in ice-water. The tube is shaken to thoroughly mix the precipitate with the wash liquid, the precipitate is allowed to settle, and the supernatant liquid is poured back

¹ Franklin and Kraus: *Am. Chem. J.*, 23, 285 (1900).

into *G*. This operation is repeated as many times as may be necessary for the complete washing of the precipitate. The liquid is then allowed to evaporate slowly through *E*, after which the tubes are sealed apart at *h*. In case the precipitate is very explosive the two arms are cooled off in a bath of liquid ammonia and the separation at *h* made with the precipitate protected by a covering of liquid ammonia inside the tube. The leg *F*, containing the washed and dried substance, and having now the form shown in Fig. 2, is attached to the mercury pump and evacuated, then detached and weighed. After removing the contents the tube is again evacuated and weighed, thus giving the weight of the substance for analysis. When it is desired to pour the salt solution into the solution of potassium amide a three-legged tube is used as follows:



Metallic potassium and platinum sponge are introduced into the leg *K*, and the salt into *G* as described above. After the conversion of the metal into the amide the solution is poured from the platinum sponge and bits of glass into *F* and the third leg *K* is sealed off at *h*. The further operations are then carried on as described above.

RESULTS.

Silver Amide, AgNH₂.—When a solution of potassium amide is run into an excess of silver nitrate solution a pure white precipitate separates which settles fairly well and hence may be washed by the decantation method described above. To avoid the certainty of explosion, which follows, all attempts to separate the two arms

of the preparation tube after the silver amide is dried, the arm *F* containing the precipitate protected by a deep layer of liquid ammonia, is immersed in a bath of liquid ammonia to reduce the internal pressure to that of the atmosphere. The stop-cock *C* is then opened and the preparation tube sealed apart at *h*, after which the liquid in *F* is allowed to evaporate very slowly through the stop-cock *C*, and the residual gas is removed by exhaustion on a Sprengel pump. To remove the product for analysis the tube is held in a clamp and a small quantity of dilute sulphuric acid is allowed to enter in such a manner as not to come into direct contact with the amide. The tube is then allowed to stand until the amide is decomposed and has lost its explosive properties. The residue is then brought into contact with the dilute acid and the solution thus formed removed for analysis. The ammonia was determined by the usual volumetric method and the silver precipitated and weighed as silver chloride.

From some twenty or more attempts to prepare the substance for analysis, the most of which terminated in violent explosions, the following results were obtained:

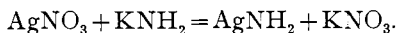
- I. 0.484 gram substance gave 0.0609 gram N and 0.5505 gram AgCl.
- II. 0.340 gram substance gave 0.0438 gram N and 0.3849 gram AgCl.
- III. 0.300 gram substance gave 0.0382 gram N and 0.3434 gram AgCl.
- IV. 0.262 gram substance gave 0.0318 gram N and 0.2992 gram AgCl.
- V. 0.549 gram substance gave 0.0617 gram N and 0.6361 gram AgCl.

	Calculated for AgNH ₂ .	Found.				
		I.	II.	III.	IV.	V.
N.....	11.19	12.6	12.9	12.7	12.1	11.2
Ag.....	87.2	85.6	85.3	86.3	86.0	87.4

The results given under I, II, III and IV are from preparations which, in all probability, were not free from adsorbed ammonia, for it was found with preparation V that, after evacuation at laboratory temperature, prolonged pumping, accompanied by gentle heating, removed additional gas from the tube. The tubes containing preparations I and II were not evacuated, but were weighed filled with ammonia gas. It seems unnecessary, however, to give

the details of the corrections for these two analyses, especially as the last three analyses leave no doubt as to the composition of the compound.

The action of potassium amide on silver nitrate in solution in liquid ammonia is therefore represented by the equation



In order to avoid exposing good analytical balances to danger of destruction from explosion the silver amide in its containing-tube was weighed on an old balance which could not be depended upon to give results nearer than about 2 mg.

Silver amide separates as a pure white, rather bulky, precipitate, which dissolves in solutions of ammonium salts. It is not soluble in excess of silver nitrate, but dissolves readily in excess of potassium amide, a behavior which probably indicates the formation of some such compound as silver potassium amide, AgNHK . The precipitate is darkened by the action of light. On drying, it shrinks very much in bulk and is left in the bottom of the tube in the form of more or less strongly discolored, sometimes black, detached masses, which explode with the greatest violence and upon the slightest provocation. During the course of this work many tubes exploded without assignable cause, shattering the containing tubes and tearing holes in several layers of stout toweling wrapped around the tube for the protection of the operator.

The above analyses were all made on silver amide prepared from silver nitrate. It seems worth while to state, however, that the formation of a precipitate, identical in appearance, by the action of potassium amide on a solution of silver iodide, shows that the reaction between a soluble ammono-base and a soluble silver salt is a general one.

The formation of an explosive substance by the action of *aqua ammonia* on silver oxide was observed by Berthollet¹ over a hundred years ago. Because, however, of the extreme instability of Berthollet's compound its composition is even yet uncertain although Raschig² concludes from determinations of the ratio of nitrogen to silver that the compound is to be represented by the formula Ag_3N .

Mercuric Nitride, Hg_3N_2 .—Mercuric iodide is abundantly soluble in ammonia, forming a dense colorless solution and leaving

¹ *Crell. Ann.*, 2, 390 (1788).

² *Ann. Chem.* (Liebig), 233, 93 (1886).

undissolved a small quantity of an ammono-basic iodide, the formation of which is prevented by the addition of ammonium iodide. The dense liquid thus formed, unlike the liquid $\text{HgCl}_2 \cdot 12\text{NH}_3$, obtained by Franklin and Kraus,¹ is miscible with ammonia in all proportions. Mercuric bromide is also very soluble in liquid ammonia with the separation of an ammono-basic salt, soluble in ammonium bromide. Like mercuric iodide and unlike mercuric chloride the ammonia addition product of mercuric bromide does not form two liquid phases in the presence of excess of liquid ammonia.

When a solution of mercuric iodide, or bromide, is run into an excess of a solution of potassium amide, a chocolate-colored precipitate is formed, which, on standing, becomes darker in color and changes from a bulky mass into a dense powder, which is easily washed. The precipitate is insoluble in excess of potassium amide, but is converted by an excess of the mercury salt into an ammono-basic salt, as described below. It dissolves readily in ammonia solutions of ammonium salts and in aqueous acid solutions. Dry mercuric nitride is very explosive, but is not so sensitive as is silver amide. It explodes on coming in contact with water and must consequently be removed from the preparation tube with all the precautions described above for removing silver amide. A number of attempts at preparing the compound ended in explosions.

For analysis the compound was dissolved in dilute hydrochloric acid. Mercury was precipitated as the sulphide and the ammonia was separated from the filtrate by distillation with the following results:

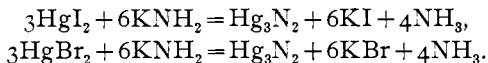
- I. 0.208 gram substance gave 0.2236 gram HgS and 0.0109 gram N.
- II. 0.4755 gram substance gave 0.5145 gram HgS and 0.0233 gram N.
- III. 0.4512 gram substance gave 0.4982 gram HgS and 0.0218 gram N.
- IV. 0.5254 gram substance gave 0.5730 gram HgS and 0.0244 gram N.
- V. 0.5626 gram substance gave 0.0245 gram N.
- VI. 0.4714 gram substance gave 0.5180 gram HgS .

¹ *Am. Chem. J.*, **23**, 299 (1900).

VII. 0.5844 gram substance gave 0.6445 gram HgS and 0.0275 gram N.

	Calculated for Hg ₃ N ₂ .	Found.						
		I.	II.	III.	IV. ¹	V.	VI. ²	VII. ²
Hg.....	95.6	92.8	93.3	95.2	94.4	95.6	95.4
N.....	4.46	5.3	4.9	4.8	4.6	4.4	4.7

Mercuric nitride therefore separates from ammonia solutions in accordance with the equations:



Since contradictory statements are found in the literature concerning the existence of mercuric nitride it seems worth while to insert here a short résumé of previous investigations upon this compound. More than sixty years ago Plantamour³ prepared a dull brown powder which he assumed to be mercuric nitride, by passing a current of ammonia gas over precipitated mercuric oxide heated to 150°. The substance was not analyzed for the reason that he was unable to free his preparation from considerable quantities of metallic mercury and unchanged mercuric oxide. Plantamour describes mercuric nitride as a dark brown (flohbraun) powder which, when heated in small portions of the size of a mustard seed, detonates with a violence scarcely less than that of nitrogen iodide.

In an abstract of his investigations upon the action of ammonia on mercuric oxide, Hirzel⁴ is reported as having made analyses confirming the formula Hg₃N₂ for Plantamour's compound.

Weyl⁵ rejects the conclusions of Plantamour and Hirzel to the effect that the product is impure mercuric nitride containing mercury and unchanged mercuric oxide, and insists that the substance is a compound containing oxygen. Weyl reports having obtained the compound Hg₂NOH at 80° to 85°, and (NHg₂)₂O at 100° by the action of ammonia on mercuric oxide.

Much more recently Hofmann and Marburg⁶ have heated both Millon's base and mercuric oxide in an atmosphere of ammonia gas and find in each case that the end-product is a loose, dark

¹ Prepared from mercuric bromide.

² Direct tests for iodine proved this element to be absent from these preparations.

³ *Ann. Chem.* (Liebig), **40**, 115 (1841).

⁴ *Ibid.*, **84**, 258 (1852).

⁵ *Pogg. Ann.*, **121**, 601, and **131**, 524.

⁶ *Ann. Chem.* (Liebig), **305**, 204 (1899).

brown, very explosive compound of the formula Hg_2NOH . They were unable to obtain mercuric nitride.

Mercuric Iodo-Nitride, Ammono-Basic Mercuric Iodide, Hg_2NI or $Hg:N-Hg-I$. (Dimercuri-ammonium Iodide.)—When potassium amide solution is added to excess of mercuric iodide in solution in liquid ammonia a reddish yellow precipitate of an ammono-basic mercuric iodide is formed. Special care must be taken to thoroughly mix the contents of the tube and to have mercuric iodide in excess, otherwise the precipitate will be contaminated with mercuric nitride. During the course of the work on this substance it was suspected that the compound Hg_2NI undergoes gradual ammonolysis during the process of washing, thus giving for analysis a mixture containing mercuric nitride or some other compound more basic than Hg_2NI . All the analytical results given below are more or less in harmony with this supposition. However, Analysis V, which was made of a specimen of the basic salt during the preparation of which special care was given to the agitation of the precipitate with an excess of mercuric iodide and to continued and thorough washing, has led to the conclusion that the results of the earlier analyses are probably due to the lack of thorough action of excess of mercuric iodide on the precipitate.

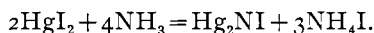
For analysis the substance was digested with dilute hydrochloric acid and metallic zinc to separate the mercury. Ammonia was then distilled off and determined volumetrically while the iodine was recovered by boiling the acidified solution with ferric chloride. The mercury in V was determined electrolytically.

- I. 0.7878 gram substance gave 0.6944 gram HgS and 0.0228 gram N.
- II. 0.7826 gram substance gave 0.6810 gram HgS , 0.0241 gram N and 0.1720 gram I.
- III. 0.4422 gram substance gave 0.0138 gram N and 0.0940 gram I.
- IV. 0.8720 gram substance gave 0.0247 gram N and 0.1880 gram I.
- V. One-fourth of 1.7463 grams substance gave 0.01183 gram N and 0.1012 gram I. Another fourth of 1.7463 grams substance gave 0.01175 gram N and 0.1003 gram I and 0.3217 gram Hg.

	Calculated for Hg ₂ Nl.	Found.				
		I.	II.	III.	IV.	V.
Hg.....	74.0	75.7	75.1	73.7
N.....	2.6	2.9	3.1	3.1	2.8	2.7
L.....	23.4	22.0	21.3	21.6	23.1

A determination of mercury in 82 mg. of the insoluble residue formed by the action of liquid ammonia on mercuric iodide gave 78 per cent. mercury. There is consequently little doubt that the product of the ammonolysis of mercuric iodide is Hg₂Nl.

The compound Hg:N-Hg-I has, therefore, been prepared from ammonia solution in accordance with the equations



This ammono-basic mercuric iodide is obtained as a dense, litharge yellow powder, which is soluble in ammonia solutions of ammonium salts, and by potassium amide is converted into mercuric nitride. It dissolves readily in aqueous solutions of ammonium iodide and is converted by dilute hydrochloric acid into a mixture of mercuric chloride, mercuric iodide and ammonium chloride. Heated in a closed tube it decomposes freely, but without explosion, yielding a sublimate of metallic mercury and mercuric iodide.

The compound Hg₂Nl was first prepared by Weyl¹ by the action of liquid ammonia upon the oxyiodide of mercury, 3HgO.HgI₂, formed by fusing together mercuric oxide and mercuric iodide in the proportions indicated by the formula. Weyl describes his product as a brown powder which explodes when heated to 130°.

A non-explosive compound of the same formula has been prepared by François² by the action of a large excess of aqua ammonia on mercuric iodide. François obtained the anhydrous compound in the form of almost black crystals.

Mercuric Brom-Nitride, Ammono-Basic Mercuric Bromide, Hg₂NBr or Hg-N-Hg-Br. (Dimercuri-ammonium Bromide).—When potassium amide solution is added to an excess of solution of mercuric bromide a pure yellow precipitate of an ammono-basic mercuric bromide is formed which soon settles to the bottom of the tube as a dense powder. As first formed the precipitate is always more or less mixed with the brown mercuric nitride which is formed

¹ *Loc. cit.*

² *Compt. Rend.*, 130, 332 and 571 (1900).

at the junction of the two liquids, along with the basic salt, when the two solutions are brought together. When, however, the precipitate is shaken with an excess of mercuric bromide the brown areas disappear, after a time, and the whole precipitate takes on the pure yellow color of the ammono-basic salt. The compound is soluble in ammonia solutions of ammonium salts and in aqueous acid solutions. Potassium amide converts it into mercuric nitride.

For analysis the substance was dissolved in dilute sulphuric acid, from which solution the mercury was separated as sulphide. The filtrate from mercuric sulphide was divided into two parts, from one of which the ammonia was separated by boiling with potassium hydroxide. The bromine was removed from the other half as silver bromide after oxidizing the hydrogen sulphide by means of ferric sulphate.

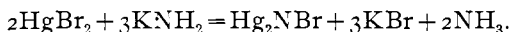
- I. 0.3230 gram substance gave 0.3049 gram HgS. One-half of 0.3230 gram substance gave 0.00558 gram N; the other half gave 0.0570 gram AgBr.
- II. 0.9176 gram substance gave 0.8686 gram HgS. One-half of 0.9176 gram substance gave 0.01715 gram N; the other half gave 0.1623 gram AgBr.

	Calculated for Hg ₂ NBr.	Found.	
		I.	II.
Hg.....	81.0	81.4	81.7
N.....	2.8	3.46	3.7
Br.....	16.2	15.0	15.0

These results, which were obtained from two entirely separate preparations, do not point to a pure compound. The low results for bromine and the slightly high content of mercury may be due to the presence of mercuric nitride formed either when the solutions of mercuric bromide and potassium amide were mixed or later as the result of the ammonolysis of the basic compound during the process of washing the precipitate for analysis. The high results for nitrogen may perhaps be accounted for by the presence of adsorbed ammonia. Both specimens were dried *in vacuo* at laboratory temperature.

Notwithstanding these rather unsatisfactory results, there seems to be but little doubt that an ammono-basic mercuric bromide is

formed by the action of potassium amide upon an excess of mercuric bromide in liquid ammonia solution as follows:



Dimercuri-ammonium bromide has previously been made by the action of aqueous ammonia on mercuric bromide solution.¹

Mercuric Chloramide, Ammono-Basic Mercuric Chloride, NH₂HgCl. (Infusible white precipitate. Mercuri-ammonium chloride). —When mercuric chloride is brought into contact with liquid ammonia an addition-product having the composition HgCl₂.12NH₃² is formed, which is but slightly soluble in liquid ammonia.³ The compound is solid at low temperatures, melts somewhere in the vicinity of 0°, and at temperatures above its melting-point forms a two-phase system with excess of liquid ammonia. At laboratory temperature and pressure the compound HgCl₂.12NH₃ loses ammonia and is converted into the well-known fusible white precipitate HgCl₂.2NH₃. The action of ammonia on mercuric chloride is accompanied by the formation of a small quantity of a white residue insoluble in liquid ammonia, but readily converted into the liquid HgCl₂.12NH₃ in the presence of ammonium chloride. A specimen of the substance, which showed itself to be the well-known infusible white precipitate, NH₂HgCl, was prepared by treating some 25 grams of mercuric chloride with excess of liquid ammonia, pouring the ammonia and heavy liquid HgCl₂.12NH₃ from the residue, and washing the latter in the usual manner for analysis.

I. 0.6825 gram substance gave 0.6291 gram HgS; one-half of 0.6825 gram substance gave 0.0194 gram N; the other half gave 0.2000 gram AgCl.

	Calculated for NH ₂ HgCl.	Found.
Hg	79.7	79.5
N	5.7	5.6
Cl	14.1	14.5

Liquid ammonia, therefore, reacts with mercuric chloride in accordance with the equation



which also represents the behavior of the same salt towards

¹ Pesci: *Gazz. chim. ital.*, 19, 509.

² Franklin and Kraus: *Am. Chem. J.*, 23, 299 (1900).

³ The statement of Weyl, *loc. cit.*, to the effect that mercuric chloride is very soluble in liquid ammonia is therefore erroneous.

aqueous ammonia. In liquid ammonia solutions the presence of a small quantity of ammonium chloride prevents the formation of the ammono-basic salt. In aqueous ammonia solution, on the contrary, a large excess of ammonium chloride is necessary to insure a pure precipitate of $\text{HgCl}_2 \cdot 2\text{NH}_3$.

Mercuric chloramide is also formed by the action of sodium amide upon excess of mercuric chloride. Neither of these substances dissolves freely in liquid ammonia. The heavy liquid addition-product of mercuric chloride was therefore poured in large excess upon the sodium amide and the mixture allowed to stand several days with occasional shaking. The residue was then washed by the method described above to remove sodium chloride and excess of $\text{HgCl}_2 \cdot 12\text{NH}_3$. Excess of sodium amide changes the color of the white product thus obtained to dark brown, a result undoubtedly due to the formation of mercuric nitride.

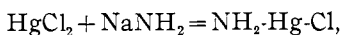
The analysis of the substance, which was conducted as described above, follows:

1.5847 grams substance gave 1.4915 grams HgS ; 22/50 of 1.5847 grams substance gave 0.3778 gram AgCl , and 28/50 of 1.5847 grams substance gave 0.0482 gram N .

	Calculated for NH_2HgCl .	Found.
Hg	79.7	81.4
N	5.6	5.5
Cl	14.1	12.7

Evidently the product was not pure HgClNH_2 . An admixture of a small quantity of a more basic chloride or of mercuric nitride would not be surprising in view of the nature of the mixture from which the preparation was separated.

The equations:



and



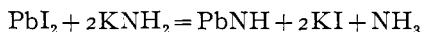
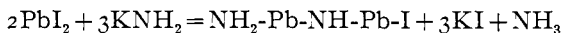
therefore represent the action of sodium amide upon mercuric chloride in ammonia solutions.

Reactions between Lead Nitrate and Potassium Amide.—Lead nitrate dissolves readily in liquid ammonia, forming a milky solution which is cleared up by the addition of a small quantity of an ammonium salt. Addition of potassium amide to this solution

gives a precipitate of a white basic salt. Further quantities of potassium amide increase the amount of the precipitate and at the same time change the color through darker shades of yellow to an orange-red. This orange-colored precipitate which is at first flocculent and voluminous, after a time becomes darker in color and changes into a dense powder. Excess of potassium amide dissolves the precipitate completely with the formation, probably, of lead potassium imide, $PbNK$, or lead potassium amide. Attempts to isolate the compound thus formed have been made, but so far have not led to satisfactory results, for the reason, principally, that the compound is very soluble in ammonia, and is, therefore, difficult to separate from the solution in a pure form. Lead, nitrogen and potassium determinations on an impure specimen gave results roughly approximating the formula $PbNH_2NHK$ or $PbNK.NH_3$. A second purer specimen of colorless, efflorescent crystals was lost by its violent explosion, which occurred on bringing dilute acetic acid into contact with the compound preparatory to analysis. Further attempts to isolate and analyze this compound will be made.

Reactions between Lead Iodide and Potassium Amide.—When lead iodide is brought into contact with gaseous ammonia no action takes place at the ordinary pressure and temperature. Under increased pressure, however, a white addition-product is formed which dissolves freely in liquid ammonia, leaving behind a white or slightly yellowish precipitate of an ammono-basic salt. Addition of a little ammonium iodide gives a perfectly clear, colorless solution. Potassium amide added to this solution gives, as with lead nitrate, first a precipitate of a white basic salt, which is changed by further addition of the ammono-base into lead imide, which latter then dissolves in excess of potassium amide.

The following equations represent the action of potassium amide upon lead iodide solutions:



Similar equations represent the action of potassium amide upon lead nitrate.

Lead Imide, $PbNH$.—The preparation of pure lead imide is attended with considerable difficulty, principally for the reason

that the absence of a basic salt cannot be insured by the use of an excess of the precipitant. An excess of potassium amide immediately dissolves the precipitate. A number of attempts were made to prepare lead imide by the action of potassium amide upon lead nitrate in ammonia solution all of which, however, gave products more or less contaminated with basic salt. After the first preliminary experiments, the following results were obtained:

- I. 0.5612 gram substance gave 0.7452 gram PbSO_4 and 0.0353 gram N.
- II. 0.3056 gram substance gave 0.4028 gram PbSO_4 and 0.0206 gram N.
- III. One-half of 2.0229 grams substance gave 1.0360 grams PbS and 0.0019 gram K_2SO_4 .¹ The other half of 2.0229 grams substance gave 0.0672 gram nitrogen and 0.0486 gram NO_3 .
- IV. 0.1670 gram substance gave 0.2178 gram PbSO_4 and 0.0109 gram N.
- V. 0.8930 gram substance gave 0.9432 gram PbS and 0.0533 gram N.

	Calculated for PbNH .	Found.				
		I.	II.	III.	IV.	V.
Pb.....	93.3	90.7	90.2	88.7	89.2	91.7
N.....	6.3	6.25	6.75	6.7	6.55	6.0
NO_3	4.8

In support of the assumption that the low percentage of lead in these preparations is due to the presence of basic salt are the observations that all these preparations were distinctly lighter in color than the lead imide prepared from lead iodide as described below. Furthermore, tests for nitrates in Preparation III showed them to be present to the extent indicated.

After the failure of the above-described attempts to prepare pure lead imide the following procedure was found to give a nearly pure product. Lead iodide solution was added slowly and in small portions at a time to a solution of potassium amide until a considerable quantity of the orange-red precipitate was formed.

¹ 0.0019 gram potassium sulphate is the equivalent of 0.0022 gram or 0.21 per cent. potassium nitrate, the amount left in the lead precipitate after washing.

The contents of the tube were thoroughly agitated, and the precipitate was allowed to stand for twenty-four hours, or more, in contact with the mother-liquor during which time the precipitate took on a darker color and changed to a dense, pulverulent mass. After washing in the usual manner with liquid ammonia, and drying *in vacuo* at laboratory temperature, the following analytical results were obtained:

- I. 0.1956 gram substance gave 0.2101 gram PbS.
- II. 0.5689 gram substance gave 0.7674 gram PbSO₄ and 0.0365 gram N.

	Calculated for PbNH ₃ .	Found.	
		I.	II.
Pb.....	93.3	93.2	92.2
N.....	6.3	(5.6) ¹	6.4

Iodine was proved, by direct tests, to be absent from both these preparations.

Dry lead imide is obtained by the above process in the form of a dense, amorphous mass of reddish brown color. It explodes violently when heated or on coming in contact with water or dilute acids. After decomposition by the slow action of water vapor it dissolves readily in dilute acetic acid or potassium hydroxide solution.

Ammono-Basic Lead Iodide, Pb₂N₂H₃I or NH₂-Pb-NH-Pb-I, or Pb : N-Pb-I.NH₃, or PbNH.PbNH₂I.—When potassium amide solution is poured upon a solution of lead iodide a precipitate which is orange-red on the upper surface and pure white below is formed at the junction of the two solutions. From the lower side of the mass of precipitate occupying a zone between the two solutions, the white basic iodide gradually falls through the lead iodide solution to the bottom of the tube, while from the upper surface of the precipitate the orange-colored lead imide goes into solution in the excess of potassium amide. Agitation of the tube, so long as the lead iodide is in excess, converts the lead imide into basic salt. The substance is thus obtained as a bulky white precipitate which refuses to settle to a small volume. Thorough washing of the precipitate by decantation is, therefore, a time-consuming operation. On allowing the ammonia to escape, the substance is left in the bottom of the tube in the form of white, detached masses which lose ammonia and change in color through

¹ Large losses of ammonia were known to have occurred.

shades of yellow to a dark brown when the temperature is raised gradually to 200°. Basic lead iodide is soluble in ammonia solutions of ammonium salts, and is converted by potassium amide into lead imide after which further addition of potassium amide dissolves the precipitate to form a potassium derivative, probably of the formula $PbNK$ or NH_2PbNHK , as indicated above. The compound is not explosive.

The following analytical results were obtained:

- I. This specimen lost its pure white color and was changed to a lemon-yellow when dried *in vacuo* at 100°. 1.0912 grams of the substance gave 0.8898 gram PbS and 0.0647 gram N.
- II. This specimen, dried at laboratory temperature, was yellowish in color, the result probably of loss of ammonia or of an admixture of a small quantity of lead imide. 0.2582 gram of the substance gave 0.2709 gram $PbSO_4$ and 0.0541 gram iodine.
- III. This preparation was heated *in vacuo* at gradually increasing temperature to 200° until ammonia was no longer given off. The color of the compound was changed to a dark brown by this treatment. 0.7370 gram of the white compound, on heating to 200°, lost 0.0252 gram NH_3 . Calculated for the loss of one molecule of ammonia from $Pb_2NI.2NH_3$, 2.9 per cent. Found, 3.4 per cent. 0.6758 gram of the substance, after heating to 200°, gave 0.7185 gram $PbSO_4$ and 0.0332 gram N.

	Calculated for		Found		
	$Pb_2NI.NH_3$	$Pb_2NI.2NH_3$	I.	II.	III.
Pb.....	72.4	70.3	70.8	71.7	72.8
N.....	4.9	7.1	5.9	4.9
I.....	22.2	21.6	20.9

The white substance is, therefore, probably the compound $Pb_2NI.2NH_3$. There can be no doubt that the formula $Pb_2NI.NH_3$, or better perhaps $NH_2PbNHPbI$, represents the composition of the dark brown compound formed by heating the white salt to 200° *in vacuo*.

Ammono-Basic Lead Nitrate, $Pb_2N(NO_3).nNH_3(?)$.—The basic compound formed as described above by the action of potassium amide upon a solution of lead nitrate is obtained as a white, or

slightly yellow, amorphous precipitate which does not settle well and which is therefore washed with considerable difficulty. Small portions of the dry product dropped upon water are vigorously decomposed; in the case of larger pieces the decomposition is sometimes accompanied by explosions. Heated in a glass tube the substance explodes. All that can be said at the present time concerning this product is that determinations of lead and ammonia in two poorly washed specimens show it to be an ammono-basic mixture. Analyses of two specimens gave, respectively, 79.0 and 79.8 per cent. lead, 7.6 and 7.2 per cent. nitrogen and 4.9 and 1.0 per cent. potassium nitrate, which had not been removed during the washing of the precipitate. The results of further work on this compound will be given in a later paper.

Bismuth Nitride, BiN.—When bismuth iodide is brought into contact with liquid ammonia it goes rapidly into solution, leaving behind a reddish brown residue, presumably of a basic salt, which is increased in amount by the addition of potassium amide to the solution. When bismuth iodide is run into a solution of potassium amide, a darker brown precipitate is formed, and there is deposited at the same time more or less metallic bismuth as a mirror on the walls of the containing tube. The precipitate settles well and is easily washed. When the precipitate is dried its color changes to very dark brown, almost black, and it seems always to undergo gradual decomposition as is indicated by the fact that metallic bismuth is always left behind on treating the dried precipitate with dilute hydrochloric acid preparatory to analysis. The dry substance explodes on being heated or on coming into contact with water or dilute acids. It is indeed so sensitive that four of the eight attempts to prepare the compound ended in inexplicable explosions. For analysis, the dry substance was decomposed by the slow action of water vapor, after which in the case of Specimen I it was dissolved in nitric acid, while Specimens II and III were treated with dilute hydrochloric acid. Complete solution accompanied by the evolution of red fumes followed the treatment of the first preparation with nitric acid. Residues of metallic bismuth remained undissolved after the action of dilute hydrochloric acid on the other two specimens.

Bismuth bromide also dissolves freely in liquid ammonia with the separation of a bulky, white mass of a basic salt which dissolves in excess of ammonium bromide. This solution gives the same

brown precipitate of bismuth nitride when added to a solution of potassium amide. Preparation III below was made from bismuth bromide.

- I. 0.0986 gram of the substance, after solution in dilute HNO_3 , gave 0.1070 gram Bi_2O_3 and 0.0037 gram N.
- II. One-half of 0.2779 gram substance treated with dilute HCl gave 0.1380 gram Bi_2O_3 and 0.00821 gram N; the other half of 0.2779 gram of the substance gave 0.1377 gram Bi_2O_3 and 0.00821 gram N. The insoluble residue was lost. The ratio of Bi to N in the soluble portion is 1.015 to 1.000.
- III. 0.2376 gram substance left on treatment with dilute HCl 0.0335 gram of residue and gave 0.2350 gram Bi_2S_3 and 0.0128 gram N.

	Calculated for BiN.	Found.		
		I.	II.	III.
Bi.....	93.7	97.3	89.2	80.4
N.....	6.3	3.7	5.9	5.4
Residue.....	0.0	lost	14.1

If the percentages of bismuth and nitrogen in the soluble portions only of Specimens II and III are calculated, then the following results are obtained:

	Calculated for BiN.	Found.	
		I.	II.
Bi.....	93.7	93.7	93.6
N.....	6.3	6.2	6.3

These are in the best of agreement with the formula BiN . The product obtained, as described above, is therefore, a mixture of bismuth nitride and metallic bismuth. A similar reducing action of the potassium amide solution, the cause for which is not obvious, has been observed many times in connection with the experiments on the silver, lead, mercury and copper compounds.

Bismuth nitride has been prepared from both bismuth iodide and bismuth bromide in accordance with the equations



and



Action of Potassium Amide on Aluminum Iodide.—Aluminum iodide reacts vigorously with ammonia gas, much heat is evolved, and, if the action is allowed to proceed rapidly, much ammonium iodide is volatilized and condensed on the cooler portions of the tube. On condensing ammonia upon the reaction-mixture everything goes into solution with the exception of a small quantity of a white residue which may be either an ammonio-basic salt or possibly an impurity from the aluminum iodide used. When aluminum iodide is added to a potassium amide solution a white precipitate is formed, which dissolves immediately in excess of the latter solution. A permanent precipitate is formed when the aluminum iodide is in excess. This precipitate is white, very bulky, and refuses to settle well, so that complete washing by decantation is practically impossible. When the solution of the white precipitate in excess of potassium amide is evaporated, the solution becomes thick and viscous without showing any signs of crystallization, whence it appears that the prospects for the isolation of a potassium aluminum derivative of ammonia are not promising.

The results of the analyses of two separate preparations of the white basic precipitate gave respectively: for aluminum 20.7 and 21.6 per cent., for nitrogen 30.9 and 29.6 per cent., and for iodine 41.8 and 44.0 per cent., while a third specimen gave 23.6 per cent. nitrogen. These results lead to no very probable compound, but agree roughly with either of the formulas Al_2IN_5 and Al_2IN_6 . The precipitate, therefore, may be an equimolecular mixture of aluminum amide, $Al(NH_2)_3$, and aluminum iodo-amide, $AlI(NH_2)_2$. It is in any case an ammonio-basic product.

Action of Ammonia on Antimony Iodide.—Ammonia gas acts upon antimony iodide with the evolution of heat and the formation of a white addition product, which by the action of liquid ammonia is gradually converted into a pure yellow, pulverulent mass. The product is apparently insoluble in ammonia, or in a solution of either ammonium iodide or potassium amide.

The analysis of a specimen which was allowed to lie in contact with a solution of potassium amide over night gave 74.3 per cent antimony, and 9.6 per cent. nitrogen. Iodine was not determined quantitatively, but was proved to be present by a qualitative test. Analysis of the product of the action of ammonia

alone on antimony iodide gave as the results of two separate experiments, 70.8 and 73.4 per cent. antimony, 10.8 and 9.8 per cent. nitrogen and 15.1 and 15.7 per cent. iodine. Calculation from the mean of these results leads approximately to the formula $\text{Sb}_5\text{N}_6\text{I}$. This formula may be interpreted as the basic compound $(\text{NH}_2)_2\text{SbI}_{.4}\text{SbN}$, or what is perhaps more probable, the reaction mass is simply a mixture of antimony nitride with unchanged antimony iodide. A mixture of one molecule of $\text{SbI}_{3.4}\text{NH}_3$ with 14 molecules of SbN would have a composition close to that of the products of the above experiments.

The impure antimony nitride as above prepared is pure yellow in color, and explodes, but with little violence, when heated or when dropped into water or dilute acids.

The antimony and aluminum derivatives of ammonia will receive further attention in this laboratory.

SUMMARY.

In this paper attention is called to the striking parallelism between the physical properties of the two electrolytic solvents, water and ammonia.

The close analogy between the relations of the acid amides, the metallic amides, and the metallic derivatives of the acid amides to ammonia on the one hand, and the relations of the ordinary oxygen acids, bases and salts to water on the other, is emphasized, and a system for naming the former class of derivatives is proposed.

The ammonia derivatives bearing to ammonia the relations which the ordinary salts, bases and acids bear to water are given the names, *ammono-salts*, *ammono-bases* and *ammono-acids*.

The word *ammonolysis* is offered as a suitable designation for a class of reactions in which ammonia plays a part analogous to the action of water in ordinary hydrolytic reactions.

The so-called mercuri-ammonium compounds of the literature are interpreted as belonging to one of three classes of ammonia derivatives: first, compounds related to ammonia as ordinary basic compounds are related to water; second, salts with ammonia of crystallization; and third, mixed compounds basic to both ammonia and water.

In the experimental part are given details of work from which the following general conclusions are drawn:

Salts of the heavy metals in solution in liquid ammonia react with the soluble amides of the alkali metals to form amides, imides or nitrides of the former in a manner analogous to the formation of insoluble hydroxides and oxides in aqueous solutions.

Certain metallic salts undergo ammonolysis in liquid ammonia in a manner analogous to hydrolytic decomposition in water.

Many metallic salts, when in excess, react with soluble metallic amides to give ammono-basic salts after the manner of the formation of ordinary basic salts in water solutions.

The insoluble metallic amides, imides, and nitrides, as well as the ammono-basic salts, dissolve in liquid ammonia solutions of ammonium salts in a manner analogous to the solution of the corresponding oxygen compounds in aqueous acids.

Certain ammono-bases dissolve in excess of potassium amide solution in a manner analogous to the solution of certain metallic hydroxides in aqueous potassium hydroxide.

The following compounds have been prepared from liquid ammonia solutions:

- Silver amide, AgNH_2 .
- Mercuric nitride, Hg_3N_2 .
- Ammono-basic mercuric iodide, Hg_2NI .
- Ammono-basic mercuric bromide, Hg_2NBr .
- Ammono-basic mercuric chloride, HgNH_2Cl .
- Lead imide, PbNH .
- Ammono-basic lead iodide, $\text{Pb}_2\text{NI}\cdot\text{NH}_3$.
- Bismuth nitride, BiN .

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THE BOILING-POINTS OF AMMONIA, METHYL AMINE, METHYL CHLORIDE AND SULPHUR DIOXIDE.

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THE VALUES given in the literature for the boiling-points of a number of low-boiling liquids have been determined almost exclusively by means of measurements of the vapor-pressures, and as there is a great lack of agreement in the various results, the writer has undertaken a criticism and revision of the earlier work and a direct determination of the boiling-points. Improved meth-