of the same order as that shown by the individual salts in solutions of hydrochloric acid.[1] It is much more pronounced for sodium chloride than for the potassium salt, so that the curves representing these two solubilities intersect at a point corresponding to 16.2% of hydrochloric acid. Here the solubilities of the two salts are equal, amounting to 4.4%. As the acid solution becomes still more concentrated the saturated mixture contains an increasingly larger proportion of potassium than of sodium chloride. However, in such strong acid solutions the solubility of both salts is very small, amounting to only 2.9% of potassium chloride and 2.2% of sodium chloride in the constant boiling point (20.3%) acid. Apparently this precludes the consideration of hydrochloric acid as a reagent in the commercial separation of the two salts in question.

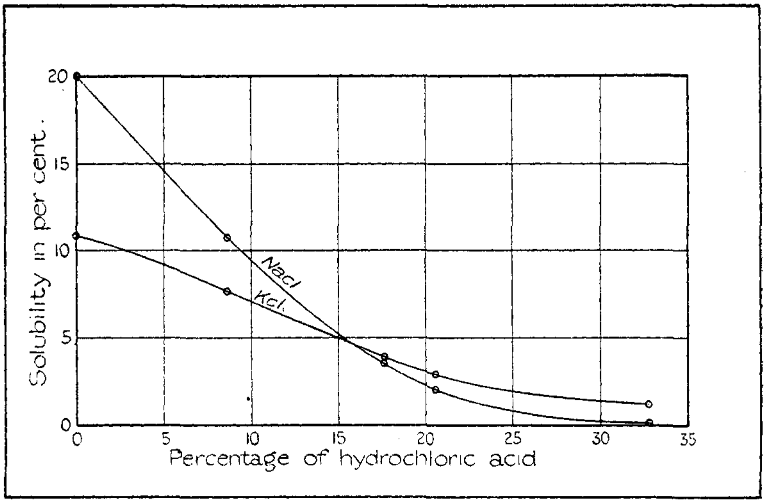

Fig. 2.

WASHINGTON, D. C.

AMMONOBASIC ALUMINIUM IODIDES.

BY EDWARD C. FRANKLIN.

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Introduction.

Some years ago the observation was made that very considerable quantities of potassium amide may be added to liquid ammonia solutions of aluminium iodide without causing the formation of a permanent precipitate. With further additions of the alkaline amide a precipitate is formed which then dissolves again in an excess of potassium amide.[2]

In the light of the many demonstrated analogies between the reactions

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[1] Engel, *Ann. de Chim. Phys.*, [6] 13, 374 (1888).

[2] THIS JOURNAL, 27, 849 (1905).

which take place in the two solvents ammonia and water the probable explanation of these observations is, first that the solution to which a limited amount of potassium amide has been added contains a soluble ammonobasic iodide of aluminium; second, that the precipitate is either an insoluble ammonobasic iodide or aluminium amide and, third, that the solution of the precipitate in an excess of potassium amide results in the formation of an ammonoaluminate of potassium.

It was for the purpose of attempting the isolation of a soluble ammonobasic aluminium iodide that the present investigation was undertaken. At the same time it was hoped that the experience in the manipulation of liquid ammonia solutions gained in the interim might enable the experimenter to isolate an ammonoaluminate of potassium and to show the insoluble precipitate studied several years ago[1] to be an ammonobasic salt of definite composition. A beautifully crystalline ammonobasic iodide of aluminium has been isolated and the existence of an insoluble ammonobasic salt is shown to be probable, but the extreme solubility of the product of the action of excess of potassium amide on aluminium iodide has so far rendered ineffectual all attempts to isolate an ammonoaluminate of potassium.

Preparation of Aluminium Iodide.—For the purposes of this investigation a quantity of aluminium iodide was synthesized by the interaction of aluminium turnings and iodine and prepared for use by distillation in vacuum into long glass tubes after the manner described by Fitzgerald.[2] The salt distills over as a clear, colorless liquid which soon solidifies to a crystalline solid. As a check on the purity of the salt an analysis was made, with the result that it was found to contain 6.6% aluminium and 93.1% iodine. Theoretically aluminium iodide should contain 6.6% aluminium and 93.4% iodine.

Ammonated Aluminium Iodide, $AlI_3.6NH_3$ and $AlI_3.20NH_3$.—When ammonia gas is brought into contact with aluminium iodide vigorous absorption takes place which, unless the action be restrained, produces sufficient elevation of the temperature to volatilize some of the material. When the salt is introduced into the reaction apparatus contained in sections of glass tubing cut from the containers described by Fitzgerald[1] then the action of the solvent on the salt is accompanied by more or less active boiling of the liquid in immediate contact with the salt, but the large mass of liquid and the small surface of contact between the liquid and the salt effectively prevents too great a rise in temperature. Aluminium iodide is extremely soluble in liquid ammonia. At —33° the very concentrated solution solidifies to a mass of crystals containing about 20 molecules of ammonia of crystallization. At 8° to 13° these

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[1] *Loc. cit.*

[2] THIS JOURNAL, 29, 1694 (1907).

crystals melt, but before fusion is complete there begins the separation of crystals containing less ammonia of crystallization, presumably a compound of the composition represented by the formula $AlI_2.6NH_3$. On further elevation of the temperature the quantity of this latter salt separating from the solution greatly increases. On cooling, these crystals again go into solution but usually before they are completely dissolved the whole liquid solidifies to a mass of the more highly ammonated salt. One obviously here observes a transition point similar to the many familiar examples taking place in water solutions.

The composition of one ammonated salt is fixed by the following analytical data. The composition of other more highly ammonated salts remains uncertain though the existence of a compound of the formula $AlI_3.20NH_3$ seems to be established.

A portion of the ammonated salt dried in vacuum at 100° to 190° weighed 1.0730 g., one-fourth of which gave 0.0289 g. Al_2O_3. Another fourth gave 0.3703 g. AgI and a third fourth gave 0.0531 g. N. At —33° this specimen of salt retained in one experiment 0.4763 g. NH_3, in another 0.5065 g. NH_3.

	Calculated for $AlI_3.6NH_3$.	Found.
Al	5.3	5.7
I	74.7	74.6
N	20.0	19.8

Calculated for $14NH_3$, 46.7; found, 44.4 and 47.2.

Soluble Ammonobasic Aluminium Iodide, $Al(NH_2)_3.AlI_3.6NH_3$.—Pure aluminium iodide dissolves in liquid ammonia to a perfectly clear, colorless solution.[1] When potassium amide is added to such a solution a white, amorphous precipitate is formed which redissolves on mixing the contents of the reaction tube. This operation is continued until a very considerable amount of potassium amide has been added, but is stopped short of the formation of a permanent precipitate. The work described below shows that there is in solution a soluble ammonobasic salt formed in accordance with the equation

$$2AlI_3 + 3KNH_2 = Al(NH_2)_3.AlI_3 + 3KI,$$

and that the permanent precipitate formed by further additions of potassium amide to the solution of aluminium iodide is another ammonobasic salt containing much less iodine.

In order to isolate the soluble ammonobasic salt, the solution prepared as described above its evaporated until a satisfactory crop of crystals is deposited but not so far as to bring about the separation of any crystals of potassium iodide from the solution. The mother liquor is then poured into the second arm of the reaction tube and sufficient solvent is distilled

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[1] The suggestion made in an earlier paper (THIS JOURNAL, 27, 849 (1905)) that an insoluble residue left on dissolving aluminium iodide in liquid ammonia was probably an ammonobasic salt is, therefore, erroneous.

from the mother liquor back upon the crystals to bring them into solution. Such portions of the solvent are again evaporated away as will result in a good crop of crystals when the mother liquor is again drained from the crystals. This operation is repeated until, in the judgment of the operator, the compound is pure or until the crop of crystals becomes so small as to render further recrystallization inadvisable. The leg containing the salt is then sealed off from the reaction tube and, after evaporating the excess of ammonia, is weighed preparatory to analysis, for which latter purpose the salt is first hydrolyzed by water and then dissolved in dilute sulfuric acid. The aluminium, iodine and ammonia in the solution thus obtained are determined by the well-known methods; aluminium as the oxide, iodine as silver iodide and ammonia by distillation with sodium hydroxide and titration after the usual manner. Following are recorded the experimental results obtained:

Preparation I.—The salt prepared as described above was recrystallized twice and dried in vacuum at 20°. The specimen weighed 0.5007 g., of which one-fourth gave 0.0222 g. Al_2O_3. Another fourth gave 0.0287 g. N and another fourth gave 0.1416 g. AgI.

Preparation II.—In this experiment 7.5 g. of aluminium iodide were used and the first crop of crystals obtained was recrystallized three times. Dried in vacuum at 100° the specimen weighed 1.5820 g. One-fourth gave 0.0692 g. Al_2O_3, another fourth gave 0.4757 g. AgI, one-tenth gave 0.0346 g. N and another tenth gave 0.0343 g. N.

Preparation III.—Ten grams of aluminium iodide were used and the basic salt was recrystallized three times. Dried in vacuum at 130° the specimen weighed 1.7605 g. One-fourth of the specimen gave 0.0783 g. Al_2O_3, another fourth gave 0.5273 g. AgI and one-tenth gave 0.0365 g. N.

Preparation IV.—This specimen was obtained from the mother liquor from Preparation III. It was recrystallized three times and dried in vacuum at 200°. It weighed 0.7964 g. One-fourth gave 0.0356 g. Al_2O_3, another fourth gave 0.0425 g. N and one-half gave 0.4802 g. AgI.

Preparation V.—This specimen was made from 4.4 g. of aluminium iodide and was recrystallized four times preparatory to analysis. After sealing apart the two legs of the reaction tube the solution of the salt was found to be milky from the presence of some impurity, presumably a small quantity of the insoluble ammonobasic salt described below. Dried at 165° in vacuum the specimen weighed 1.7343 g., one-fourth of which gave 0.0773 g. Al_2O_3. Another fourth gave 0.5280 g. AgI and one-tenth gave 0.0370 g. N.

	Calculated for $Al(NH_2)_3.AlI_3.6NH_3$.	Found.				
		I.	II.	III.	IV.	V.
Al	9.2	9.3	9.2	9.4	9.5	9.4
I	65.1	61.2	65.0	64.8	65.3	65.8
N	21.6	22.2	21.6	20.7	21.4	21.3

A soluble ammonobasic iodide of aluminium therefore results from the action of potassium amide on aluminium iodide in liquid ammonia solution in accordance with the equation given above. It is readily soluble in liquid ammonia, the solubility greatly increasing as the temperature is lowered. At laboratory temperatures the salt separates in beautifully formed crystals containing six molecules of ammonia which are not given off even at a temperature of 200°. As the temperature of the solution in equilibrium with the hexammonate crystals is lowered, the crystals dissolve and at the still lower temperature furnished by a bath of liquid ammonia the solution solidifies to a mass of needle-like crystals of the composition represented by the formula $Al(NH_2)_3.AlI_3.18NH_3$.[1] This salt melts in the neighborhood of zero, more or less of the hexammonate separating from the solution at the same time. Obviously one has to do with a transition point similar to that shown by aluminium iodide described above.

Insoluble Ammonobasic Aluminium Iodide, $Al(NH_2)_3.Al(NH_2)_2I.NH_3$ and $Al(NH_2)_3.Al(NH)I$.—When potassium amide is added to a solution of the soluble salt described above an amorphous, bulky precipitate of an insoluble basic salt is formed which settles very sluggishly and never to small bulk. The process of washing is therefore exceedingly tedious and time consuming, for which reason the preparation of a second specimen has not been attempted. The precipitate was washed 18 times by decantation, but since only about one-third of the liquid could be removed at each washing there is no certainty that the precipitate was thoroughly washed. The product was prepared for analysis in a manner similar to that described above for the soluble salt.

The specimen, dried in vacuum at 20°, weighed 0.4870 g. Dried at 160° it weighed 0.4135 g. One-fourth of the specimen dried at 160° gave 0.0414 g. Al_2O_3, another fourth gave 0.0224 g. N and a third fourth gave 0.1043 g. AgI.

From the data thus recorded the following results have been calculated:

	Calculated for $Al(NH_2)_3.AlNHI$.	Found.
Al	22.2	21.2
N	22.9	21.6
I	52.0	54.4

	Calculated for $Al(NH_2)_3.Al(NH_2)_2I.NH_3$.	Found.
Al	19.4	18.1
N	30.2	30.8
I	45.6	46.2

It seems probable, therefore, that an ammonobasic iodide of aluminium of the composition represented by the formula $Al(NH_2)_3.Al(NH_2)_2I.NH_3$ is formed by the action of potassium amide on a solution of aluminium

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[1] As is the case with the more highly ammonated iodide of aluminium the amount of ammonia contained in this compound above six molecules appears to be difficult to fix. Four determinations of the amount of ammonia retained by the hexammonate at —33° gave 36.0, 38.3, 40.6 and 38.8%. Twelve molecules require 34.9%, 14 molecules requires 40.7%. Because of the time-consuming nature of the operations involved in establishing equilibrium between an ammonated salt and ammonia in the case of ammonated salts showing a considerable vapor tension at low temperatures further attempts to fix the composition of this compound were abandoned.

iodide[1] and that the compound thus formed loses two molecules of ammonia on being heated to 160°. In view of the amorphous character of the precipitate, however, the existence of a definite compound of the composition given cannot be certain. At all events it is an insoluble ammonobasic product.

Summary.—A soluble ammonobasic iodide of aluminium is formed in accordance with the reaction represented by the equation $2AlI_3 + 3KNH_2 = Al(NH_2)_3.AlI_3 + 3KI$, when potassium amide in limited amount is added to a liquid ammonia solution of aluminium iodide. At ordinary temperature the salt separates from solution with six molecules of ammonia of crystallization as represented by the formula $Al(NH_2)_3.AlI_3.6NH_3$, at low temperatures a highly ammonated salt containing from 18 to 20 molecules of ammonia separates from the solution.

An insoluble ammonobasic iodide of aluminium, the composition of which is represented by the formula $Al(NH_2)_3.Al(NH_2)_2I.NH_3$ is precipitated when potassium amide is added to a solution of the above soluble basic salt. When heated this compound loses two molecules of ammonia to form a product to which the formula $Al(NH_2)_3.AlNHI$ has been given.

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POTASSIUM AMMONOARGENTATE.

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Some years ago while studying the action of potassium amide on liquid ammonia solutions of silver salts, the observation was made that silver amide dissolves readily in excess of potassium amide solution.[2] Since this is a behavior which recalls the similar action of water solutions of potassium hydroxide on certain metallic hydroxides it was surmised that the observed action of potassium amide solution on silver amide probably results in the formation of an ammonoargentate of potassium.

It was for the purpose of attempting the isolation of such a compound that this investigation was undertaken.

When, in one of the two-legged reaction tubes which have been elsewhere described,[3] a liquid ammonia solution of potassium amide is run into a similar solution of a silver salt a precipitate of silver amide is formed which, as the addition of potassium amide is continued, increases in amount until all the silver is precipitated. With further addition of the precipitant the precipitate dissolves to a clear, colorless solution. When, after a proper adjustment of the concentration, the solution thus obtained is cooled in a bath of liquid ammonia a crop of beautiful crystals separates from the

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[1] Cf. analytical results given in THIS JOURNAL, 27, 849 (1905).

[2] THIS JOURNAL, 27, 835 (1905).

[3] *Ibid., loc. cit.*