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Some Problems in the Stabilization of Low Oxidation States

THE REACTION OF POTASSIUM WITH ALUMINUM(III)

IODIDE IN LIQUID AMMONIA SOLUTION

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A SURVEY OF EARLIER WORK CONCERNED WITH THE LIQUID AMMONIA CHEMISTRY  
OF ALUMINUM

The behavior of aluminum and aluminum(III) compounds in liquid ammonia has been the subject of several investigations through the years. As might be expected, the experiments performed in different laboratories over a period of years have varied considerably as to the objectives of the work and the experimental techniques used. These diverse experiments, however, may be grouped, in a rather arbitrary fashion, into certain categories for more detailed consideration. These reports must be examined carefully as background material for the present experimental work to be presented below.

First, the previous work may be considered in the light of those investigations designed to demonstrate the main course of the particular reaction and identify the gross products of that reaction. Such experiments involved either replacement or metathetical reactions and were usually performed on a macro scale in a relatively simple, purely chemical manner.

Over against this type of investigation may be contrasted those experiments involving some electrical property of the system under scrutiny. Often such experiments did not permit the isolation of reaction products because of either unstable species present or quantities too small for the usual chemical analyses.

Franklin [J. Am. Chem. Soc. 27, 849(1905)] first observed that aluminum(III) iodide is freely soluble in liquid ammonia at its boiling point. It was also reported at that time that the addition of potassium amide to aluminum(III) iodide solutions in liquid ammonia eventually gave a solid product containing both aluminum and iodide ions. Franklin [J. Am. Chem. Soc. 37, 847-52(1915)] later resumed the work on the amide-aluminum iodide reaction with the result that two ammonobasic iodides of aluminum were isolated and characterized. The products isolated corresponded to the addition of 1.5 and 2.5 equivalents of amide per atom of aluminum respectively.

The first of these ammonobasic iodides was found to possess a negative temperature coefficient of solubility; so that at the boiling point of ammonia it was readily soluble but at room temperature it separated from solution in beautifully crystalline form. The product was dried in vacuo at temperatures ranging between 20 and 200° and in all cases the analyses indicated the same product. On the basis of chemical analyses for aluminum, iodide, and nitrogen, Franklin assigned the formula  $AlI_3 \cdot Al(NH_2)_3 \cdot 6NH_3$  to the first ammonobasic iodide.

The ammonobasic iodide resulting from the addition of 2.5 equivalents of amide separated from solution as an amorphous mass both at -33° and at room temperature. The light, amorphous nature of this product caused difficulties in purification under the prevailing experimental methods of that time. Nevertheless, Franklin's analyses were in substantial agreement with the formula  $Al(NH_2)_2I \cdot Al(NH_2)_3 \cdot NH_3$  for the insoluble ammonobasic iodide.

Bergstrom prepared the remaining two types of basic aluminum(III) compounds which are aluminum amide [J. Phys. Chem. 32, 434(1925)] and tetramidoaluminate (J. Am. Chem. Soc. 45, 2788-94(1923) and J. Am. Chem. Soc. 46, 1545-51(1924)]7.

Potassium amidoaluminate,  $KAl(NH_2)_4$ , was prepared by the reaction of either potassium metal solutions or potassium amide solutions with amalgamated aluminum in liquid ammonia. In a similar manner the corresponding sodium compound was prepared. It is interesting to note that Bergstrom found that sodium solutions reacted with the amalgamated aluminum at a rate two or three fold faster than did potassium. Both amidoaluminates were found to be readily soluble at room temperature and became somewhat less soluble as the temperature was decreased to -40°. In earlier work Franklin observed that the ammonobasic iodides dissolved in an excess of potassium amide. This was also evidence for the amphoteric nature of aluminum in liquid ammonia and for the existence of amidoaluminate complexes. The amidoaluminates were found to be extremely reactive toward water.

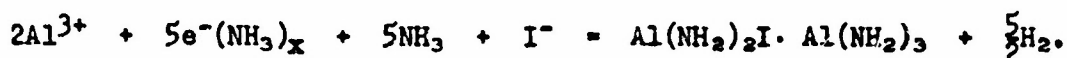
The reaction with water liberated ammonia but no other gases such as nitrogen or hydrogen. Bergstrom also found that when the amidoaluminate complexes were heated in vacuo at 50°, ammonia was readily lost and compounds formulated as  $\text{Al}(\text{NH}_2)_2\text{NHNa}$  and  $\text{Al}(\text{NH}_2)_2\text{NHK}$  were formed.

Aluminum amide, the simplest of the basic aluminum compounds in ammonia, was the most difficult to prepare in a pure form. Bergstrom first reported its preparation by the reaction of ammonium bromide with sodium amidoaluminate. The compound formed should perhaps best be referred to as ammonous aluminum nitride since it was found to possess a remarkable resemblance in properties to the analogous hydrous aluminum oxide precipitated from aqueous solutions.

The experiments involving electrical properties of aluminum and its compounds in liquid ammonia are not as closely related as are those investigations just outlined. The remaining background work is presented in chronological order.

McElroy, Bennett, Kleinberg, and Davidson [J. Am. Chem. Soc. 72, 5178-80 (1950) and J. Am. Chem. Soc. 71, 377(1949)] found that when aluminum iodide was electrolyzed between an aluminum anode and a platinum cathode in liquid ammonia, intensely blue colorations were obtained at the cathode. On prolonged electrolysis this blue color spread throughout the entire solution. Experiments performed with these blue solutions showed that the cathode reaction consisted of the dissolution of electrons, which were then capable of existence with an appreciable concentration of aluminum ions. Stated in another way, the blue solutions were the result of the presence of ionized metallic aluminum in a condition entirely analogous with the more familiar ammonia solutions of the alkali metals. The aluminum-in-ammonia solutions were not very stable when electrolysis was terminated. The products of reaction with the solvent were hydrogen and an ammonobasic aluminum iodide corresponding to the formula  $\text{Al}(\text{NH}_2)_2\text{I} \cdot \text{Al}(\text{NH}_2)_3 \cdot 2\text{NH}_3$ . It will be noticed that this has essentially the same composition as the insoluble ammonobasic iodide prepared by Franklin from the reaction of potassium amide with

aluminum iodide. The overall ionic reaction, without mention of mechanism, for the formation of the ammonobasic iodide is presented here and will be referred to again later.



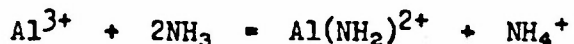
The next work to be mentioned was also performed at the University of Kansas and reported by Bennett, Davidson, and Kleinberg [J. Am. Chem. Soc. 74, 732 - 5 (1952)7]. It was found that in an electrolytic medium containing nitrate ion, anodic oxidation of pure aluminum metal gave rise to mean initial valence numbers of less than three for the aluminum. The apparent initial valence numbers were determined from coulometric data. When a number of metallic nitrates were used alone as the electrolyte, values of the initial oxidation state of aluminum fell near 2.7 with no apparent dependence upon the specific cation present. If, however, mixed electrolytes of sodium bromide and sodium nitrate or ammonium bromide and ammonium nitrate were used the initial oxidation state of the aluminum reached a minimum of about 1.5 when the electrolyte ratio was about two moles of nitrate to one mole of halide.

No compound containing aluminum in an oxidation state of less than three could be isolated from the reaction mixtures. It was found, however, that nitrate ion was reduced to nitrogen in the anode compartment. Such a reduction could hardly be the primary electrode reaction at the anode but could very well result from the oxidation of unstable species of lower valent aluminum. Experiments in which the loss of nitrate ion was determined and others in which the amount of nitrogen evolved was collected supported the hypothesis that some unstable lower valent state of aluminum was formed at the anode. From the coulometric data, it seems very probable that this lower oxidation state species was aluminum(I).

Watt, Hall, and Choppin [J. Phys. Chem. 57, 567-70(1953) and J. Am. Chem. Soc. 73, 5920(1951)7] studied the reaction of potassium with ammonia solutions of aluminum iodide by means of potentiometric titration. A plot of the data gained from titration with potassium yielded a curve with two breaks corresponding to

the addition of one and two equivalents of metal. Similar titration with potassium amide also yielded a curve with two breaks but these corresponded to the addition of three and four equivalents of the amide.

An interpretation given to the curve obtained from the titration with metal was that the reaction consisted of stepwise reduction to aluminum(II) and aluminum(I) by the addition of one and two equivalents, respectively, of potassium. It was recognized that at least one other explanation of the data presented itself. This alternative was the titration of ammonium ion resulting from ammonolysis of the aluminum ion, possibly in accordance with the following equations:



The titrations with amide were made to throw light upon mechanism of reaction. It was reasoned that if the changes in potential resulted from ammonolytic reactions, then titration with amide should yield essentially the same results as corresponding titrations with the alkali metal. Since the curves resulting from the titrations with the two different reagents differed, the interpretation involving reduction to lower oxidation states of aluminum was favored.

These investigators also reported some preliminary work on measuring the amount of hydrogen liberated in the reaction between potassium and aluminum iodide. It was found that substantially the stoichiometric quantity of hydrogen was evolved when the reaction was carried out rapidly. When the potassium was added very slowly, however, the amount of hydrogen collected decreased sharply. It was pointed out that this work was incomplete and that the results of experiments in which hydrogen was collected were not consistent with each other.

The final work to be mentioned here was reported by McElroy and Laitinen [*J. Phys. Chem.* 57, 566-67(1953)]. This involved a polarographic study of the aluminum ion in liquid ammonia. The single wave polarogram obtained from the

"reduction" of aluminum iodide at the dropping mercury electrode yielded a half-wave potential of almost exactly the same value as that observed for the reduction of ammonium ion. The observed values of the diffusion current constant were considerably larger than the calculated values for a three electron reduction. Such behavior was also attributed to a side reaction consisting of the reduction of ammonium ion.

Further experiments were performed in which the dropping mercury electrode was inserted as the anode into systems in which aluminum had just been oxidized anodically in ammonium bromide-ammonium nitrate media. In still another experiment the dropping mercury electrode, as anode, was inserted into a solution of aluminum iodide to which 1.6 equivalents of potassium had been added and allowed to react completely. In neither case was there any evidence for oxidizable aluminum species as would be expected if lower oxidation states of aluminum were present in the solutions.

These investigators also found that hydrogen was liberated from the reaction between potassium and aluminum iodide. The quantity of hydrogen collected corresponded to the amount required for the reaction  $K + NH_3 = 1/2 H_2 + NH_2^- + K^+$ .



II

THE AMMONATION OF ALUMINUM IODIDE AND THE SOLUBILITY OF THE AMMONATED  
PRODUCT IN LIQUID AMMONIA

Anhydrous aluminum(III) iodide absorbs ammonia with the evolution of a large quantity of heat. Uncontrolled ammoniation in an atmosphere of pure gaseous ammonia resulted in the fusion of the solid, a darkening of the color of the material, and the volatilization of a white finely dispersed substance. The major product of ammoniation is probably hexamminealuminum(III) iodide,  $\text{Al}(\text{NH}_3)_6\text{I}_3$ , [Franklin, J. Am. Chem. Soc. 27, 849(1905)]<sup>7</sup>. It is very likely that some ammonolysis takes place even with gaseous ammonia and that the white volatile material contains some ammonium iodide [see Franklin, Loc.cit. and Nicholson, Winter, and Fineberg, Inorganic Syntheses 3, 35(1950)]<sup>7</sup>. The final product of the uncontrolled ammoniation usually had a pale yellow cast indicative of the presence of some free iodine.

It was found that ammonolysis during the ammoniation process could be kept at an experimental minimum by maintaining a temperature of about  $\pm 70^\circ$  around the vessel containing the aluminum iodide. Ammonia was introduced slowly by means of a stream of dry, oxygen free nitrogen which was bubbled through a separate vessel containing dried liquid ammonia. Ammonated in this manner the resulting product consistently was pure white in color. It is not known if or how much ammonolysis does occur under these controlled conditions.

Franklin reported aluminum iodide to be freely soluble in ammonia at room temperature and at  $-33^\circ$ . In the present work it was found qualitatively that the high solubility at  $-33^\circ$  diminished sharply with decreasing temperature. For example, a sample of approximately one millimole of aluminum iodide readily dissolved in about fifty milliliters of ammonia to give a clear solution at  $-33^\circ$  but separated from solution to yield a milky white suspension at  $-70^\circ$ .

These ammoniation and solubility phenomena are not of extreme importance to the data and interpretations to follow but are described here to indicate more fully the physical nature of the systems under study.

III

A DESCRIPTION OF THE REACTION OF POTASSIUM WITH SOLUTION OF AMMONATED  
ALUMINUM IODIDE : THE APPARENT END POINT

It was found that potassium, added either as pieces of the solid metal or in ammonia solution, gave a vigorous initial reaction with solutions of ammonated aluminum(III) iodide. This reaction was characterized by an immediate discharging of the blue color of potassium in ammonia, an evolution of gaseous material insoluble in ammonia from the whole of the solution, and an evolution of heat. Hydrogen was qualitatively identified as a product of the reaction.

The time required for the blue color of the alkali metal to disappear, with successive increments of approximately equal magnitude, has been taken as a rough measure of the rate of reaction. This rate was found to decrease from the rapid initial reaction to a very slow rate of reaction which approached the limiting rate or that of the reaction between the metal and solvent. The gradual decrease in rate of reaction noted in the earlier stages of the addition of metal did not continue uniformly until the very slow rate was reached. Instead, when somewhat more than one and one-half equivalents of potassium had been added an apparent end point appeared. The metal continued to react after this point and so it is impossible to ascribe a true end point to this system. That a sharp break in the course of reaction did appear, however, is evidenced by the repeated observation that the time required for the blue color of approximately equal increments of metal to disappear suddenly changed from the order of five minutes to the order of one hour. For example, in a typical experiment in which titration of 1.4 millimoles of aluminum iodide in approximately 60 milliliters of ammonia was done with a 0.10 molar potassium solution the data in Table I were found.

Table I

Successive volume readings, milliliters	K increments in equivalents	Time required for blue color to disappear
0 -22.2	0 -1.60	ca. 10 min. total for a number of added portions
22.2-22.7	1.50-1.64	3 min.
22.7-23.1	1.64-1.67	60 min.

IV

THE NUMBER OF EQUIVALENTS OF POTASSIUM CONSUMED AT THE APPARENT END POINT

A total of sixteen experiments were made in which the purpose was to ascertain the apparent end point. These titrations were made immediately after adding the aluminum iodide to liquid ammonia at approximate  $-70^{\circ}$ .

The mode of ammoniation of the aluminum iodide varied greatly in these experiments. Although a poorly ammoniated product may indeed give an apparent end point value different from that of a well ammoniated product, it was found that this difference was no larger than unexplained differences arising in successive runs under supposedly nearly identical conditions. Since there are experimental difficulties in weighing and handling such reactive substances as anhydrous aluminum iodide and metallic potassium, variations may well be expected. Also there abide inherent errors in the titration procedures used.

An attempt has been made to minimize all of the possible errors and sources of variable values. The result was that twelve of the sixteen values for the apparent end point gave an average value of  $1.6 \pm 0.1$  equivalents. The other four values were much larger than the average and for the most part were suspected of error even before the apparent end point value was calculated. The average value of 1.6 equivalents of potassium, then, is given with considerable confidence as a correct indication of the location of the apparent end point.

The apparent end point was found to have essentially the same value when titrations were made near the boiling point of ammonia ( $-33^{\circ}$ ) instead of at  $-70^{\circ}$ . The break at the higher temperature was not as sharp as that at the lower temperature and more difficult to determine experimentally because of the increased rate of the succeeding reaction or reactions at the much higher temperature.

It was found, however, that prolonged standing of the aluminum iodide in ammonia solution gave rise to appreciable increases in the apparent end point values. This effect did not increase uniformly with the passage of time but

appeared to level off at a value just less than 2.0 equivalents of potassium. Here again the factors causing variable results, which were mentioned earlier, probably contributed to a scattering of the values. The eight experiments involving the effect of standing in solution upon the apparent end point are summarized in Table 2. In all cases the temperature was kept below  $-55^{\circ}$ .

Table 2

Hours between solution and titration	Apparent end point equivalents of K
12	1.6
12	1.7
12	1.95
14	1.95
16	1.8
18	1.95
20	1.9
24	1.9

It is seen that these apparent end point values are distinctly above those of the immediate titrations. In no case did the value reach or exceed 2.0 equivalents, however.

REACTION PAST THE APPARENT END POINT : THE APPEARANCE OF SOLID PRODUCTS

As mentioned previously the qualified expression apparent end point is used because potassium continued to be consumed, slowly, past the initial break.

Shortly before the apparent end point was reached, the reaction mixture became turbid. Upon filtering the reaction mixture after the apparent end point was reached, a very small amount of grayish-white solid remained. Most of these experiments involved about 0.5 gram (near one millimole) of aluminum iodide and about 1.6 millimoles of potassium. The solid isolated at the apparent end point weighed less than ten milligrams. The analyses of this product and of others isolated will be presented in the next section.

Between the apparent end point and 2.0 equivalents of alkali metal very little more solid appeared, the amount still being of the order of ten milligrams. Past 2.0 equivalents, however, relatively large amounts of precipitate appeared as more and more potassium was consumed. Throughout the remaining reactions which were studied up to the consumption of four and one-half equivalents of metal, solid products were always present and the reaction mixture was heterogeneous.

As pointed out above the fading of the blue color of potassium after the apparent end point was reached proceeded very slowly. The rate of the successive reaction or reactions was not constant but appeared to vary from experiment to experiment. It should be pointed out that when precautions were taken to exclude rigorously all traces of air and moisture from the apparatus and materials and to control carefully the ammoniation process, the rate of successive reaction, beyond the apparent end point, was no faster than that expected if the potassium were reacting with pure ammonia. Since such non-specific things as solids in general, poorly cleaned surfaces, and light are known to catalyze the potassium-ammonia reaction it is not surprising that differences in that total reaction time should arise. To illustrate the points of this paragraph some representative values are presented in Table 3.

Table 3

Total equiv. K. reacted	Total time in hours required for reaction
1.7	2
1.9	5
2.1	4
2.1	7
2.2	2
2.2	14
2.5	15
2.5	18
2.6	8
2.6	18
2.6	75
3.1	96
3.2	70
3.7	44
4.2	44
4.2	190

It should also be pointed out that temperature changes could drastically affect the rate of reaction. All of these experiments were started at approximately -70°. In cases of long reaction times, however, standing overnight was mandatory and some temperature rise was inevitable. The temperature factor is believed to be one of the most important causes of such widely diverse values.

VI

ANALYSES OF SOLID PRODUCTS FORMED

As indicated in an earlier section, solid products were present in the reaction mixture when the apparent end point was reached and remained throughout the entire range of reactions studied. Between the apparent end point and two and one-half equivalents of metal consumed the precipitates varied in composition, depending roughly upon the quantity of metal consumed, but always contained aluminum, iodide, and amide and/or ammonia nitrogen as major constituents and were undoubtedly mixtures of ammonobasic iodides. Potassium was usually found as a minor constituent. The solids were thoroughly washed with ammonia before analysis and so it is unlikely that much of the potassium found resulted from soluble impurities.

The analytical data indicated that the composition of the solid product formed in a reaction depended primarily upon the number of equivalents of alkali metal consumed. From about two and one-half equivalents on up to approximately four, essentially all of the aluminum was precipitated. This will be treated more fully in the next section.

The amount of potassium found in the precipitates also increased as more and more metal reacted. Whereas the aluminum and potassium percentages increased with increasing potassium consumption, iodide was found to decrease correspondingly. The solids from these reactions in which more than four equivalents of potassium were consumed contained no trace of iodide. The complete removal of iodide from the solid occurred at a point somewhere between three and four equivalents.

The data from the solid analyses are summarized below in Table 4. It will be seen that there is often considerable divergence in values corresponding to the same number of equivalents of metal reacted. Perhaps this is primarily the



result of experimental difficulties in working with the very small quantities of material found near the apparent end point. Also, evidence will be presented later that the solids were susceptible to ammonolysis during the washing processes and on standing in contact with ammonia. The nitrogen content of the solids was very sensitive to the moisture of the air. No satisfactory nitrogen determination was obtained from the three experiments in which more than four equivalents of potassium reacted.

In Table 4 those nitrogen values marked (calcd.) were obtained by difference from the analyses of the other constituents.

Table 4

SOLID ANALYSES

EQUIV. K REACTED	ATOMIC RATIOS I: Al: K: N	PERCENTAGE COMPOSITION
1.6	1.0:1.5:0.0:--	
1.6	2.0:1.0:0.0:--	
1.6	1.0:3.0:0.1:--	
1.7	1.0:1.4:0.0:--	
1.8	1.0:1.7:0.0:--	
1.8	1.0:1.6:0.4:5.5	45.4 I; 15.3 Al; 5.0 K; 27.3 N
1.9	1.0:1.6:0.3:5.3 (calcd)	47.7 I; 16.2 Al; 4.1 K
2.0	1.0:1.7:0.1:5.4 (calcd)	47.2 I; 16.9 Al; 1.9 K
2.0	1.0:2.1:0.1:--	
2.1	1.0:1.7:0.1:5.7 (calcd)	47.0 I; 17.1 Al; 1.4 K
2.2	1.0:2.2:0.2:7.2 (calcd)	40.5 I; 19.2 Al; 2.0 K
2.2	1.0:2.2:0.3:5.2	
2.2	1.0:2.1:0.1:--	
2.5	1.0:2.2:0.1:--	
2.5	1.0:1.8:0.1:4.8	50.2 I; 19.2 Al; 0.7 K; 26.5 N
2.6	1.0:3.3:0.1:--	
ca. 2.8	1.0:3.7:0.3:9.2	
ca. 2.8	1.0:2.6:0.5:7.7	38.5 I; 21.0 Al; 5.6 K; 32.5 N.
ca. 2.8	1.0:3.5: ? :9.4	31.2 I; 23.1 Al; 32.5 N
3.1	0.1:2.6:1.0:--	29.3 Al; 16.4 K; Ca. 5 I
3.1	0.1:1.0:0.2:3.0 (calcd)	31.3 Al; 5.6 I; 7.9 K
ca. 4.2	0.0:1.0:1.1:3.2 (calcd)	
4.2	0.0:1.0:1.2:2.8 (calcd)	
4.2	0.0:1.2:1.0:5.6 (calcd)	

VII

FILTRATE ANALYSES

The usual procedure followed in these experiments was to filter the reaction mixture, at the appropriate time, collecting the filtrate in a dry filter flask. The filtrates, then, consisted of the ammonia soluble components of the system. When the solvent ammonia had evaporated out of the filter flask, the solid materials remaining were subjected to analysis for aluminum, iodide and potassium. Such analyses were made with the idea in mind that a knowledge of the composition of the filtrates might be as helpful in understanding the nature of the reaction as the corresponding analyses of solid products.

It was found that at the apparent end point, the filtrates contained aluminum, iodide and potassium. The amount of aluminum found in the filtrates decreased as more and more potassium reacted beyond the apparent end point. Finally when two and one-half equivalents of metal had reacted with the aluminum iodide, no aluminum was found in the filtrate. In reactions in which from two and one-half to four equivalents of metal were consumed, the filtrates contained no detectable or only very small quantities of aluminum.

The analytical data from a number of representative experiments are tabulated below. The quantities in the third column of the table are simply the differences between the total number of cation charges determined and the total number of anion charges determined. These interesting observations will be referred to later in the discussion of the results. It should be pointed out that the filtrates afforded very convenient samples with which to work and the results are believed worthy of considerable confidence as to their accuracy.

Table 5  
FILTRATE ANALYSES

EQUIV. K REACTED	ATOMIC RATIOS Al: K: I	TOTAL DETERMINED CATION CHARGES MINUS TOTAL DE- TERMINED ANION CHARGES
1.6	1.0:5.9:7.3	1.6
1.6	1.0:4.7:6.2	1.5
1.7	1.0:1.7:3.2	1.5
1.7	1.0:2.3:3.7	1.6
1.9	1.0:2.3:3.7	1.6
1.9	1.0:2.7:4.1	1.6
1.9	1.0:3.8:5.2	1.6
2.0	1.0:4.9:6.5	1.4
2.1	1.0:3.4:4.7	1.7
2.2	1.0:7.2:9.0	1.2
ca. 2.2	1.0:4.6:6.3	1.3
2.5	0.05:1.00:1.15	0.0
2.5	O: 1.0:1.0	0.0
2.5	O: 1.0:1.1	-0.1
2.6	O: 1.0:1.1	-0.1
3.1	0.01:1.0:1.0	0.03
3.2	0.04:1.0:1.0	0.1
4.2	O: 1.2:1.0	0.2

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Results varied from experiment to experiment but all showed the same general

The analyses are summarized in the table below.

Table 6

Experiment	Time of Standing	Atomic Ratios
1	60 hours	Solid: 5.3Al : 1.OI 3.6Al : 1.OI  (Samples collected from different parts of the reaction cell)  Filtrate: 1.OI : 1.2K : 0.14Al
2	87 hours	Solid: 7.2Al : 1.OI : ?K  Filtrate: 1.OK : 1.4Al : 2.8 I

Very small amounts of solid material available for analysis made accurate determinations very difficult. Nevertheless, it is believed that the above results at least indicate the correct order of magnitude of the atomic ratios.

IX

INDICATOR EXPERIMENTS

Aqueous solutions of aluminum salts are known to be distinctly acid as a result of an appreciable degree of hydrolysis of the small, highly charged aluminum ion. Ammonolysis is involved in one of the possible interpretations of the reaction between aluminum iodide and potassium in ammonia. For this reason, it was desirable to attempt to determine whether or not ammonia solutions of aluminum iodide gave acid reactions with acid-base indicators.

Thoroughly dried phenolphthalein imparted a red-violet coloration to pure, dry ammonia. It was found that solutions of aluminum iodide were colored less intensely by the indicator under comparable conditions. An increase in acidity sufficient to discharge the basic color of the indicator was not observed, even in solutions kept overnight at temperatures near the boiling point of ammonia.

Similar results were found using dried thymolphthalein as indicator. This substance has a pKa value greater than that of phenolphthalein and thus should require a smaller amount of acid to effect a color change. In an experiment in which the solution of aluminum iodide was allowed to stand sixty-seven hours, the blue color of the basic form of the indicator was still visible. The intensity of the coloration appeared slightly diminished from that of the indicator in pure ammonia.

Recently more evidence for ammonolysis has been found in another laboratory (Dr. G. W. Watt, private communication). X-ray diffraction patterns of samples of ammonated aluminum iodide, prepared by dissolving the salt in ammonia and then allowing the solvent to evaporate contained lines attributable to ammonium iodide. The total amount of ammonium iodide present was apparently very small.

X

TESTS FOR REDUCING POWER

If stable compounds containing lower valent species of aluminum were present in the reaction mixture, the average oxidation state of the aluminum present could be determined by evaluating the extent of reduction of a convenient oxidizing agent. By similar reasoning, failure to reduce the oxidizing agent would cast doubt upon the existence of stable species containing a lower oxidation state of aluminum.

Dr. V. J. Christensen, in this laboratory, developed and used with success a very convenient test for reducing power utilizing silver(I) nitrate as the oxidizing agent. This technique was used in the present work. The criterion for reducing power then, would be the formation of metallic silver.

The silver nitrate was usually added as the dried solid. It should be remembered that in all of these experiments the silver nitrate was added after the blue color, signifying unreacted potassium, had disappeared. Such procedure was necessary because potassium would readily reduce silver nitrate.

In a number of experiments the filtrate was dropped onto solid silver nitrate when the reaction mixture was filtered. In most of these cases the reaction mixture was filtered after the apparent end point had been reached. In some instances, however, the filtration onto silver nitrate was performed before the apparent end was reached.

Similar experiments were carried out in which the silver nitrate was added to the entire reaction mixture both before and after the apparent end point was reached. In still other cases silver nitrate was added to an ammonia suspension of the previously washed solid product.

In no case was there ever any detectable amount of metallic silver formed. In those experiments in which the silver nitrate contacted the ammonobasic aluminum iodides, dark colored heterogeneous products were often formed in small quantity. These products, soluble in dilute hydrochloric acid, gave tests for silver, aluminum, and iodide ions and were apparently mixtures possibly containing ammonobasic silver compounds.



XI

EXPERIMENTS USING POTASSIUM AMIDE INSTEAD OF POTASSIUM METAL

Since the analytical data indicated the presence of amide ions in the reaction mixture and since some of the potentiometric titrations reported by Watt, Hall, and Choppin used potassium amide, it was deemed of interest to compare the results obtained with potassium in the present work with similar experiments involving potassium amide.

Potassium solutions were converted to pale yellow solutions of potassium amide under the influence of a shiny iron wire catalyst. Since ammonia solutions of potassium amide have no distinctive color, it was not possible to obtain such a value as the apparent end point.

It was found that as amide was added to solutions of ammoniated aluminum iodide the reaction mixture first became turbid and, finally, precipitates settled out much in the same manner as in the reactions with potassium. Therefore, the experiments with potassium amide were designed to locate the point of permanent turbidity and to yield analyses of products obtained by the reaction of known equivalents of amide.

In titrating with amide to detect the turbidity point the temperature of the aluminum iodide solution was maintained at about  $-50^{\circ}$ . The purpose of this precaution was to insure the maintenance of a perfectly clear solution of the aluminum iodide. As closely as could be determined, the point of permanent turbidity occurred at or slightly before the addition of 1.6 equivalents of amide. Filtration at this point yielded a very small quantity of grayish-white material.

In experiments in which more than four equivalents of amide were added, the precipitate which finally formed almost entirely dissolved, leaving only a slightly turbid reaction mixture. The reaction mixture from one experiment in which 4.2 equivalents of amide were added was allowed to stand for sixty-seven hours at approximately  $-70^{\circ}$ . At the end of this time the quantity of solid in the mixture was not noticeably greater than that present before the standing period.

Finally, a mixed titration using both amide and metal was conducted. In the experiment, 0.90 equivalent of amide was added to the aluminum iodide solution. Potassium was then added from the buret until the blue color persisted for approximately forty-five minutes. The quantity of potassium required to reach this point was 0.87 equivalent. The sum of amide and metal added was 1.8 equivalents.

The results of these and other experiments with amide are summarized in Table 7. Some potassium data are included to allow convenient comparison.

Table 7

EQUIVALENTS OF METAL OR AMIDE	SOLID ANALYSES Atomic Ratios	FILTRATE ANALYSES
1.6 KNH <sub>2</sub>	4.7 Al:1.0 I:0.4 K	1.0 Al:1.7 K: 3.4 I cation charges minus anion charges 1.3
1.6 K	1.5 Al:1.0 I:0.0 K 3.0 Al:1.0 I:0.1K	1.0 Al:4.7 K:6.2 I cation charges minus anion charges 1.5
2.6 KNH <sub>2</sub>	2.4 Al:1.0 I:0.1 K:6.1 N	1.0 K:1.0 I:0.0 Al
2.5 K	2.2 Al:1.0 I:0.1 K:--	1.0 K:1.0 I:0.0 Al
3.0 KNH <sub>2</sub>	1.0 Al:0.2 K:0.06 I Percentages: 32.1 Al; 7.2 K; 9.5 I	1.0 K:1.0I:0.0 Al
3.1 K	1.0 Al:0.2 K:0.04 I Percentages: 31.3 Al; 7.9 K; 5.6 I	1.0 K:1.0 I: 0.0 Al
4.1 KNH <sub>2</sub>	1.7 Al: 1.0 K: 0.0 I	1.0 Al: 4.9 K: 4.0 I
4.2 KNH <sub>2</sub>	1.0 Al: 1.2 K: 0.0 I	1.0 Al: 4.8 K: 3.6 I cation charges minus anion charges 4.2
4.2 K	1.2 Al: 1.0 K: 0.0 I	0.0 Al: 1.2 K: 1.0 I

XII

DISCUSSION

The reducing power experiments produced no evidence for the presence of stable species containing aluminum in an oxidation state of less than three. This is in accordance with the observations of McElroy and Laitinen who found no readily oxidizable constituent in the system by means of the dropping mercury electrode. These experiments do not preclude the formation of lower valent species of aluminum. The inference is that if such species are present they are so extremely short lived that their identification and isolation by chemical means cannot be accomplished.

The products isolated from both the solid and the filtrate of the reaction mixtures then, must be composed of aluminum(III) compounds. In view of the liberation of hydrogen from the system and the observed properties of the solids isolated it is believed that these solids consist of ammonobasic aluminum(III) compounds. This is even more strongly indicated by the repeated observation of the disparity between the total cation charges and the total anion charges determined in the filtrates. To preserve electrical neutrality some other anion must be present along with the iodide ion. Amide ion, either free or in some kind of combination, is the only apparent possibility in this system. Also, this ion is formed in quantities of the same order of magnitude as those of the other reactants.

It is proposed that the amide ion originates from the ammonolysis of the aluminum iodide. The indicator and x-ray evidence available strongly indicates that some ammonolysis takes place. Still stronger evidence for ammonolysis is presented by the observation that solid products, consisting of mixtures of ammonobasic iodides and aluminum amide, separate from solution upon prolonged

contact with liquid ammonia. The evidence also indicates that the extent of ammonolysis is extremely small. It is believed, however, that the addition of potassium disrupts the ammonolytic equilibrium in that the ammonium ion, formed concurrently in ammonolysis, is irreversibly removed with the liberation of hydrogen. Thus the ammonolytic equilibrium would be continuously displaced as more potassium was added resulting in the accumulation of amide in the solution. This behavior is believed to account for the initial rapid reaction of potassium with the aluminum iodide solutions.

Further, it is proposed that when the apparent end point is reached all of the aluminum has been effectively tied up as a comparatively stable complex containing amide. The filtrate analyses of Table 5 clearly show that the cation charges - anion charges disparity, which reflects the presence of amide, has its largest values before two equivalents of metal are consumed, or, in general, in the region of the apparent end point. It would seem that if this amide were present as the free ion it would react almost immediately to precipitate the insoluble ammonobasic aluminum iodide first reported by Franklin. On the other hand, if the amide were present in an aluminum complex of relatively high stability, it would be expected that further reaction with potassium and/or with the solvent would proceed only slowly.

It might be suggested that the aluminum ion present in some manner catalyzes the otherwise very slow reaction between the alkali metal and ammonia. Such an explanation, however, would not account for the sudden loss of catalytic activity when the apparent end point was reached. It should also be pointed out here that if species of lower valent aluminum had transitory existence in the reactions the end result could very well be the same as postulated in the preceding paragraph. This would be expected since the lower valent aluminum must needs react immediately with the solvent giving hydrogen and amide along with trivalent aluminum. It would then be impossible to distinguish between the two mechanisms in a chemical manner.

Analyses of the solids obtained (Table 4) demonstrate that they were mixtures of basic aluminum compounds. The succession of these basic aluminum(III) compounds may be conveniently formulated as  $AlI_3 \longrightarrow Al(NH_2)I_2 \longrightarrow Al(NH_2)_2I \longrightarrow Al(NH_2)_3 \longrightarrow KAl(NH_2)_4$ . Such a formulation simply presents a convenient stepwise picture. There is no conclusive evidence for the existence of  $Al(NH_2)I_2$  and  $Al(NH_2)_2I$  as stable solid phases, although the solid phases isolated may be thought to consist of mixtures of such compounds.

It would seem reasonable to postulate that the solids isolated were composed of varying proportions of  $Al(NH_2)I_2$ ,  $Al(NH_2)_2I$ ,  $Al(NH_2)_3$  and  $KAl(NH_2)_4$ . The relative proportions of the individual components would depend primarily upon the number of equivalents of potassium which reacted. Probably all four of the compounds listed above would not be capable of simultaneous existence. There is evidence, however, that any adjacent three of the entities may contribute to the solid products isolated. For example, the solid isolated from an experiment in which 3.1 equivalents of metal were consumed gave an aluminum percentage within about one per cent of the theoretical value for aluminum amide. The solid also contained, however, 5.6 per cent iodide and 7.9 per cent potassium.

With regard to the proposed aluminum complex at the apparent end point, a further bit of speculation proved of interest. For example in an experiment in which 1.6 equivalents of potassium were consumed the filtrate gave the ratios of 1.0 Al:4.7K : 6.2I. The cation charges minus the anion charges, or amide present, would then be 1.5. Now if all of the potassium in the filtrate were assumed to be present as potassium iodide, the iodide remaining would be 6.2 - 4.7 or 1.5 atom. This would leave the ratios of 1.0Al : 1.5I : 1.5NH<sub>2</sub> which is exactly that required for the soluble ammonobasic iodide reported by Franklin and formulated as  $AlI_3 \cdot Al(NH_2)_3 \cdot 6NH_3$ . The specific example given was by no means an isolated case since calculations with almost all of the filtrate analyses near the apparent end point gave similar results.

The reactions past the apparent end point are believed to involve a complex series of equilibria and competing reactions. Since at the apparent end point essentially all of the aluminum is probably tied up in the relatively stable soluble complex containing amide, further reactions must be instigated by attack upon and reaction of this complex. The two most obvious possible reactions involving the soluble complex are ammonolysis, with the separation of insoluble ammonobasic iodides, and reaction with amide derived from the excess potassium present, also yielding insoluble ammonobasic iodides. After such reactions had begun there would be the further possibility of interactions among the several possible solid ammonobasic compounds. Also, experiments have shown that the insoluble ammonobasic iodides tend to ammonolyze and lose iodide simply on prolonged contact with ammonia. Still another reaction which must be considered is that between potassium and ammonia under whatever catalytic influence the solid phases may exert.

It is seen that most of these reactions would involve a precipitate and its surroundings and must be of a heterogeneous nature. As might be expected the rates of these reactions are all apparently very slow since the reactions past the apparent end point proceed very slowly. Since such a large number of possible reactions exist, it is no surprise that mixtures of solid products are invariably isolated from the system under consideration.

In summary, the solid products may be said to consist of mixtures of compounds. The predominating compound at 2.5 equivalents is the insoluble ammonobasic iodide reported by Franklin and later by McElroy, Kleinberg and Davidson and formulated as  $\text{Al}(\text{NH}_2)_2\text{I} \cdot \text{Al}(\text{NH}_2)_3 \cdot 1-2\text{NH}_3$ ; that at 3.0 equivalents is aluminum amide; and that at 4.0 equivalents is potassium tetramidoaluminate.

It is also believed that the course of reaction is the same whether potassium or potassium amide is used. In Table 7 it was seen that corresponding experiments using either amide or metal showed a marked similarity to one

another, both qualitatively and quantitatively. In one titration in which amide was added first and then the reaction was completed with potassium, the sum of the equivalents of the two titrants was only slightly greater than that expected for the usual apparent end point with potassium alone.

There was one point in which the amide reactions differed greatly from the metal reaction. This occurred in those experiments in which approximately four equivalents of the respective reagent was consumed. In the case of the reaction with potassium a large amount of solid remained at the completion of the reaction and the filtrate contained no aluminum. This solid was very reactive toward the moisture of the air but the analyses indicate fairly well that the compound was potassium tetramidoaluminate. With the amide, however, the product formed was almost entirely soluble as might be expected considering the amphoteric nature of aluminum. The filtrate analyses could well be interpreted to indicate the presence of the amidoaluminate in solution. The small quantity of solid in one case also analyzed fairly well for the amidoaluminate. When one of the amide solutions was kept for sixty-seven hours it was found that the quantity of solid did not increase appreciably. There is no satisfactory explanation at present for this great difference in behavior. The major difference in the two cases was the rate of reaction. The reaction with potassium was extremely slow whereas that with the amide was almost instantaneous.

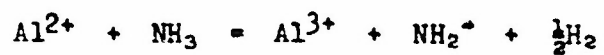
McElroy, Kleinberg, and Davidson in their electrolysis experiments found that when aluminum ions, iodide ions, and the ammoniated electron species were all present in the same solution the insoluble ammonobasic iodide,  $\text{Al}(\text{NH}_2)_2\text{I}\cdot^-$   $\text{Al}(\text{NH}_2)_3\cdot 2\text{NH}_3$ , was always formed. In the present work with potassium and aluminum iodide, exactly the same constituents are present along with potassium ions. The two systems are believed to be essentially equivalent. In this work the presence of an excess of solvated electrons and of potassium ions allows further

reaction involving, eventually, the amphoteric character of aluminum. Thus from consideration of the earlier work, the precipitation of ammonobasic compounds of aluminum(III) should be expected in the reaction between potassium and aluminum iodide.

Finally a few words will be written concerning the interpretation of the potentiometric titration data of Watt, Hall, and Choppin. If reduction of aluminum to lower oxidation states takes place, the species formed must react instantaneously with the solvent since it has not been possible to detect any reducing power in the reaction mixtures. With aluminum(II) as the specific example, this reaction would be  $Al^{2+} + NH_3 = Al^{3+} + NH_2^- + \frac{1}{2}H_2$ . Now if the aluminum (II) reacted immediately after its formation the effective concentration of aluminum(II) in the system would remain essentially constant and nearly equal to zero. Since aluminum(III) is regenerated from the lower state its effective concentration should also remain essentially constant until the accumulation of base would cause a change in the aluminum(III) species present. If the potentiometric data are to reflect reduction of aluminum(III) to aluminum(II) the change in potential must result from changes in the concentration ratio  $Al(III)/Al(II)$ . As pointed out above, however, the concentrations of both of these species would be expected to remain nearly constant. Therefore no change in potential would occur as the result of reduction and no break in the curve would be found. Furthermore, it would appear reasonable to expect that if lower valent species were present for a sufficient length of time to allow their detection by the rather slow process of potentiometric titration, they would also be detectable by the various means already mentioned.

If the potential changes observed resulted from reaction between aluminum(III) and amide generated from the reaction of lower valent aluminum with ammonia, the following sample reactions may be thought to occur:





The end result of such a sequence would be exactly the same as that postulated above involving original ammonolysis of aluminum(III). Thus, again it would be impossible to distinguish between the two mechanisms.