

REACTIONS OF SOME ALKALI AND ALKALINE EARTH METALS
WITH ALUMINUM(III) IODIDE IN LIQUID AMMONIA

by

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Finally, it has been a pleasure to work on the beautiful University of Kansas campus. Our years in Lawrence have been happy ones.

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INTRODUCTION

STATEMENT OF THE PROBLEM

The investigation forming the basis of this thesis was undertaken as the result of previous work done at the University of Kansas by William E. Bennett and Albert D. McElroy under the direction of Professors A. W. Davidson and Jacob Kleinberg. These projects involved study of the anodic oxidation of aluminum, gallium, indium, and thallium in liquid ammonia.

Except for thallium, in which the most stable oxidation state is plus one, compounds of these elements which possess the group valence of three are far more stable than those of lower oxidation states. These lower states of aluminum, gallium, and indium, although they have been reported, are, in most cases, neither widely known nor completely characterized.

Data from the anodic oxidations provided evidence for the existence, in the systems studied, of unstable compounds of lower valent aluminum (1), gallium, and indium (2). However, no solid product containing lower valent species of any of these metals could be isolated.

In the light of the results obtained from anodic oxidations, it seemed of interest to attempt to prepare compounds containing lower valent entities of these elements by reduction of trivalent starting materials. Liquid ammonia was chosen as the reaction medium because the properties of that solvent permit use of the alkali metals as very strong and relatively simple reducing agents.

Other factors contributing to the choice of ammonia as solvent for this work were the success of a number of previous reduction studies in this medium and also the tradition of liquid ammonia chemistry at the University of Kansas.

The first element investigated was gallium; and it was soon found that reaction of the triiodide with potassium resulted in reduction to the metal. Independently conceived studies at another laboratory (3) confirmed this finding and further reported the same type of result for the reduction of indium(III) iodide with potassium.

With these facts in mind, full attention was focused upon the aluminum(III) iodide - potassium reaction since it was found not to involve reduction to metallic aluminum. Qualitative experiments indicated that reducing power attributable to lower oxidation states of aluminum could not be detected at any time during the course of reaction. Quantitative analyses of reaction products further showed that, in order to explain the path of reaction, it is unnecessary to assume the formation of aluminum(II) and aluminum(I) in the system, as had been postulated (3), although the transitory existence of these lower states was not ruled out. Thus the major goal of the work reported herein was to arrive at a consistent explanation of the experimental data and to seek a mechanism for the overall reaction.

To obtain a complete picture of the reaction system,

five metals of the alkali and alkaline earth families were treated with aluminum(III) iodide. The ratio of metal to original aluminum iodide was varied over a wide range. Whenever possible, complete analyses were obtained for all reaction products, both in the solid and liquid phase.

LOWER VALENT ALUMINUM

The purpose of this section is to sketch very briefly what is known about the lower oxidation states of aluminum. Most of this material is taken from a recent review by McGeer (4).

Since thallium is known to possess a very stable unipositive oxidation state, it may be thought that, by reason of periodic relationships, lower valent aluminum, under the proper conditions, also should be found. A consideration of the ionization potentials of aluminum indicate that monovalent aluminum particularly should be capable of existence. Recent heat-of-formation calculations by means of the Born-Haber cycle indicated that the formation of aluminum monohalides, both solid and gaseous, at 25°C is not energetically impossible. These calculations, however, did not consider the possibility of disproportionation of the monohalide into the trihalide and free metal.

Although the existence of lower halides of aluminum had been suspected for many years, it was not until 1943 that Klemm and Voss actually demonstrated that these substances were monohalides. These workers heated, at temperatures above 750°, pure aluminum and aluminum(III) fluoride in a high vacuum. The white sublimate formed was repeatedly

sublimed with more aluminum. Finally, the aluminum to fluorine ratio in the sublimate became one to one, indicative of the formation of aluminum(I) fluoride. X-ray diffraction examination of the cooled product having the empirical composition of AlF showed only the presence of aluminum and the trifluoride. The monofluoride, stable at high temperatures, underwent disproportionation when cooled.

Klemm and his co-workers later reported the preparation of a number of other aluminum(I) compounds which are summarized in Table 1. In each case, the monovalent material was prepared at high temperatures in high vacuum, and cooling resulted in complete disproportionation to aluminum metal and aluminum(III) compounds.

Table 1

Monovalent aluminum compounds

Reaction	Temperature range
$2Al + AlX_3 = 3AlX$	750 - 1200°
$Al + AgBr = AlBr + Ag$	800 - 1000°
$2Al + MnCl_2 = 2AlCl + Mn$	800 - 1000°
$2Al + X_2 = 2AlX$	1000 - 1200°
$4Al + Al_2Y_3 = 3Al_2Y$	1100 - 1200°
X = F, Cl, Br, I	
Y = S, Se	

The first reaction listed in Table 1 has been used as the basis of a process for the preparation of very pure aluminum from the impure metal or from alloys containing

aluminum.

Brewer and Searcy found that oxides of both aluminum(II) and aluminum(I) were formed at high temperatures. Aluminum(II) oxide was the primary dissociation product of alumina; whereas the aluminum(I) oxide resulted from reduction of the sesquioxide with aluminum.

The first isolation of a material stable at room temperature which contained aluminum(I) was accomplished by Schumb and Rogers (5). By use of an electrodeless discharge produced at low pressures and at temperatures below 50° in the vapor of aluminum(III) iodide, vapors of iodine and a non-volatile solid were obtained. Exhaustive extraction of the solid with anhydrous benzene, followed by vacuum drying, yielded a buff-colored solid of which the chemical analysis and X-ray diffraction data were consistent with the presence of a mixture of metallic aluminum and a monoiodide, $(AlI)_n$.

In work done at the University of Kansas (6), evidence for monovalent aluminum has been obtained from experiments involving anodic oxidation of aluminum in anhydrous acetic acid containing suitable electrolytes. No monovalent compound could be isolated from the systems studied.

Evidence obtained in ammonia as the reaction medium for the existence of lower oxidation states of aluminum is discussed in a later section dealing with the liquid ammonia chemistry of aluminum.

NATURE AND USES OF METAL-AMMONIA SOLUTIONS

In the pages which follow, repeated reference is made to ammonia solutions of the alkali and alkaline earth metals. Since these solutions have no counterpart in aqueous medium it seems advisable at this point to outline briefly some of their physical properties, theories proposed about their nature, and typical reactions which such solutions undergo. Material for the discussion has been gleaned primarily from reviews by Yost and Russell (7) and by Kraus (8).

It should be pointed out that elucidation of the nature of metal-ammonia solutions has proved to be a difficult problem. An entirely satisfactory picture, consistent with all the experimental data, has not yet been found.

The solubility of potassium and sodium in ammonia was first observed some ninety years ago. Since that time all of the other alkali metals and the alkaline earth metals have been found to be readily soluble in ammonia. Magnesium is slightly soluble, and solutions of aluminum have been prepared electrolytically (9). Presumably, other active metals, such as the lanthanide elements, should be capable of dissolution under the same conditions as those used for aluminum.

Except for lithium, evaporation of the ammonia from freshly prepared alkali metal solutions yields the unchanged metal. The alkaline earth metals form rather unstable amines which have the formula $M(\text{NH}_3)_6$. Lithium apparently gives a very unstable tetraamine, $\text{Li}(\text{NH}_3)_4$. Metallic aluminum cannot be recovered from its solutions; removal of

solvent yields ammonobasic materials.

To present some idea of the degree of solubility of the alkali metals in ammonia, the data, in grams of metal per hundred grams of ammonia at -33° , reported for lithium, sodium, and potassium are 10.9, 24.6, and 49.0, respectively. The solubility changes only slightly with temperature.

When dilute, the metal-ammonia solutions possess a blue color. The absorption spectra of dilute solutions of different metals are identical at the same concentrations. This means that the blue color is attributable to the same substance in all cases. Concentrated solutions have a bronze-like reflection.

At all concentrations, the equivalent conductance of the metal solutions is greater than that found for any known salt in any known solvent. The limiting equivalent conductance is some three fold greater than that of solutions of the best conducting salts in ammonia. The specific conductivity of concentrated solutions is very high and is of the order of magnitude of metal conductance.

A large positive volume change accompanies the dissolution of a metal in ammonia. Consequently the densities of these solutions are very low. For example, the density, at 19° , of a saturated lithium solution is 0.477 g./ml., making it the lightest known liquid at room temperature.

Transference data, obtained from EMF measurements of concentration cells containing sodium solutions, indicate that the ratio of current carried by the negative constituent to that carried by the positive has a limiting value

of seven in extremely dilute solutions. This ratio increases with increasing metal concentration and has a value of two hundred eighty for a one normal solution.

There seems to be little question that the concentrated metal-ammonia solutions behave essentially as a metal. It is not known whether the ammonia plays any definite role other than to serve as diluent. For most purposes the concentrated metal-ammonia solutions may be viewed as alloys of the metal with an insulator, ammonia.

The transference experiments and conductivity data indicate that the negative constituent of dilute solutions is the electron. Even in dilute solutions the conductance is best considered as essentially metallic, in view of the fact that no detectable material effects accompany the passage of electrons from the solution into or out of the electrode surfaces.

The optical properties of dilute solutions are best explained on the basis of interaction between the electrons and ammonia molecules. Magnetic susceptibility measurements indicate, however, that there is no large concentration of solvated electrons. On the other hand, the susceptibilities are too low to support the conclusion that the valence electrons are in the same state as in the free metals.

Further work on the visible absorption spectrum of dilute sodium solutions has produced evidence that actually two colored components are present and that the equilibrium between them is dependent upon concentration and tempera-

ture (10). It is proposed that these colored components consist, respectively, of electron pairs and single unpaired electrons. Such an assumption would tend to bring the optical and magnetic data into better agreement.

To summarize, the most widely accepted interpretation of the nature of dilute metal-ammonia solutions is that such solutions contain metal ions as the positive component; an equilibrium mixture of paired and unpaired electrons constitutes the negative component. All of these charged particles are solvated to some extent. The conductance of these dilute solutions is essentially metallic rather than electrolytic.

Attention will now be turned from the physical nature of metal-ammonia solutions to a consideration of typical reactions into which these solutions enter with inorganic substances. Watt (11) has prepared an extensive review of this subject which is the source of most of the present discussion.

Perhaps the most characteristic reaction of the metal solutions is the slow reaction with the solvent ammonia, to yield amide ion and hydrogen. The rate of this reaction is accelerated tremendously by finely divided metals, oxides and solid phases in general, and by ultraviolet light. Stabilities of the various metal solutions vary in accordance with the general chemical reactivities of the different elements as indicated by ionization potentials. For example, cesium solutions are the least stable of all the alkali metals, potassium less stable than sodium,

barium less stable than calcium, and so forth. Of course the stability of a solution, as measured by the time required for disappearance of the blue color, will depend upon the total amount of metal present. In general, however, pure solutions of potassium, more concentrated than one normal, may be kept for several days before appreciable decomposition takes place. Similar solutions of sodium are stable for several weeks. These data are quoted to emphasize that the amide reaction is extremely slow as compared with typical ionic reactions.

Another characteristic reaction of the metal solutions is the instantaneous reaction with ammonium ion, the strongest acid which can exist in ammonia, to give ammonia and hydrogen. Since molecular hydrogen is evolved, this reaction is irreversible.

Since the metal-ammonia solutions contain essentially free electrons, these solutions are powerful reducing agents. Reducible cations of simple salts which are not extensively ammonolyzed, are usually reduced first to the free metal. In some cases the finely divided product will react with excess metal solution to form intermetallic compounds. With ammonolyzed ions the primary reaction generally is the reduction of ammonium ion. No general statement can be made about the products of anion reduction since such products depend upon the nature of the original anion. Coordination compounds which are neither ammonolyzed nor appreciably dissociated in solution are often capable of reduction to substances containing a lower oxidation state

of the central metal ion. A particularly interesting example is the addition of potassium solution to tetracyanonickelate(II) ion to yield potassium tetracyanonickelate(0).

This section is concluded by mentioning an interesting observation made by Bergstrom (12). Since the metal-ammonia solutions contain metal ions and electrons, a system which contains a finite concentration of another metal ion co-existent with the alkali or alkaline earth metal may be regarded as a solution of the other metal in ammonia.

LIQUID AMMONIA CHEMISTRY OF ALUMINUM

Reports on the behavior of aluminum compounds in liquid ammonia date back to 1905, in the early days of Franklin's work. Since that time a number of investigations have been made which involve aluminum and aluminum compounds in ammonia as the solvent medium. 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. Only those investigations which are pertinent to and necessary for an understanding of the experimental work and conclusions to be presented in this thesis are considered in this section.

The diverse experiments constituting this background material may be grouped, in a rather arbitrary fashion, into two categories for more detailed examination.

First, the previous work may be considered in the light of those investigations designed to demonstrate the main course of a particular reaction and identify the

gross products of that reaction. Such experiments involved either replacement or metathetical reactions which usually were performed on a macro scale in a relatively simple, purely chemical manner.

This type of investigation may be contrasted with those experiments involving some electrical property of the system under study. Often such work did not permit the isolation of reaction products because of the presence of unstable chemical species, or because use of elaborate equipment required quantities of materials too small for the usual chemical analyses.

Franklin (13) first observed that aluminum(III) iodide is freely soluble in liquid ammonia at its boiling point. It was also reported at that time that addition of potassium amide to ammonia solutions of aluminum iodide eventually gave a solid product containing both aluminum and iodide ions. Franklin later resumed work on the amide-aluminum iodide reaction with the result that two ammonobasic iodides of aluminum were isolated and characterized (14). The products isolated corresponded to the addition of 1.5 and 2.5 equivalents of potassium 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 crystalline form. The product was dried under reduced pressure at temperatures ranging between 20 and

200°, and in all cases the analyses indicated the same compound. On the basis of chemical analyses for aluminum, iodide, and nitrogen, Franklin assigned the formula $\text{AlI}_3 \cdot \text{Al}(\text{NH}_2)_3 \cdot 6\text{NH}_3$ to the first ammonobasic iodide.

The ammonobasic iodide resulting from addition of 2.5 equivalents of amide separated from solution as an amorphous mass of low density both at -33° and at room temperature. The light, non-crystalline 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 $\text{Al}(\text{NH}_2)_2\text{I} \cdot \text{Al}(\text{NH}_2)_3 \cdot \text{NH}_3$ for the material when dried at room temperature under reduced pressure. When this basic salt was heated to 160° under reduced pressure, two moles of ammonia were evolved leaving a product formulated as $\text{Al}(\text{NH})\text{I} \cdot \text{Al}(\text{NH}_2)_3$.

Bergstrom found that amalgamated aluminum dissolved readily in solutions of potassium (15) or sodium (16) in liquid ammonia. Solutions of the corresponding alkali metal amides also effected this solution process and gave final reaction products identical with those obtained from solutions of the metals. Pure aluminum, however, even when finely divided, was not attacked by either the alkali metal or amide solutions. Amalgamation apparently was necessary to prevent the coating of the aluminum surface by insoluble basic compounds. Pure ammonia did not attack amalgamated aluminum. Reaction of amalgamated aluminum with the metal solutions resulted in gas evolution

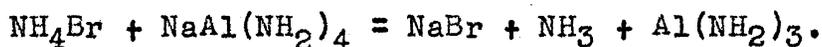
(hydrogen) and discharge of the characteristic blue color of those solutions. The pale yellow solutions of potassium amide and suspensions of sodium amide, which is only slightly soluble in ammonia; reacted with amalgamated aluminum to yield opaque blue colorations which subsequently became colorless. The fading of the blue color again was accompanied by hydrogen evolution.

The products obtained from these reactions were potassium and sodium tetraamidoaluminate, $KAl(NH_2)_4$ and $NaAl(NH_2)_4$. The preparation of these compounds demonstrated the amphoteric nature of aluminum nitride, or amide, in ammonia. Both amidoaluminates were readily soluble at room temperature and became slightly less soluble as the temperature was decreased to -40° . Isolation of the solid compounds was accomplished by crystallization from concentrated solution at -40° . The amidoaluminate compounds were found to be extremely reactive toward water; such reaction liberated ammonia as the only gaseous product. Prolonged contact with liquid ammonia resulted in slow ammonolysis of the amide complexes. Bergstrom also found that heating of $KAl(NH_2)_4$ to 50° and $NaAl(NH_2)_4$ to 90° , under reduced pressure, resulted in a ready loss of one molecule of ammonia from the complexes. The solid materials which remained were $KAl(NH_2)_2NH$ and $NaAl(NH_2)_2NH$.

Lithium tetraamidoaluminate also has been reported (17). The slightly soluble salt was prepared by reaction of amalgamated aluminum with lithium amide. The formation of the tetraamidoaluminate complexes is analogous to the

dissolution of metallic aluminum in aqueous solutions of the alkali metal hydroxides.

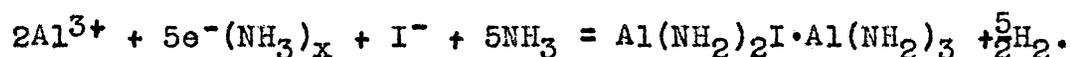
Aluminum amide, the simplest in formula, of the ammonobasic aluminum compounds was the most difficult to prepare in pure form. Bergstrom (18) first reported its preparation by reaction of ammonium bromide with sodium tetraamidoaluminate. The equation for this reaction is:



The compound formed should perhaps best be referred to as ammonous aluminum nitride, $\text{AlN} \cdot x\text{NH}_3$, since it was found to possess a remarkable resemblance in properties to the analogous hydrous aluminum oxide precipitated from aqueous solution.

McElroy, Bennett, Kleinberg, and Davidson (9,19) 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 represented by the equation:



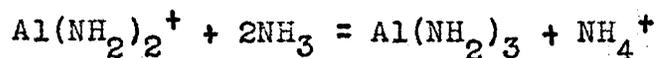
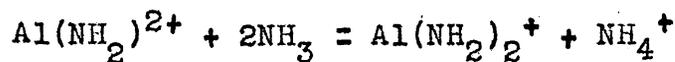
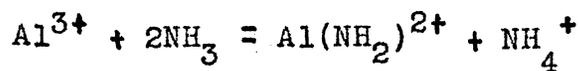
The next work to be mentioned was also performed at the University of Kansas and reported by Bennett, Davidson, and Kleinberg (1). It was found that in an electrolytic medium containing nitrate ion, anodic oxidation of pure aluminum metal gave rise to mean initial valence numbers of less than three for 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 (3,20) 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 per atom of aluminum. 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.

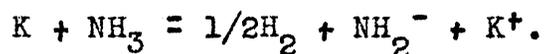
These investigators also reported some preliminary work on measuring the amount of hydrogen liberated in the reaction between potassium and aluminum iodide. It was found that substantially the stoichiometric quantity of hydrogen was evolved when the reaction was carried out rapidly. When the potassium was added very slowly, however, the amount of the 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 self consistent.

The final work to be mentioned here was reported by McElroy and Laitinen (21). 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 per atom of aluminum had been added and allowed to react completely. In neither case was there any evidence for oxidizable aluminum species as would be expected if stable 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:



EXPERIMENTAL

Two general techniques for the handling of liquid ammonia in laboratory experiments have been described in the literature. With the older method the experiments are carried out at room temperature which necessitates the use of sealed tubes capable of withstanding high pressures. The other technique makes use of cooling baths so that the reactions may be performed at atmospheric pressure. This second method has been used exclusively in the present work. The temperature extremes obtainable with this technique are -33° , the boiling point of ammonia, and -78° , the sublimation temperature of the carbon dioxide coolant.

MATERIALS

The cooling baths used in this work were prepared by adding pieces of solid carbon dioxide to cellosolve (ethylene glycol monoethyl ether) contained in Dewar flasks.

The aluminum(III) iodide starting material was prepared by the method of Watt and Hall (22). In this synthesis the elements are combined directly at $500-600^{\circ}$ in an evacuated system. The marked success of the method is attributable to the passage of the aluminum iodide through a long tube of heated aluminum which acts as a scavenger for the last traces of unreacted iodine. Reagent grade aluminum and iodine were employed and the product was pure white in color. The high purity of the product obtained is indicated by the following analytical data:

calculated for AlI_3 : 6.62% Al, 93.38% I; found: 6.6% Al, 93.4% I. Aluminum(III) iodide is an extremely hygroscopic material. Consequently, the preparation was sealed off in a number of small tubes which were opened only in a dry box.

Since aluminum iodide avidly absorbs ammonia, the actual material to which the metal solutions were added consisted of the ammoniation products of aluminum iodide. The ammoniation process is highly exothermic and if not in some way controlled sufficient heat accumulates to fuse the aluminum iodide. When this happens ammonolysis also occurs and ammonium iodide is vaporized from the melt (13). The final solid obtained from uncontrolled ammoniation was always tinged yellow by the presence of some free iodine which probably resulted from decomposition of ammonium iodide.

It was found that whether or not the ammoniation were moderated had little or no effect upon the results of the experiments, so long as none of the material was removed from the reaction vessel by the process. It seemed desirable, however, to keep ammonolysis at an experimental minimum and to use as clean a product as possible. To accomplish this control, three precautions were taken whenever possible. First, the aluminum iodide was taken from the preparation tubes in the form of small pellets, rather than as a powder, in order to expose as little surface to the ammonia as possible. Second, the vessel containing the iodide was surrounded by a

cooling bath maintained at approximately -70° . Finally, the ammonia passed over the aluminum iodide was highly diluted with nitrogen. This was accomplished by bubbling a slow stream of nitrogen through a reservoir of purified ammonia, the temperature of which was kept at about -40° .

The product obtained when these precautions were observed was a fine white powder. A typical sample gave the following analyses: 5.2% Al, 74.8% I, 20.2% NH_3 ; calculated for $\text{Al}(\text{NH}_3)_6\text{I}_3$: 5.3% Al, 74.7% I, 20.0% NH_3 . The analytical data indicate that the ammoniated product was essentially hexamminealuminum(III) iodide.

The nitrogen used in the experiments was taken from cylinders of the commercial water pumped product. The gas was passed successively through two 500 ml. bottles of chromium(II) sulfate solution to remove oxygen, and through drying towers of concentrated sulfuric acid, sodium hydroxide pellets, and granular magnesium perchlorate. The chromium(II) solutions were prepared by reduction of violet chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ with amalgamated zinc. The reduced solutions were approximately 0.25N in chromium and 0.1N in sulfuric acid.

The ammonia utilized in this work was the synthetic anhydrous product obtained from the Spencer Chemical Company. In each experiment gaseous ammonia was taken from the cylinder and condensed over a mixture of metallic sodium and sodium amide to insure complete removal of traces of water and oxygen.

Baker and Adamson reagent grade sodium and potassium

were employed. The other metals, lithium, calcium, and barium, were high quality commercial materials. All of the metals were obtained in bar form and were kept under anhydrous benzene to prevent oxidation.

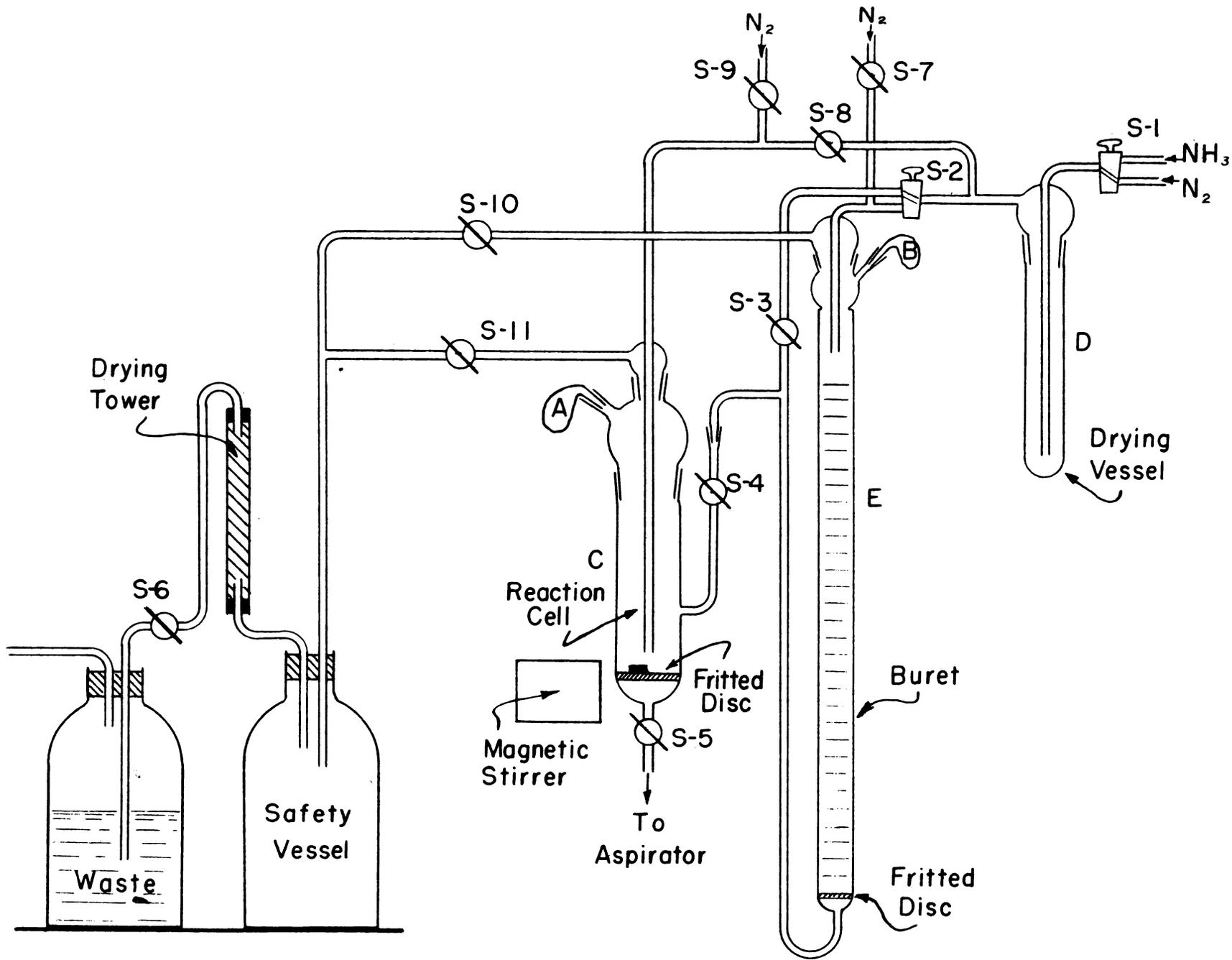
Chemicals required in the analyses and for other purposes were all of reagent grade as obtained from leading chemical manufacturers.

APPARATUS

The apparatus employed in this investigation combined, with some modification, the best features of three previously reported designs (23,24,25). The main parts of the set up are shown in the accompanying figure. The distinct advantage of this apparatus over those previously used was that the buret and main reaction vessel could be used independently of one another.

The large pieces of equipment were fabricated from Pyrex glass and connections were made by means of standard taper ground joints. The pieces of tubing and stopcocks, also Pyrex, which served to complete the apparatus system were joined by means of flexible Tygon tubing. It was impractical to depict all of the connecting tubes in the drawing. Hence it should be pointed out that when every piece was in place the entire reaction system was closed to the atmosphere except at the tube leading from the waste collector.

Stopcocks S-1 and S-2 were the three way, 3 mm. type. The remaining stopcocks were of the two way, 2 mm.



oblique design. The connective glass tubing was the standard 8 mm. material.

The main reaction cell C had a convenient working capacity of approximately 100 ml. If necessary, a maximum volume of 150 ml. could be accommodated in C. The sintered glass disc, of medium porosity, and stopcock S-5 made possible the separation and washing of solid phases without exposure to the atmosphere. The large 45/50 joint by which C was connected to the cell head facilitated removal of reaction products for analysis or for cleaning of the vessel. The reaction chamber C was united with the buret assembly by means of a small 14/35 joint located just above S-4. A standard quart size, wide mouth, silvered Dewar flask contained the cooling bath for C. The magnetic stirrer was placed next to the Dewar flask. Stirring bars cased in glass were used exclusively. Bars coated with Teflon and other plastic materials were found unsuitable because of their tendency to react with the metal solutions.

Buret E was of 45 ml. capacity and was graduated at 0.1 ml. intervals. The fritted disc, of medium porosity, was sealed in level with the last graduation thus obviating the calibration of an unetched volume. All of the tubing between the buret disc, through S-4, and the junction with C was of 1 mm. capillary material. The capillary tubing aided greatly the transference of the metal solutions from the buret into C. The Dewar flask used around the buret was a large 10 x 40 cm. vessel obtained from the H. S. Martin Company. The flask was strip silvered so that buret

readings on the deeply colored metal solutions could be made without removal of the cooling bath.

Addition bulb A served to admit the ammoniated aluminum iodide into the reaction cell. Similarly, bulb B was used to introduce the metal into the buret. The volumes of both A and B were approximately 25 ml. These bulbs were connected to the rest of the apparatus by means of 19/38 joints.

The vessel D, employed for the drying of ammonia, was simply a large tube of about 200 ml. capacity.

The safety vessel and waste container were five gallon carboys. The waste bottle contained water to absorb the waste ammonia. Functions served by the safety vessel were to help damp sudden pressure fluctuations which accompany the condensation of ammonia; and to receive any water sucked back from the waste absorption carboy under low pressure conditions.

The waste ammonia delivery tube extended some three or four inches below the surface of the water. This provided a positive pressure within the reaction system roughly equivalent to the several inches head of water. It should be pointed out that no other regulatory or safety device was included in the apparatus. In particular, it is believed that the commonly used mercury traps are hazardous and give chance for contamination of the system to such an extent as to outweigh the points in their favor.

The drying tower located between the two carboys was added as a further precaution against the admittance of water vapor into the reaction system. Sodium hydroxide pellets were employed as the desiccant.

The entire reaction system was mounted at a convenient working height, upon a steel rack situated on a vacuum bench. By means of the appropriate clamps the various pieces of glassware were made stationary upon the rack.

A homemade dry box was constructed from a five gallon solvent drum. The box contained two arm ports, a window, a light fixture, and gas entrance and exit tubes. Materials were placed into and taken from the dry box through one of the glove holes. Phosphorus(V) oxide served as the desiccant. An atmosphere of nitrogen was maintained within the box.

EXPERIMENTAL PROCEDURE

Reaction cell C and bulbs A and B were cleaned and dried overnight in an oven at 125°. The buret was not readily detached from the rack and so it was cleaned and dried in place. After the water washings, several portions of distilled acetone were forced through the buret. Finally, dry nitrogen was passed through the buret overnight to insure complete removal of the acetone. While the detachable parts of the apparatus were apart from the main system, the resulting open places in the tubing network were stoppered to prevent the entrance of air and moisture.

When the various pieces of equipment were assembled

in their proper positions, reaction cell C was flushed with nitrogen for at least one hour. Concurrently, condensation of ammonia was begun in the drying vessel. The buret had been thoroughly swept out with nitrogen in the cleaning process.

Bulb A was taken from the oven, stoppered, cooled in a desiccator, weighed, and placed in the dry box. In a nitrogen atmosphere, aluminum iodide was transferred from the preparation tube to the addition bulb. After removal from the dry box the tightly stoppered bulb was again weighed in order to ascertain the quantity of aluminum iodide taken for the experiment. In most experiments, the amount of aluminum iodide used was from 0.5 to 1.0 gm. or, roughly, 1-2 millimoles. The bulb containing the aluminum iodide was then quickly placed in its position above C. The aluminum iodide was then ammoniated in bulb A by means of the nitrogen diluted ammonia stream in accordance with the controlled procedure described previously. When ammoniation was complete, nitrogen was no longer passed into C; instead, a full stream of ammonia was admitted and some 50 ml. were condensed in the reaction cell. Ordinarily the ammoniated aluminum iodide was not transferred from A to the liquid in the main reaction vessel C until just before the titrations were begun.

The quantities of aluminum iodide normally employed in the titrations required the weighing of 100-500 mg. of metal, the exact amount depending upon the particular weight

of the aluminum iodide and the equivalent weight of the metal. Reasonably accurate weighings, to 1 mg., of such reactive substances as the alkali metals proved to be no simple task. Since the metals were stored under benzene the initial cutting operation on potassium, sodium, and lithium was done under the benzene. Calcium and barium were too hard to be cut with the paring knife used for the other metals; so these were cut into small pieces with a hacksaw. Mineral oil was poured over the metal being sawed to prevent undue exposure of the freshly cut surfaces to the atmosphere.

Only the most satisfactory weighing procedure found is described here. Pieces of the metal with untarnished surfaces were obtained, under benzene, by cutting the alkali metals and by scraping the previously sawed pieces of the alkaline earth metals. These pieces were then transferred, by means of a "spear" made from a glass rod, from the benzene medium to another vessel containing low boiling Skellysolve. The very volatile Skellysolve was blotted quickly with a circle of filter paper and the metal piece was dropped into a tared 50 ml. glass stoppered erlenmeyer flask which contained dry xylene. The flask which contained the xylene and metal was then weighed. Xylene was removed by again washing the metal with Skellysolve. The metal pieces were then placed into bulb B which had been flushed with gaseous ammonia and which contained a sufficient quantity of Skellysolve to cover the metal surfaces. Bulb B was put into position in the apparatus and the

volatile hydrocarbon product allowed to evaporate. This procedure had several advantages: the metal surfaces were exposed to the atmosphere only momentarily; washing with the very volatile Skellysolve minimized the possibility of weighing absorbed hydrocarbon with the metal; weighing was performed in a closed flask which contained a relatively non-volatile hydrocarbon; and the metal surfaces were quickly freed of the organic protective material used in the final washing.

With stopcock S-3 open and S-4 closed, ammonia was condensed in the buret E. Since the gas inlet was at the bottom of the buret, ample stirring was readily accomplished. When a sufficient quantity of ammonia was condensed in E the metal was added from B. To make a volume reading, all of the metal solution was forced into the buret by means of an appropriate pressure of nitrogen through S-1, S-2, and S-3.

When the original buret reading was determined the titration proper was begun. The metal solution was slowly transferred through S-4 into the suspension of ammoniated aluminum iodide in C. To accomplish this stopcocks S-7 and S-11 were open and S-8, S-9, S-10, and S-3 were closed. The contents of C were mixed by means of the magnetic stirrer. When the desired amount of metal solution had been added, the remaining solution was again forced back into the buret and the volume read.

Throughout most of the titrations a cooling bath was maintained around the reaction vessel. The temperature of

the bath was not rigidly controlled but since the bath ordinarily contained an excess of Dry Ice the temperature at which most of the experiments were made was in the neighborhood of -70° . In a few cases the titrations were performed at temperatures near the boiling point of ammonia. This was done by removing the Dewar flask and allowing the temperature of the system to rise to the boiling point.

When the titration was concluded the reaction mixture was filtered. The filtrate passed through S-5 into the filter flask. Precautions were taken to insure a positive pressure within the reaction system throughout the filtration. The flask containing the filtrate was placed in the hood and the solvent allowed to evaporate.

Solid products remaining on the fritted disc were washed by repeated condensation of fresh ammonia over the solid, followed by vigorous stirring of the resulting suspension. After the final washing the ammonia stream was replaced by nitrogen and the system was allowed to warm to room temperature. The reaction vessel was then taken from the apparatus, quickly stoppered, and placed in the dry box. In the dry box, samples were transferred from the reaction cell to tared glass-stoppered weighing bottles which were then removed and the quantity of sample determined by weighing.

ANALYTICAL METHODS

Whenever possible, solutions of samples for analysis were made up to a standard volume of 250 ml. and separate known aliquots of this volume were taken for determination

of the various constituents. As a rule, both solid and filtrate samples were dissolved in dilute acid, either sulfuric or perchloric.

Lithium, sodium, and potassium analyses were made by means of a Perkin-Elmer model 52-C flame photometer. The operating procedures employed were obtained from the manufacturer (26). Calcium was determined by precipitation as the oxalate (27), followed by titration of this substance with standardized potassium permanganate solution (28). Barium was separated as barium chromate which was then dissolved in dilute acid, and the iodine liberated from an added excess of potassium iodide was titrated with standard sodium thiosulfate solution (29).

Aluminum was determined gravimetrically with 8-quinolinol, using the tartrate method of Knowles (30).

Iodide analyses were performed gravimetrically as silver iodide and, more frequently, volumetrically. The volumetric method involved addition of an excess of standard potassium iodate to the acidified solution containing iodide. The liberated iodine was removed by boiling. Unused iodate was determined by addition of excess potassium iodide to the cooled solution followed by titration of the resulting iodine with standard thiosulfate (31).

Ammonia, either physically absorbed or as ammoniate, and substances such as amide and nitride, which hydrolyze to yield ammonia, were determined together. The solid samples were put into a boiling flask and tightly stoppered

in the dry box to prevent loss of ammonia from the very reactive materials. Aqueous sodium hydroxide (approximately 10 per cent by weight) was added to the samples by means of a dropping funnel. The strongly basic solutions were then boiled and the expelled ammonia received in a saturated boric acid solution which was surrounded by an ice bath. The ammonia absorbed by the boric acid, as ammonium borate, was then titrated with standard hydrochloric acid to the bromcresol green end point (32). Since no distinction was made as to the origin of the ammonia titrated, the results of such determinations were expressed in terms of nitrogen.

In some cases the very small amount of solid product available prohibited the use of aliquot portions for the aluminum and iodide analyses. In such instances the iodide was first separated as silver iodide. Then, after removal of excess silver ion as silver chloride, by the addition of hydrochloric acid, aluminum was precipitated with 8-quinolinol.

Generally, titration data were obtained directly from the buret readings and the weight of metal taken. In some experiments, however, more accurate data could be obtained by determination of the amount of unused metal. This was particularly true in the case of lithium which has both low equivalent weight and relatively low solubility in ammonia. The quantity of unused metal was ascertained either by the usual method of determination of the metal

or by titration, with standard acid, of the hydroxide formed by reaction of the metal with water.

Directions for the various standardizations required in the analyses were obtained from the textbook by Kolthoff and Sandell (28).

RESULTS AND DISCUSSION

THE APPARENT END POINT

The solubility of the ammoniated aluminum iodide in ammonia was found to diminish sharply with decreasing temperature. For example, many of the titrations performed involved approximately 0.5 gm. of aluminum iodide in about 50 ml. of ammonia. At -33° the ammoniate was completely soluble in this quantity of ammonia but as the temperature was lowered to -70° , a considerable amount of solid phase separated from solution.

It was found that the metals gave a vigorous initial reaction with the suspension of ammoniated aluminum(III) iodide. This reaction was attended by immediate discharge of the blue color of the metal solutions; evolution of hydrogen, which was identified qualitatively, from the whole of the reaction mixture; and liberation of heat.

Shortly after the addition of metal solution was begun all of the solid phase originally present at -70° passed into solution, possibly as the result of an increase in temperature attributable to the exothermic reaction. Another important factor possibly contributing to the increased solubility of the aluminum iodide ammoniate is the disturbance of the solubility equilibrium caused by removal of one of the equilibrium components.

The time required for the blue color of the metal solutions to disappear, on addition of successive increments of approximately equal magnitude, was taken as a measure of the rate of reaction. The rate decreased from that of

the initial rapid reaction to a very slow rate which was not greatly different from the rate of reaction between the metals and pure solvent. The gradual decrease in rate of reaction noted in the early stages of addition of the metals did not continue uniformly until the very slow rate was reached. Instead, in the vicinity of 1.5 equivalents of metal per atom of aluminum, a definite break occurred. The sharpness of the break is shown by the data in Table 2.

Table 2

Titration of 1.43 Millimoles of Aluminum Iodide with
0.104 M Potassium Solution

Successive volume readings, ml.	K increments in equivalents per atom of Al	Time, in minutes, required for blue color to disappear
0 - 22.2	0 - 1.60	10
22.2 - 22.7	1.60 - 1.64	3
22.7 - 23.2	1.64 - 1.67	60

This break, observed in titrations with all of the metals studied, has been termed the apparent end point. The apparent end point then, was defined as the point at which the metal ceased to be rapidly consumed. It would seem reasonable to attribute the rapid initial rate to a reaction different from the very slow reaction observed later. Thus the apparent end point became important in interpretation of the course of reaction because it served as a demarcation between reactions of widely different rates.

The average numerical values of the apparent end point, which were obtained with the various metals, are listed in Table 3.

Table 3

The Apparent End Point at -70°

Metal	Number of titrations averaged	Average equivalents of metal per atom of aluminum
Potassium	11	1.63 \pm 0.13
Sodium	6	1.7 \pm 0.1
Lithium	2	1.6
Calcium	2	1.6
Barium	2	1.5
All metals	23	1.6 \pm 0.1

With potassium some titrations were performed at -33° in order to determine the effect of a relatively large increase in temperature upon the apparent end point. At the higher temperature, the breaks were not as sharp as at -70° . An increased rate of reaction was the only significant effect of temperature, however, since the numerical values of the apparent end point were the same for both temperatures.

If lower valent aluminum were present for an appreciable length of time in the reaction mixtures at the apparent end point, the average oxidation state of the aluminum could be evaluated from the extent of reduction of a convenient

oxidizing agent. Solid silver nitrate was employed as the reagent to test for reducing power, for which the criterion would be formation of metallic silver. The silver salt was always introduced after the blue color, attributable to unreacted metal, disappeared. This precaution was necessary since the metal solutions would readily reduce silver nitrate.

Usually, when the apparent end point was reached, the silver nitrate was added to the turbid reaction mixtures. In other experiments, the filtrates were dropped onto the silver salt in the filter flask. Also, in some cases, several portions of the reaction mixtures were filtered onto silver nitrate at various intervals before the apparent end point was reached. Still further, experiments were performed in which the silver nitrate was added to suspensions, in ammonia, of solid products which appeared in reactions carried beyond the apparent end point.

In no case, before, at, or after the apparent end point, was there any detectable amount of metallic silver formed. The work concerned with the anodic oxidation of aluminum showed that the lower valent aluminum formed was very unstable (1). In fact, evidence for lower valent species was obtained only in the presence of a reducible ion such as nitrate. Therefore, it seems unlikely that possible lower states, prepared by reduction with the metal-ammonia solutions, would be of sufficient stability to fail to reduce silver ion. From these experiments it

was concluded that only aluminum(III) was present in the reaction products analyzed and further, that if lower valent aluminum were formed in the course of reaction, the existence of such species was so transitory as to elude detection by ordinary chemical means.

As the apparent end point was approached the reaction mixtures became turbid. Except for the experiments with metallic barium solutions, filtration immediately after the disappearance of the blue color at the apparent end point yielded only a small amount of grayish solid. With metals other than barium the quantity of solid obtained at this point did not exceed 20 mg. in experiments involving approximately 500 mg. of aluminum iodide. If the reaction mixtures, at the apparent end point, were allowed to stand for several hours before filtration an increased quantity of solid product was obtained. When barium was used, relatively large amounts of solid were present at the apparent end point.

The very small quantity of solid available from experiments with potassium, sodium, lithium, and calcium did not permit division of the sample into two portions as was necessary if nitrogen were to be determined in addition to aluminum and iodide. Consequently, only the atomic ratios of iodide to aluminum were obtained. Only traces of the metal titrants, except barium, were found in the solid products at the apparent end point. In the case of barium sufficient solid was obtained to allow complete analysis.

Some typical analyses of the solid products are listed in Table 4.

For comparative purposes, the iodide : aluminum ratios required for a number of ammonobasic aluminum iodides are presented in Table 5.

Examination of the data in Tables 4 and 5 indicate that the solids analyzed do not correspond to any one of the ammonobasic iodides included in Table 5. The variance among the analyses of the products obtained from the sodium and potassium experiments suggests that mixtures rather than pure compounds were present. The predominating substance believed to be present in these solids is the insoluble ammonobasic iodide described by Franklin (14) and later by McElroy (9). In those cases in which the aluminum : iodide ratio is greater than two, aluminum amide probably was present along with the ammonobasic iodide. It is also possible that some aluminum amide occurred in the other materials.

The data obtained with barium indicate that a slightly soluble ammoniate of barium iodide was the primary constituent of the solid present at the apparent end point. That ammonia is readily lost from the ammoniate is evidenced by the widely different nitrogen ratios listed in Table 4. The product which gave the higher nitrogen ratio was taken for analysis from the ammonia atmosphere immediately after the washed material reached room temperature. The lower nitrogen ratio product was allowed to stand at room temperature, in a nitrogen atmosphere, for two days before analysis.

Table 4

Solid Products at the Apparent End Point

Metal	Atomic ratios
Potassium	I : Al 1.0 : 1.4 1.0 : 1.5 1.0 : 1.6 1.0 : 2.7 1.0 : 3.0
Sodium	I : Al 1.0 : 1.6 1.0 : 1.8 1.0 : 2.1 1.0 : 2.2 1.0 : 2.4
Lithium	1.0 I : 1.2 Al
Calcium	1.0 I : 1.2 Al
Barium	1.00 Ba : 2.07 I : 7.13 N : 0 Al 1.00 Ba : 2.03 I : 1.24 N : 0 Al

Table 5

Iodide : Aluminum Ratios for Ammonobasic Iodides

Formula	Description	Atomic ratios
		I : Al
AlI_3	starting material	1.00 : 0.33
$Al(NH_2)_2I$	hypothetical	1.00 : 0.50
$AlI_3 \cdot Al(NH_2)_3$	Franklin's soluble salt	1.00 : 0.67
$Al(NH_2)_2I$	hypothetical	1.00 : 1.00
$Al(NH_2)_2I \cdot Al(NH_2)_3$	Franklin's insoluble salt	1.00 : 2.00

In both cases the sums of the constituent analyses exceeded 99 per cent.

From the small quantity of solid obtained at the apparent end point it is seen that only a relatively small fraction, not over 10 per cent, of the reaction mixtures was present in the solid phase when potassium, sodium, lithium, or calcium were reacted with aluminum iodide. Filtrate analyses, then, must be considered in any description and interpretation of the course of reaction. The quantities of material available in the filtrates made possible the procurement of reliable analytical data. Representative filtrate analyses are shown in Table 6. The numbers in the last column were obtained by subtraction of the iodide ratios from the sum of the metal and aluminum ratios, each multiplied by the appropriate valence number.

The striking feature of the filtrate analyses is the disparity between the determined cation and anion charges. This inequality was observed in every experiment in which the reaction mixture was filtered at the apparent end point and thus is not likely to be the result of analytical error. Two explanations of this charge disparity may be considered. First, if lower valent aluminum were present, multiplication of the aluminum ratio by three would give rise to an excess of cation charges. The reducing power experiments described earlier afforded no evidence for the presence of lower oxidation states of aluminum in the filtrates and so this possibility does not

Table 6

Filtrate Analyses at the Apparent End Point

Metal	Atomic ratios			Total cation charges minus anion charges
	Al :	M :	I	
Potassium	1.00 :	2.60 :	4.17	1.43
	1.00 :	3.43 :	4.71	1.72
	1.00 :	1.66 :	3.22	1.44
	1.00 :	2.65 :	3.91	1.74
	1.00 :	5.87 :	7.30	1.57
	1.00 :	4.71 :	6.20	1.51
	1.00 :	3.77 :	5.22	1.55
	1.00 :	2.68 :	4.06	1.62
	1.00 :	2.25 :	3.65	1.60
	1.00 :	2.29 :	3.74	<u>1.55</u>
			Average	1.57 ± 0.16
Sodium	1.00 :	2.21 :	3.60	1.61
	1.00 :	2.53 :	3.97	1.56
	1.00 :	1.93 :	3.26	1.67
	1.00 :	1.61 :	3.02	1.59
	1.00 :	1.84 :	3.30	<u>1.54</u>
			Average	1.59 ± 0.07
Lithium	1.00 :	1.41 :	3.01	1.40
	1.00 :	1.55 :	3.10	<u>1.45</u>
			Average	1.43 ± 0.03
Calcium	1.00 :	0.92 :	3.47	1.37
	1.00 :	0.89 :	3.10	<u>1.68</u>
			Average	1.53 ± 0.16
Barium	1.00 :	0.120 :	1.70	1.54
	1.00 :	0.135 :	1.88	<u>1.39</u>
			Average	1.47 ± 0.07

seem plausible. The alternative explanation of the apparent violation of electrical neutrality is that some other anion was present which was not determined in the scheme of analysis. Amide ion is the only other anion which could be present in the reaction system before filtration. Consequently, the charge disparity may be used as a measure of the amide present in the filtrate.

The data in Table 7, which are simply the average values of the data in Table 6, demonstrate a particularly interesting point. That is, at the apparent end point,

Table 7

Correlation between the Apparent End Point and the Amount
of Amide Found in the Filtrate

Metal	Average apparent end point, equivalents of metal per atom of Al	Average equivalents of amide, per atom of Al, in filtrate
Potassium	1.63	1.57
Sodium	1.7	1.59
Lithium	1.6	1.43
Calcium	1.6	1.53
Barium	1.5	1.47

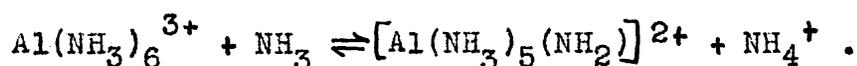
amide ion was present in quantities equivalent to the amount of metal which reacted. Actually, the agreement between the equivalents of metal, per atom of aluminum, consumed at the apparent end point and the equivalents of amide, per atom of aluminum, formed by reaction of the

metals is better than indicated by the values listed in Table 7. This results from the fact that the filtrate data represent some 90 to 95 per cent of the total aluminum whereas the apparent end point are recorded in terms of 100 per cent of the original aluminum iodide. Examination of the data in Table 4 indicates that from 2 to 3 equivalents of amide are associated with each aluminum atom in the solid products isolated at the apparent end point. Since the amide : aluminum ratio is greater for the solids than for the filtrates, the total amide values, referred to the total aluminum content, would be a little larger than the corresponding values given in Table 7 which considers only the filtrates. It should also be noted that free metal amide could not be present in the filtrate since sodium amide is only slightly soluble, and the amides of lithium, calcium, and barium are practically insoluble in ammonia. Therefore, the amide must have been tied up in a complex which was relatively stable toward dissociation.

Further information about the amide containing complex at the apparent end point was deduced from the analytical data in the following manner. Consider a typical filtrate analysis, obtained in a potassium reaction, in which the atomic ratios were 1.00 Al : 2.29 K : 3.74 I. Now, it would seem reasonable to propose that all of the potassium ion in this filtrate was associated with iodide ion since slightly soluble barium iodide was isolated from the reactions with barium. Subtraction of 2.29 from 3.74, to

account for potassium iodide, leaves the ratios 1.00 Al : 1.45 I : 1.55 NH₂ which are very near to the empirical composition of 1.00 Al : 1.50 I : 1.50 NH₂ required by the soluble ammonobasic iodide prepared by Franklin (14).

The proposed course of reaction can now be presented. It is believed that the driving force of the reaction is ammonolysis of the ammoniated aluminum ion to yield free ammonium ion and soluble ammonobasic aluminum compounds, in accordance with the equation:



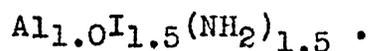
The rapid initial rate of reaction then, results from the destruction of ammonium ion by the metals. Some of the lines of evidence for ammonolysis of the original salt are as follows:

- (1) Ammonolysis is known to occur in the uncontrolled ammoniation of aluminum iodide with gaseous ammonia (13).
- (2) The small, highly charged aluminum ion should show some acidic character in ammonia as it is known to do in aqueous medium.
- (3) X-ray diffraction patterns of ammoniated aluminum iodide samples possess lines attributable to ammonium iodide (33).
- (4) A sample of ammoniated aluminum iodide was dissolved in ammonia and the solution was allowed to stand at approximately -55°. After the passage of about 24 hours the solution became

turbid. When the mixture was filtered, after 67 hours, a small quantity of solid remained. Analysis of the solid yielded the ratios of 4.31 Al : 1.00 I which indicated precipitation of ammonobasic substances. The filtrate ratios, 1.00 Al : 3.61 I, possessed a deficiency of cation charges which could be explained on the basis of the presence of ammonium ion.

The available evidence indicates that the actual degree of ammonolysis is very small. That any ammonolysis occurs is significant, however, since the ammonolytic equilibrium would be continuously displaced by the irreversible liberation of hydrogen from ammonium ion. The net result of the addition of the metals then, would be evolution of hydrogen and accumulation of amide in the solution. Since the liberation of hydrogen and production of amide result from the same sequence of reactions, the amount of amide found at the apparent end point also gives an indirect measure of the quantity of hydrogen formed. One-half mole of hydrogen would be evolved for each gram ion of amide produced.

It is proposed that the original ammonolytic equilibrium was responsible for the propagation of the reaction with the metals until sufficient amide accumulated to form a soluble complex of empirical composition



This complex was relatively stable toward both dissociation

and further ammonolysis. The stability of the complex would explain the sharp break in the rate of reaction observed when the apparent end point was reached.

It might be suggested that the aluminum ion in some manner catalyzes the otherwise very slow reaction between the metals and ammonia. Such an explanation, however, would not account for the sudden loss of catalytic activity at the apparent end point. It should also be pointed out that if lower valent aluminum had transitory existence in these reactions, the end result could very well be the same as postulated in the preceding paragraphs. This would be expected since the lower valent aluminum must react immediately with the solvent yielding hydrogen, amide, and aluminum(III). It would then be impossible to distinguish between the two mechanisms in a chemical manner.

As mentioned previously, the quantity of solid products obtained at the apparent end point was a function of the time the reaction mixtures were allowed to stand. Not only did the amount of solid increase with time but also the aluminum : iodide ratios in the solid products increased with time. These observations suggest that the solid products originated from ammonolysis of the soluble complex and, further, that the solid materials formed were themselves subject to ammonolysis. The effect of this continued ammonolysis was the production of more amide and ammonium ions and the replacement of iodide ion originally associated with the aluminum by this amide.

It seemed of interest to study the effect upon the apparent end point values, of allowing the original aluminum iodide suspensions to stand for some time before titration. The results of these experiments are presented in Table 8.

Table 8

Effect, upon the Apparent End Point, of Delayed Titration

Hours elapsed between solution and titration	Apparent end point, equivalents of potassium per atom of aluminum
12	1.72
12	1.95
14	1.95
16	1.81
18	1.95
20	1.92
24	1.87

It is seen that the apparent end point values increased as a result of delayed titration. The absence of a uniform increase with time is believed to be attributable to temperature fluctuations, since the temperature was not strictly controlled. Thus, to effect ammonolysis, a shorter time at a higher temperature could be just as effective as a longer standing period at lower temperatures. The experiment, presented earlier in the list of evidence for ammonolysis, in which aluminum iodide was allowed to stand in ammonia solution for 67 hours, showed that the extent of ammonolysis increased with prolonged standing in solution.

Similar reasoning may be used to explain the increased values for the apparent end point in the delayed titrations. These increased values, however, are believed to result not from an extension of the original ammonolytic equilibrium but rather from ammonium ion obtained from continued ammonolysis of the basic substances produced by the original ammonolysis. The data in Table 8 are cited as further evidence of the importance of ammonolytic reactions to an understanding of the course of reaction in this system.

If, as has been postulated above, a net effect of addition of the metals to ammonia solutions of aluminum iodide is an accumulation of amide in the solutions, titrations with ammonia soluble potassium amide should give results similar to those obtained with the metals. Such experiments were performed to throw more light upon the interpretation proposed. Solutions of potassium, in the buret, were converted to the amide in the presence of a shiny iron wire catalyst. Since the pale yellow ammonia solutions of potassium amide do not possess sufficiently intense color to function as self indicators, no such break as the apparent end point could be obtained in the amide titrations. Instead, titration was stopped at the first observation of permanent turbidity in the reaction mixtures. These titrations were performed at about -50° to insure complete solubility of the ammoniated aluminum iodide. The turbidity point was found to be in the

vicinity of 1.6 equivalents of amide per atom of aluminum, which is in agreement with the corresponding point in the titrations with the metals, namely, near the apparent end point. Analytical data on solid products and filtrates from amide titrations showed similar agreement with data obtained with the metals.

In another experiment, a mixed amide-metal titration was made. First 0.90 equiv. of potassium amide, per atom of aluminum, was added to the aluminum iodide solution. Then, the titration was continued with potassium until the apparent end point was reached. The amount of potassium required was 0.87 equiv., which made a total of 1.77 equiv. of potassium and amide added. This combined value is higher than but still of the same order of magnitude as the usual apparent end point values obtained with the metals. Some of the data obtained from the amide experiments are presented in Table 9. The qualitative and quantitative

Table 9

Analyses of Products from Amide Titration

Equiv. added	Solid	Filtrate	Amide in filtrate
	I : Al	Al : K : I	
1.60 KNH ₂	1.0 : 4.7	1.00 : 1.73 : 3.36	1.37
0.90 KNH ₂ plus 0.87 K	1.0 : 2.5	1.00 : 3.38 : 4.82	1.56

similarities between the metal titrations and the amide

titrations suggest that, in many respects, the overall reactions are identical. Once again, the experimental results lend support to the interpretation given to the course of reaction.

REACTION BEYOND THE APPARENT END POINT

As indicated previously the qualified expression apparent end point was coined because the metals continued to react, slowly, beyond the initial break. The rate of reaction past the apparent end point was of the same order of magnitude as that expected for the reaction of the metals with ammonia in heterogeneous medium. An indication of the time required for these slow reactions may be gained from the data in Table 10.

Table 10

Time Involved in Reactions Beyond the Apparent End Point

Metal, and equiv. reacted per atom of aluminum	Hours required for complete reaction of metal
1.91 K	4
2.04 K	4
2.16 K	14
2.55 K	75
2.57 Na	68
2.62 Li	90
3.08 K	96
4.12 Ca	92
4.21 K	190

The time values listed in Table 10 are not necessarily comparable one with another. Obviously, the time required for reaction is primarily dependent upon the quantity of metal which reacts, and the actual weights of metal consumed are not specified in the table. Also, temperature fluctuations from experiment to experiment should affect the rates of the reactions. The purpose of Table 10 is simply to illustrate that long periods of time are involved in the slow reactions. The sharpness of the break at the apparent end point again may be emphasized with the data of Table 10. For example, consider the reaction in which 75 hours were required for the consumption of 2.55 equiv. of potassium. The first 1.60 equiv. of the metal reacted in about one hour which means that the final 0.95 equiv. required some 74 hours for reaction.

Typical analytical data obtained from the products of reactions past the apparent end point are summarized in Table 11. It is felt that analyses expressed in percentages may make the atomic ratio data more meaningful. Therefore, Table 12 was constructed from some of the values given in Table 11.

The data in Table 11 indicate that the solid products obtained from reaction of from 2.0 to 2.5 equivalents of metal per atom of aluminum, possessed aluminum : iodide ratios which were not significantly different from those of the solids present at the apparent end point. In other words, the solid products obtained from reaction of up to 2.5 equivalents of metal were mixtures of ammonobasic

Table 11

Reactions Beyond the Apparent End Point

Titrant	Equiv. per atom of Al	Solid Analyses atomic ratios				Filtrate Analyses atomic ratios			Amide in filtrate
		I	Al	M	N	Al	M	I	
K	2.03	1.00	2.06	0.05	----	1.00	4.90	6.53	1.37
K	2.04	1.00	1.54	----	5.50	1.00	4.69	6.81	0.88
K	2.06	1.00	1.66	0.02	5.81	1.00	5.88	7.58	1.30
Na	2.1	1.00	1.67	0.0	5.65	-----	-----	-----	-----
K	2.16	1.00	2.10	0.05	----	1.00	7.23	9.00	1.23
Na	2.5	1.00	1.61	----	5.84	0.0	1.03	1.00	0.0
K	2.54	1.00	1.80	0.05	4.80	0.0	1.00	1.03	0.0
K	2.55	1.00	3.32	0.12	----	0.05	1.00	1.15	0.0
KNH ₂	2.55	1.00	2.44	0.12	6.06	0.01	1.00	1.04	0.0
Na	2.57	1.00	2.18	0.10	6.40	0.0	1.00	1.01	0.0
Li	2.62	1.00	2.77	----	8.71	0.04	1.00	1.13	0.0
KNH ₂	3.00	0.06	1.00	0.16	----	0.0	1.00	1.05	0.0
K	3.08	0.04	1.00	0.17	3.1	0.0	1.00	1.00	0.0
Ca	4.12	0.0	1.70	1.00	6.86	1.00	3.45	5.94	3.96
KNH ₂	4.12	0.0	1.65	1.00	----	1.00	4.87	4.01	3.86
K	4.18	0.0	1.00	1.17	----	-----	-----	-----	-----
K	4.21	0.0	1.15	1.00	----	1.00	5.68	4.92	3.76
KNH ₂	4.21	0.0	1.00	1.20	----	1.00	4.83	3.63	4.20

Table 12

Percentage Composition of Solid Products

Equiv. of metal per atom of Al	Percentage composition of solid			
	I	Al	M	N
2.04 K	47.3	15.4	-----	28.7
2.12 K	47.2	16.9	1.9	-----
2.55 KNH ₂	40.3	20.9	1.4	26.6
2.57 Na	41.0	19.0	0.7	28.9
2.62 Li	36.1	21.2	0.07	34.7
2.8 K	38.5	21.0	5.6	32.5
3.00 KNH ₂	9.5	32.1	7.2	-----
3.08 K	5.6	31.3	7.9	-----
4.12 Ca	0.0	21.6	18.9	45.3
4.21 K	0.0	19.2	24.2	-----

aluminum iodides, predominately the insoluble material of empirical composition $\text{Al}(\text{NH}_2)_3 \cdot \text{Al}(\text{NH}_2)_2\text{I}$, and, occasionally, some aluminum amide. The longer reaction times beyond the apparent end point should favor the formation of aluminum amide by ammonolysis of the ammonobasic iodides.

The quantities of solid obtained from the reactions past the apparent end point, particularly when more than 2.0 equivalents of metal were consumed, were much greater than the amounts present at the apparent end point. This is primarily attributable to the increased quantities of amide ion, which became available as more metal reacted.

When about 2.5 equivalents of metal had reacted, essentially all of the aluminum was present in the solid phase. The filtrates at this point contained only the metal iodide as a major constituent. Reaction of from 2.5 to 3.0 equivalents of metal resulted in further replacement of iodide, by amide, in the solid products. In the vicinity of 3.0 equivalents of metal reacted, the major solid product was aluminum amide. Again mixtures were present, however, for the solids at 3.0 equivalents contained both iodide and potassium. When 4.0 equivalents of metal reacted, aluminum once again was found in the filtrate as a result of formation of the fairly soluble tetramidoaluminate complexes.

From the data in Table 11 it is seen that the analytical results from the reactions which involved the use of potassium amide as titrant are very similar to those obtained from the metal reactions at the appropriate point of comparison. In one respect, however, some of the amide reactions differed greatly from those of the metals. This difference occurred in the experiments in which about 4 equivalents of the titrant reacted. In the case of the reactions with the metals, relatively large quantities of solid, involving approximately 40 per cent of the original aluminum, remained at the completion of the reaction. With potassium amide, however, only a minute amount of solid product was present when the reaction mixture was filtered. The analytical data indicate that the same products are formed with both amide and metal. The solid products appear to consist primarily of the amidoaluminate

complex which is contaminated with either metal amide or aluminum amide. For example, the atomic ratios found in the solid from the reaction of 4.12 equivalents of calcium were in excellent accord with those expected from a mixture of calcium tetraamidoaluminate and calcium amide in the ratio of 1.00 : 0.12, respectively. Incidentally, the preparation of the calcium amidoaluminate apparently has not been previously reported. It is believed that the difference between the amide and metal experiments at 4 equivalents is probably the result of an aging phenomenon which arises from the very long period of time required for the metal reaction. No experimental evidence was obtained, however, to support this view.

The formation of the solid products may be conveniently represented by the following series of steps:

$$\text{AlI}_3 \rightarrow \text{Al}(\text{NH}_2)\text{I}_2 \rightarrow \text{Al}(\text{NH}_2)_2\text{I} \rightarrow \text{Al}(\text{NH}_2)_3 \rightarrow \text{MAl}(\text{NH}_2)_4.$$
This formulation is of a speculative nature since it is not known whether or not $\text{Al}(\text{NH}_2)\text{I}_2$ and $\text{Al}(\text{NH}_2)_2\text{I}$ actually exist. The reaction products which contain aluminum, however, may be accounted for successfully on the assumption that such products consist of mixtures of the appropriate ammonobasic compounds, listed above, which were derived from aluminum iodide.

It should be stressed that the ammonobasic iodides and the amidoaluminates are subject to ammonolysis, with the ultimate formation of aluminum amide, upon prolonged contact with liquid ammonia. For example, ammonia washed samples of an ammonobasic iodide, which had aluminum :

iodide ratios of approximately 2 : 1, initially were suspended in pure ammonia and allowed to stand for long periods of time. One sample was analyzed after the passage of 60 hours and the other after 87 hours. The atomic ratios found in the solids were 5.3 Al : 1.0 I and 7.2 Al : 1.0 I, respectively. In each case, iodide ion was detected in the filtrate.

In the light of the number of possible products and the ammonolytic reactions which these products can undergo, it is not surprising that mixtures, rather than pure compounds, were always obtained from the reaction system studied.

In an entirely different type of experiment, the ammonobasic iodide mixture obtained by reaction of 2.06 equivalents of potassium per atom of aluminum, was heated to 800° in an evacuated Vycor tube. Ammonia and ammonium iodide were liberated from the heated solid, which lost approximately two-thirds of its original weight. The pertinent analytical data derived from this experiment were as follows: for the original ammonobasic iodide mixture the ratios, 1.00 I : 1.66 Al : 5.81 N : 0.02 K; for the original filtrate, 1.00 Al : 5.88 K : 7.58 I : 1.30 NH₂; and for the heated solid, 1.00 N : 1.07 Al : 0.102 I : 0.0009 K were found. The percentage composition of the heated solid was 22.0 N, 20.3 I, 45.5 Al, and 0.3 K. The analytical data from the heated solid indicate that aluminum nitride, AlN, was the primary constituent of the

of the material produced at 800° . The iodide in the heated substance possibly was present as an imide - iodide such as $\text{Al}(\text{NH})\text{I}$. The products obtained from the thermal decomposition experiment were just as would be expected from an original ammonobasic iodide mixture and afford no evidence for the presence of lower valent aluminum, either in the original solid or in the heated solid.

McElroy, Kleinberg, and Davidson (9) 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. The components of the reaction systems described in this thesis differed from those of McElroy, Kleinberg, and Davidson only in that alkali or alkaline earth metal ions were also present. Since these metal ions, as such, should have no direct effect upon the nature of the aluminum products obtained, the two systems are essentially equivalent, and ammonobasic aluminum compounds found in the electrolytic investigations should also be the result of the present experiments. In the reactions investigated in the present work, the excess of solvated electrons, which, of course, were accompanied by alkali or alkaline earth metal ions, allowed further reaction and the formation of products other than the one ammonobasic iodide obtained by McElroy and co-workers.

Finally a few words are necessary concerning the interpretation of the potentiometric titration data of Watt, Hall, and Choppin (3). If reduction of aluminum

to lower oxidation states takes place, the species formed must react almost 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 $\text{Al}^{2+} + \text{NH}_3 = \text{Al}^{3+} + \text{NH}_2^- + \frac{1}{2}\text{H}_2$. 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 $\text{Al(III)}/\text{Al(II)}$. Also, the conversion to aluminum(II) must take place in more than trace quantities. 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.

SUMMARY

Ammonia solutions of potassium, sodium, lithium, calcium, and barium react vigorously with suspensions of aluminum iodide hexammoniate in ammonia at -70° . It is believed that the rapid initial reaction is between the metals and ammonium ion which results from ammonolysis of the aluminum ion. Although the degree of ammonolysis is small, the ammonolytic equilibrium is continuously displaced by the irreversible evolution of hydrogen, and the rapid reaction continues until all of the aluminum is tied up as a soluble, stable complex of empirical composition $Al_{1.0}I_{1.5}(NH_2)_{1.5}$. When this has occurred the rate of consumption of the metals thereafter decreases greatly.

This point is termed the apparent end point, the average value of which, determined from titrations with solutions of the five above mentioned metals, is 1.6 ± 0.1 equivalents of metal per atom of aluminum. At the apparent end point not more than 10 per cent of the aluminum in the reaction mixtures is present in the solid phase, the remainder being in solution. Reducing power experiments with silver nitrate indicate that lower valent aluminum species cannot be detected in the reaction mixtures at any time during the course of reaction.

The excess of cation charges over anion charges observed from the analytical values for aluminum, metal and iodide ions gives a measure of the quantity of amide formed. The amide is present in the solid products as a

constituent of ammonobasic aluminum compounds and in the filtrates in the soluble ammonobasic aluminum iodide, $Al_{1.0}I_{1.5}(NH_2)_{1.5}$. Experiments which involve barium differ from those with the other metals in that slightly soluble barium iodide ammoniates occur in solid products at the apparent end point, whereas the iodides of the other metals are soluble in ammonia.

Consideration of the total amide found at the apparent end point, both in the solids and filtrates, shows that for each equivalent of metal which reacts one equivalent of amide is produced.

Reaction beyond the apparent end point proceeds at extremely slow rates which approximate those of the metals with the solvent. The result of these slow reactions is the production of more amide and the accumulation of larger quantities of solid products, which are mixtures of ammonobasic aluminum compounds rather than pure substances.

Titrations with potassium amide, in most cases, are qualitatively and quantitatively in agreement with the corresponding titrations with the metals.

The results of this work do not preclude the formation and transitory existence of unstable lower valent aluminum species in the reaction systems. It is believed, however, that sufficient evidence for the existence of such species in systems of this kind has not yet been presented.

SUGGESTIONS FOR FURTHER WORK

Successful reduction of simple aluminum salts to lower oxidation states in ammonia solution seems unlikely because of the preferential reduction of ammonium ion produced by ammonolysis of the small, highly charged aluminum ion.

Reduction studies on stable aluminum complexes such as the fluoro complex Na_3AlF_6 , might be worthwhile. The solubility of such compounds in ammonia is probably very small, however. Complexes containing reducible ligands should be avoided.

The present work suggests that the possibility of ammonolysis must be considered in the interpretation of reduction studies in ammonia solutions. Such investigations, regardless of the experimental technique employed, should be accompanied by complete analyses before reduction to lower oxidation states is postulated.

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