[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Reactions of Some Alkali and Alkaline Earth Metals with Aluminum(III) Iodide in Liquid Ammonia

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Ammonia solutions of potassium, sodium, lithium, calcium and barium react vigorously with suspensions of aluminum iodide hexammoniate in ammonia at −70°. No evidence has been obtained for the existence of lower oxidation states of aluminum in such systems. 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 the aluminum is tied up as a soluble, relatively stable complex of the empirical composition $Al_{1.0}(NH_2)_{1.5}I_{1.5}$. When this has occurred, the rate of consumption of the metals thereafter decreases greatly. Reaction beyond this point proceeds at rates which approximate those of the metals with the solvent, and solid products isolated are mixtures of ammonobasic aluminum compounds.

A previous report from this Laboratory presented evidence for the formation of a very unstable lower oxidation state of aluminum prepared by the anodic oxidation of the metal in a suitable electrolyte in liquid ammonia.[1] The results of potentiometric titrations of ammonia solutions of aluminum iodide with potassium solutions have been interpreted as perhaps representing a stepwise reduction to aluminum(II) and aluminum(I).[2] A polarographic investigation of ammonia solutions of aluminum iodide, either alone or after reaction with metallic potassium, failed to present evidence for the formation of lower oxidation states of aluminum in those systems.[3]

Several examples of materials, stable only at elevated temperatures, which contain aluminum in lower oxidation states have been reported in the literature.[4] Only one such substance, a monoiodide, has been isolated at a lower temperature.[5]

The present report describes the results of reactions in liquid ammonia between aluminum(III) iodide and solutions of the metals potassium, sodium, lithium, calcium and barium. In no case has reduction of aluminum(III) to a lower oxidation state been detected. Furthermore, it is not necessary to assume the transitory formation of lower states of aluminum in order to account adequately for the reaction products isolated.

Experimental

Materials.—In each experiment the "refrigeration grade" ammonia (Spencer Chemical Co.) employed was dried by condensation over a mixture of sodium and sodium amide. Commercial water-pumped nitrogen was purified by successive passage through two 500-ml. bottles of chromium(II) sulfate solution to remove oxygen and through drying towers of sodium hydroxide pellets and anhydrous magnesium perchlorate. The cooling baths, contained in Dewar flasks, consisted of solid carbon dioxide and Cellosolve.

The aluminum iodide starting material was prepared by direct combination of the elements (reagent grade) in accordance with the procedure of Watt and Hall.[6] The high purity of the product obtained is indicated by the following analytical data; calcd. for AlI_3: Al, 6.62; I, 93.38. Found: Al, 6.6; I, 93.4. The hygroscopic aluminum iodide was preserved in sealed tubes which were opened only in a dry-box.

Since aluminum iodide avidly absorbs gaseous ammonia, the actual material to which the metal solutions were added consisted of ammoniation products. 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.[7] Certain precautions were taken to minimize ammonolysis during the ammoniation of the aluminum iodide. The iodide was taken from the preparation tubes in pellet form in order to expose as little surface as possible to the ammonia. Also, a cooling bath maintained at approximately −70° was placed around the vessel (see Experimental Procedure) in which the ammoniation was performed. 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 dried 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. Calcd. for $[Al(NH_3)_6]I_3$: Al, 5.3; I, 74.7; NH_3, 20.0. Found: Al, 5.2; I, 74.8; NH_3, 20.2.

Baker and Adamson reagent grade sodium and potassium were employed. The other metals, lithium, calcium and barium, were high quality commercial materials. Compounds required in the analyses were all of reagent grade.

Apparatus.—The titration apparatus employed in this investigation combined, with some modification, the best features of three previously reported designs.[8-11] The primary parts of the apparatus were a buret of 45-ml. capacity for holding the metal–ammonia solutions and a main reaction cell which could be used independently of one another. The main reaction vessel contained a sintered glass filter plate which facilitated the isolation and washing of solid materials. Proper precautions were taken to prevent the entrance of atmospheric moisture and oxygen into the apparatus during the course of an experiment.

Experimental Procedure.—In an atmosphere of nitrogen in a dry-box, aluminum iodide was put into a tared addition bulb which was then tightly stoppered, removed from the dry-box, weighed and placed in position in the apparatus which also possessed a nitrogen atmosphere. In most experiments the quantity of aluminum iodide used was from 0.5 to 1.0 g. or about 1–2 millimoles. The aluminum iodide was ammoniated in the addition bulb. Just before the titration was begun the ammoniated material was suspended in approximately 50 ml. of ammonia in the main reaction cell. The metal–ammonia solutions were prepared in the buret, from which they were run into the reaction cell as desired. The metals used were stored and cut under dry benzene and were weighed under dry xylene in a glass stoppered flask. In most cases the titrations were performed at temperatures near −70°.

After the desired quantity of metal had reacted, the re-

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(1) W. E. Bennett, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **74**, 732 (1952).

(2) G. W. Watt, J. L. Hall and G. R. Choppin, *ibid.*, **73**, 5920 (1951); *J. Phys. Chem.*, **57**, 567 (1953).

(3) A. D. McElroy and H. A. Laitinen, *ibid.*, **57**, 564 (1953).

(4) J. P. McGeer, *J. Chem. Educ.*, **29**, 534 (1952).

(5) W. C. Schumb and H. H. Rogers, THIS JOURNAL, **73**, 5806 (1951).

(6) G. W. Watt and J. L. Hall, *Inorg. Syntheses*, **4**, 117 (1953).

(7) E. C. Franklin, THIS JOURNAL, **27**, 849 (1905).

(8) V. J. Christensen, J. Kleinberg and A. W. Davidson, *ibid.*, **74**, 2495 (1953).

(9) G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

(10) G. W. Watt and T. E. Moore, *ibid.*, **70**, 1197 (1948).

(11) A complete description and diagram of the apparatus are given in the Ph.D. thesis of William Lloyd Taylor, University of Kansas, 1954.

action mixtures were filtered. Solid products were washed with ammonia and then allowed to warm to room temperature in a nitrogen atmosphere. Further handling of the solids, prior to analysis, was done in the dry-box. The solvent was evaporated from the filtrates and the resulting solid materials were retained for analyses.

Analytical Methods.—Generally, titration data (*i.e.*, quantity of metal consumed in reaction with aluminum iodide) were obtained directly from the buret readings. In some experiments, however, more accurate data could be obtained by determination of the quantity of unused metal, either by the usual method (see below) of determination of the metal or by titration with standard acid of the hydroxide formed by reaction of the unused metal with water.

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. Calcium was determined by precipitation of the oxalate which was then titrated with standardized potassium permanganate solution. Barium was separated as the chromate which was then determined iodimetrically.

Aluminum was determined gravimetrically with 8-quinolinol. Iodide analyses were usually performed volumetrically by means of standard potassium iodate and sodium thiosulfate solutions. In some cases the small quantity of sample 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, aluminum was precipitated with 8-quinolinol.

Ammonia and substances such as amide, which hydrolyze to yield ammonia, were determined together. The ammonia, liberated by strong aqueous sodium hydroxide, was absorbed in boric acid solution and then titrated with standard hydrochloric acid. Since no distinction was made as to the origin of the ammonia, the results of this determination were calculated simply as nitrogen.

In most experiments at least 90% of the total starting materials were accounted for in the combined filtrate and solid analyses.

Results and Discussion

The Apparent End-point.—The solubility of the ammoniated aluminum iodide was found to diminish sharply with decreasing temperature. For example, the ammoniate from approximately 0.5 g. of aluminum iodide was freely soluble in about 50 ml. of ammonia at −33°. As the temperature was lowered to −70°, however, a considerable quantity of solid phase separated from solution.

The metal solutions reacted vigorously with the suspensions of ammoniated aluminum iodide at approximately −70°. This initial reaction was attended by immediate discharge of the blue color of the metal solutions, evolution of hydrogen, 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.

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, not greatly different from that observed for the reaction between the metals and pure solvent. The transition from the initial rapid rate of reaction to the final slow rate took place rather abruptly in the vicinity of 1.6 equivalents of metal per atom of aluminum. To illustrate the sharpness of the change in reaction rate, data from a typical titration of 1.43 millimoles of aluminum iodide with 0.104 *M* potassium solution are presented. Some 13 minutes were required for the addition, in several portions, and complete reaction of 22.7 ml. of the metal solution corresponding to a total of 1.64 equivalents of metal per atom of aluminum. However, the blue color which resulted from addition of another 0.5 ml. of metal solution, or only 0.03 equivalent more, persisted for 60 minutes. This sort of break, observed in titrations with all of the metals studied, has been termed the *apparent end-point*, which is defined as the point at which the metals ceased to be rapidly consumed. The only observed effect of an increase in temperature upon the apparent end-point was a diminution of the sharpness of the break. Titrations performed at −33° yielded the same apparent end-point values as were found at −70°. The average numerical values of the apparent end-point are listed in Table I. The origin and significance of the data in the last column will be discussed shortly.

TABLE I

THE APPARENT END-POINT

Metal	No. of titrations	Av. apparent end-point, equiv. of metal/g. atom of Al	Av. equiv. of amide/g. atom of Al, in filtrate
Potassium	11	1.63 ± 0.13	1.57 ± 0.16
Sodium	6	1.7 ± 0.1	1.59 ± .07
Lithium	2	1.6	1.43 ± .03
Calcium	2	1.6	1.53 ± .16
Barium	2	1.5	1.47 ± .07
All metals	23	1.6 ± 0.1	1.55 ± .16

If a lower oxidation state of aluminum were present for an appreciable length of time in the reaction mixtures, the average oxidation state of the aluminum could be evaluated from the extent of reduction of an oxidizing agent. Silver nitrate was employed as the reagent to test for reducing power, for which the criterion would be the formation of metallic silver. The silver salt was always introduced after the blue color of unreacted metal had disappeared since the metal solutions would readily reduce silver ion. In no case, before, at, or beyond the apparent end-point, was there any detectable quantity of metallic silver formed. A previous investigation concerned with the anodic oxidation of aluminum in ammonia showed that evidence for the existence of a lower oxidation state of aluminum was obtained only in the presence of a reducible ion such as nitrate.[1] Therefore, it seems unlikely that a lower state, prepared by reduction of tripositive aluminum with the metal solutions, would possess sufficient stability to fail to reduce silver ion. From these experiments it was concluded that aluminum was present exclusively as aluminum(III) in the materials analyzed.

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, *i.e.*, at the apparent end-point, yielded only a small amount of grayish solid. This quantity of material in the solid phase represented only about 10%, or less, of the total reaction mixtures. Consequently, the composition of the material in solution at the apparent end-point must be considered in any description and interpretation of the course of reaction. Analysis of the solids left on evaporation of the solvent revealed an interesting and significant fact. Although in some instances the atomic ratios of aluminum:alkali (or alkaline earth) metal:iodide varied over fairly wide limits, the total cation equivalents (aluminum being considered to be present only in the tripositive state) exceeded the iodide equivalents by an amount which corresponded closely with the quantity of metal consumed. Since amide ion is the only other anion which could exist in the reaction mixtures before filtration, the disparity between the number of cation and iodide equivalents may be used as a measure of amide present in the filtrate (see last column of Table I).

The presence of amide ion in the filtrate in quantities equivalent to the amount of metal which reacted is consistent with the observation of McElroy and Laitinen[3] that reaction between potassium and aluminum iodide in liquid ammonia results in the liberation of hydrogen in accordance with the equation

$$K + NH_3 = K^+ + NH_2^- + {}^1/_2H_2$$

The agreement between the values for the equivalents of metal consumed at the apparent end-point and the equivalents of amide formed by reaction of the metals is actually somewhat better than indicated by the respective values in Table I. This results from the fact that the filtrate data represent some 90 to 95% of the total aluminum whereas the apparent end-point data are recorded in terms of 100% of the original aluminum iodide. The solid products also were found to contain amide, and furthermore the amide:aluminum ratios in these solids were greater than the corresponding ratios for the filtrates. Therefore, consideration of the total amide present, referred to the total aluminum content, would give values slightly larger than those in Table I which are calculated on the basis of the filtrates alone.

It should be noted that free amide ion could not be present in the filtrates since, of the metals studied, only potassium yields an appreciably soluble amide. The amides of lithium, calcium and barium are practically insoluble in ammonia. Consequently, the amide in the filtrates must have been tied up in a complex, undoubtedly with aluminum.

With the exception of the experiments with barium, the small quantities of solid product isolated at the apparent end-point permitted only the accurate determination of the atomic ratios of iodide to aluminum. If the reaction mixtures at the apparent end-point were allowed to stand for several hours before filtration an increased quantity of solid was obtained. Typical solid products isolated from reactions between aluminum iodide and sodium and potassium contained no detectable alkali metal, and the iodide–aluminum atomic ratios varied over rather wide limits (*e.g.*, from 1.0:1.4 to 1.0:3.0 for reactions with potassium). Thus it appears that mixtures of ammonobasic iodides rather than pure compounds were obtained. The materials isolated may be simply and conveniently represented as mixtures of varying proportions of $Al(NH_2)_2I$ and $Al(NH_2)_3$.

Analysis of the solid products obtained at the apparent end-point from titrations with barium indicated that an unstable ammoniate of barium iodide was produced. Thus in two experiments the following Ba:I:N atomic ratios were obtained; 1.00:2.07:7.13, and 1.00:2.03:1.24N. The product which had the higher nitrogen content was analyzed immediately after the ammonia washed solid had been allowed to come to room temperature, whereas the product with lower nitrogen content was allowed to stand at room temperature for two days before analysis. The solids contained no aluminum, and in both cases the sums of the constituent analyses exceeded 99%.

The Proposed Course of Reaction.—It is believed that ammonolysis of the ammoniated aluminum ion, to yield free ammonium ion and soluble ammonobasic aluminum compounds, is responsible for the initial reaction. The ammonolysis reaction may be expressed by the equation

$$[Al(NH_3)_6]^{3+} + NH_3 = [Al(NH_3)_5(NH_2)]^{2+} + NH_4^+$$

Thus the initial rapid rate of reaction results from the destruction of ammonium ion by the metal solutions. Some lines of support for ammonolysis of the original salt are as follows.

(1) Ammonium iodide, resulting from ammonolysis, is volatilized as the result of uncontrolled ammoniation of aluminum iodide with gaseous ammonia.[7]

(2) The small, highly charged aluminum ion should exhibit some acid character in ammonia as it is known to do in aqueous solutions.

(3) A sample of ammoniated aluminum iodide was dissolved in ammonia and the solution was allowed to stand at approximately −55°. After the passage of some 24 hours the mixture became turbid. When the mixture was filtered, after 67 hours, a small quantity of solid remained, which upon analysis gave the atomic ratios of 4.31Al: 1.00I. This analysis clearly indicates that ammonobasic aluminum compounds, which could arise only from ammonolysis, were precipitated.

The available evidence suggests that the actual degree of ammonolysis is quite 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 would be evolution of hydrogen and accumulation of amide in the solution. It is believed that ammonolysis of aluminum iodide was responsible for the propagation of the reaction with the metals until sufficient amide accumulated to form a soluble, relatively stable complex which effectively tied up all of the aluminum.

Further information about the amide-containing complex at the apparent end-point was deduced from the filtrate analyses. Consider a typical filtrate analysis, obtained from a potassium titration, in which the atomic ratios were 1.00Al:2.29K: 3.74I. It seems reasonable to propose that all of the potassium ion in this filtrate is accompanied by iodide ion, since the slightly soluble barium iodide was isolated from the titrations with barium. Therefore, subtraction of 2.29 from 3.74, to account for the potassium iodide, leaves the ratios 1.00Al:

1.45I:1.55NH_2 which are very near to the empirical composition of 1.00Al:1.50I:1.50NH_2 required by the ammonia-soluble ammonobasic iodide prepared by Franklin[12] and formulated as $AlI_3 \cdot Al(NH_2)_3 \cdot 6NH_3$. This compound did not lose ammonia when heated to 200° under reduced pressure. The stability of this complex toward dissociation would explain the sharp break in the rate of reaction observed when the apparent end-point was reached.

The quantity of solid products obtained at the apparent end-point was a function of the time the reaction mixtures were allowed to stand. Furthermore, the aluminum:iodide ratios in the solids also increased with time. These observations suggest that the solid products originated from ammonolysis of the soluble complex and that the solids formed were themselves subject to ammonolysis. It was found that the effect upon the solid products of prolonged exposure to liquid ammonia was a replacement of iodide ion by amide.

If a net effect of the addition of the metal solutions to the aluminum iodide is an accumulation of amide in the reaction systems, titrations with ammonia-soluble potassium amide should yield results similar to those obtained with the metals. The potassium amide solutions are not distinctly colored as are the metal solutions and so a direct determination of the apparent end-point was not possible with the amide titrant. However, the products obtained from experiments utilizing the amide were both qualitatively and quantitatively similar to those found in comparable titrations with the metals. A mixed amide–metal titration was also made. First, 0.90 equivalent of potassium amide per atom of aluminum was added to the aluminum iodide. Then the titration was continued with potassium solution until the characteristic apparent end-point was reached. The amount of potassium required was 0.87 equivalent, which made a total of 1.77 equivalents of metal and amide added. This combined value is greater than but still of the same order of magnitude as the usual apparent end-point values obtained with the metals alone. The data are summarized in Table II.

TABLE II

ANALYSES OF PRODUCTS FROM AMIDE TITRATIONS

Equiv. added	Solid atomic ratios I:Al	Filtrate atomic ratios Al:K:I	Equiv. amide in filtrate
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

Reaction beyond the Apparent End-point.—The rate of reaction beyond the apparent end-point was extremely slow and of the order of magnitude expected for the reaction between the metals and ammonia alone. For example, in experiments involving the usual quantities of aluminum iodide, 2.55 equivalents of potassium per atom of aluminum required 75 hours for complete reaction; 2.62 equivalents of lithium required 90 hours; and 190 hours elapsed before 4.21 equivalents of potassium reacted completely.

The sharpness of the break at the apparent end-point again may be emphasized by the data just given. For example, in the lithium experiment the first 1.6 equivalents of lithium reacted in about one hour, which means that the other 1.0 equivalent required some 89 hours for complete reaction.

Typical analytical data obtained from the products of reactions past the apparent end-point showed that the solid materials isolated from the reaction of from 2.0 to 2.5 equivalents of metal contained little or no alkali metal and possessed aluminum:iodide ratios which were not greatly different from those of the solids present at the apparent end-point. That is, the solid products obtained from reaction of up to 2.5 equivalents of metal may be conveniently accounted for in terms of mixtures of the appropriate ratios of $Al(NH_2)_2I$ and $Al(NH_2)_3$.

The quantities of solid obtained when more than 2.0 equivalents of metal were consumed were much greater than the amounts present at the apparent end-point. This is attributable to the increased quantities of amide which became available as more metal reacted. When 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. In the vicinity of 3.0 equivalents of metal consumed, the major solid product was aluminum amide, although mixtures rather than pure compounds were still obtained. When 4.0 equivalents of metal had reacted, aluminum once again was found in the filtrates, as a result of formation of soluble tetraamidoaluminate complexes which contain the uninegative anion $[Al(NH_2)_4]^-$.[13]

Potassium amide reactions differed somewhat from reactions with metallic potassium and calcium in experiments in which some 4 equivalents of titrant were consumed. The amide titrations were performed rapidly and yielded little solid, whereas the reactions with the metals, which required long periods of time for completion, yielded relatively large quantities of solid involving some 40% of the total aluminum. There seemed to be no great difference in the composition of the solid and filtrate materials obtained from the amide and metal reactions.

Miscellaneous Experiments and Remarks.—The ammonobasic aluminum 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: ratios for the original solid ammonobasic iodide mixture, 1.00I:1.66Al:5.81N:0.02K: for the original filtrate, 1.00Al:5.88K:7.58I:1.30N; and for the heated solid, 1.00N:1.07Al:0.102I:0.009K were found. The percentage composition of the heated solid was 22.0N, 20.3I, 45.5Al and 0.3K. The analytical data indicate that aluminum nitride was the principal constituent of the material produced at

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(12) E. C. Franklin, THIS JOURNAL, **37**, 847 (1915).

(13) F. W. Bergstrom, *ibid.*, **45**, 2791 (1923); **46**, 1548 (1924).

800°; this is what would be expected from the thermal decomposition of an ammonobasic iodide mixture. This experiment affords no evidence for the presence of a lower oxidation state of aluminum either in the original solid or in the heated solid.

McElroy, Kleinberg and Davidson[14] found that when aluminum ions, iodide ions and the ammoniated electron species were all present in the same solution, an insoluble ammonobasic iodide, $Al(NH_2)_2I \cdot Al(NH_2)_3 \cdot 2NH_3$,[15] was always formed. The components of the reaction systems described in this report 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 aluminum products obtained, the two systems are essentially equivalent, and ammonobasic aluminum compounds 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.[2] 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 $Al^{2+} + NH_3 = Al^{3+} + NH_2^- + {}^1/_2H_2$. 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 (amide ion) 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). Furthermore, the conversion to aluminum(II), and subsequently to aluminum(I), must take place to a major extent in order to change the ratios which cause a potential change. 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. 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.

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[14] A. D. McElroy, J. Kleinberg and A. W. Davidson, THIS JOURNAL, **72**, 5178 (1950).

[15] This compound is similar to the insoluble ammonobasic iodide isolated by Franklin (ref. 12) by reaction in liquid ammonia between potassium amide and aluminum iodide in the formula weight ratio 2.5:1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA A. AND M. COLLEGE]

Activities of Transition Metal Chlorides in Aqueous Hydrochloric Acid Mixtures. I. Nickel(II) Chloride and Cobalt(II) Chloride[1]

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The activities of each of the components in ternary H_2O–HCl–$NiCl_2$ or $CoCl_2$ mixtures have been determined at 30° by measurement of the HCl and H_2O partial pressures and integration of the Gibbs–Duhem equation for 3 components. The measurements were made on series of solutions each having constant HCl concentration (from 4.69 and 8.86 *m*) and variable salt concentrations (from 0.5 *m* to saturation). The Stokes and Robinson treatment of the activity coefficients of concentrated binary solutions of electrolytes has been extended to ternary mixtures and the experimental results have been treated according to this extended theory. For $CoCl_2$–HCl mixtures where the theory does not hold, spectrophotometric evidence is presented for association of cobalt and chloride ions forming $CoCl_2$.

Recent studies of the solvent extraction of salts from aqueous solutions have shown that the distribution coefficients of many transition metal chlorides are greatly increased when the salts are dissolved in concentrated hydrochloric acid.[2] The literature, however, contains almost nothing of the thermodynamic properties of such acid–salt–water mixtures. As a part of a program of study of the factors affecting the 2-octanol extraction of certain transition metal halides, the activities of each of the components in the ternary systems $NiCl_2$–HCl–H_2O and $CoCl_2$–HCl–H_2O were determined over a wide range of acid and salt concentrations.

Since no satisfactorily reversible electrodes have been found for metals such as nickel or cobalt,[3] it was necessary to make use of the Gibbs–Duhem equation applied to a ternary system and to calculate the salt activity from experimental values of

[1] Presented in part at the 9th Southwest Regional meeting of the American Chemical Society, New Orleans, La., 1953. Supported under Contract AT(11-1)-71 No. 1 with the U. S. Atomic Energy Commission.

[2] H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

[3] W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 210.