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I hereby recommend that the thesis prepared under my supervision by Francis Richard Holden

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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

Approved by:

W. M. Burgess. Director

W. M. Burgess, Chairman

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A STUDY OF THE REDUCTION OF INORGANIC SALTS BY ALKALI AND ALKALINE EARTH METALS IN LIQUID AMMONIA

A dissertation submitted to the

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by

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I. THE PHYSICAL AND CHEMICAL NATURE OF SOLUTIONS OF THE ALKALI AND ALKALINE EARTH ELEMENTS IN LIQUID AMMONIA.

A. Physical Nature:

In 1864, Weyl(1) discovered that the alkali metals, sodium and potassium, were soluble in liquid ammonia. He treated these metals with ammonia gas under pressure and obtained solutions whose color varied from a copper-red when concentrated to a deep blue when dilute. He postulated that there was compound formation between the alkali metals and the ammonia and called the products metal ammoniums, i.e. sodammonium, $NaNH_3$. In 1871, Seely(2) condensed ammonia on sodium in a manner similar to that of Weyl, but was unable to detect any discontinuity of the optical properties. He concluded that a true solution of sodium in liquid ammonia, rather than a compound, was formed. Due to manipulative difficulties encountered in studying these solutions, very little experimentation was done until some time after Seely's work.

In 1890, Joannis(3) published a series of papers dealing with liquid ammonia chemistry, in which he presented the first quantitative measurements of solutions of the alkali metals in liquid ammonia. He determined the vapor pressures at various temperatures and the boiling points of differently concentrated solutions. His results led him to conclude as had Weyl, that the compounds, sodammonium and potassammonium, were formed. This opinion was dominant for two decades and is still accepted by many European chemists.

Shortly after Joannis' work, investigators including Moissan(4) and Guntz(5) added lithium, rubidium, caesium, calcium, barium and strontium to the list of soluble metals. Cottrell(6) found that magnesium is slightly soluble.

Later work by Ruff and Giesel(7) and Kraus(8) proved conclusively the non-existence of the alkali metal ammoniums. Kraus reasoned from the phase rule as follows: If the compound, alkali metal ammonium, existed the two component system, alkali metal and ammonia, would be invariant providing that the four phases, alkali metal, metal ammonium, saturated solution and ammonia gas, were all present. According to Joannis, when ammonia gas was continuously removed from the unsaturated solution of the alkali metal in liquid ammonia, the vapor pressure varied regularly until the solution became saturated and the compound metalammonium appeared. Then the pressure remained constant until all the solution disappeared and the compound had broken down and only alkali metal remained. This same result was observed at several different temperatures. Joannis considered that after the solution disappeared, the compound broke down into metal and ammonia without change in pressure and that the four phases, vapor, saturated solution, solid compound and alkali metal, could co-exist at several different temperatures. However, according to the phase rule such a system was invariant and could exist at but one temperature. Therefore, one phase, obviously metalammonium, must be non-existent.

However, the vapor pressure curves for the system, alkaline earth metal-ammonia, has presented quite a different situation. Kraus, Mentrel(9) and Roederer(10) prepared the definite alkaline earth compounds, calcium, barium and strontium hexammonates. Kraus considered these compounds as ammonates similar to ammonated salts of the type $CaCl_2.6NH_3$. There was no evidence for assuming that there are metal ammoniums in which the metal was joined to the nitrogen in the ammonium radical.

It is also interesting to note that whereas the alkali metals are dissolved in liquid ammonia with an inappreciable heat of solution, the alkaline earth metals are dissolved with considerable heat of solution. This is an indication of a combination between the alkaline earth metals and ammonia.

Kraus made an extensive study of the electrical properties of solutions of metals in liquid ammonia. He found that these solutions conduct the electric current to an extraordinary degree and that the alkali and alkaline earth metals are ionized like salts. Kraus has summed up the results of his studies of the conductivities of solutions of metals in liquid ammonia as follows:(11)

"These solutions, therefore, constitute a connecting link between metallic and electrolytic conductors. In dilute solutions the process is, at least in part, electrolytic. A portion of the current is carried by the positive carriers as they appear in solutions of the common salts. The negative carrier is chemically uncombined, but is associated with one or more molecules of the solvent. These carriers are identical for the solutions of all metals, and, when the discharge occurs at the anode, the only material process which takes place is that a portion of the solvent is left behind in the immediate neighborhood of this electrode. As the concentration of the solution increases, the nature of the phenomenon changes only in so far as the combination of the negative carrier with ammonia is affected. At the higher concentrations, the negative carriers are free from association with the ammonia molecules to a greater and greater extent. And, since under these conditions the negative carrier is associated with no material of atomic dimensions, it follows that all the material effects cease so far as these carriers are concerned. It is not to be understood that a given carrier is free from association with the solvent molecules for any considerable period of time. Obviously, an equilibrium must exist between the free carriers and the combined carriers and ammonia, which results in a constant interchange between the free and bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in metals. As the concentration is further increased, the number of free carriers constantly increases. It is evident that their number in the more dilute solution, for example in the neighborhood of normal, must be relatively small, since at the higher concentrations the equivalent conductance reaches values some one hundred times as great as that at normal concentration. It is not possible to determine the actual number of carriers in the more concentrated solutions. In the more dilute solutions, however, it appears that the number of carriers decreases with increasing concentration just as it does in the case of normal electrolytes in ammonia.

There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radioactive and other phenomena."

Determinations of the molecular weight of sodium in liquid ammonia,(12) using solutions less than 0.1 normal, showed that the apparent value is less than 23. This gave further evidence pointing to the dissociation of the alkali and alkaline earth metals in liquid ammonia solution.

Kraus' work may be summarized as follows: The alkali and alkaline earth metals are ionized in liquid ammonia solution according to the equation,

$$M + xNH_3 \longrightarrow M^{m+} + m\bar{e}(NH_3)_x$$

M represents an alkali or alkaline earth metal, $\bar{e}(NH_3)_x$ represents a solvated electron and $m = 1$ for alkali metals, and $m = 2$ for alkaline earth metals. The value of x varies with the concentration of the alkali or alkaline earth metal, being larger in dilute solutions. The solvated electron is the main carrier of the electric current.

The solution of calcium in liquid ammonia is also of interest in that it forms two phases even at room temperatures. The more concentrated phase of the calcium in liquid ammonia tends to cling to the walls of the container and contains most of the calcium. Kraus(8) reports that the dilute phase in no case holds more than 1/10 of a g. atom of calcium per liter of solution. At -33° C. the solubility of calcium in liquid ammonia is 1 g. atom of calcium per 7.0 g. moles of ammonia. This corresponds to 84 times the concentration of calcium present in the dilute solution. Kraus also states that the difference in specific gravity between the two layers is too little to allow a separation.

The phenomena of forming two phases of alkali metal in liquid ammonia solution has been found to occur only at very low temperatures. The alkalis are very soluble. Their solubilities are found to be of the order of 1 g. atom of sodium per 5.48 g. moles of ammonia and 1 g. atom of potassium per 4.95 g. moles of ammonia at -33° C. The solutions vary from a color of aniline blue to a coppery-red as the concentration of alkali metal increases. The blue color is visible at dilutions of .000025 N. This sensitivity is of great importance in determining the end point of reactions involving the removal of the alkali or alkaline earth metal from solution.

B. Chemical Nature:

The alkali and alkaline earth metals are known to react very slowly with the solvent ammonia according to the equation,

$$M + m NH_3 \longrightarrow M(NH_2)_m + \frac{m}{2} H_2$$

M represents an alkali or alkaline earth metal and $M(NH_2)_m$ represents a metallic amide. The value of m is 1 for alkali metals and 2 for alkaline earth metals. The presence of certain substances greatly accellerated this reaction. Kahler(13) has made a study of several catalysts and found that platinum black, ferrous oxide powder and powdered iron are among the best.

Due to the presence of free electrons the solutions of the alkali and alkaline earth metals in liquid ammonia have been found to be excellent reducing media. Their reactions with inorganic salts may be classified as follows:

1. A soluble salt is reduced by the alkali or alkaline earth metal producing another salt and a metallic precipitate. This may be illustrated by the following equation,

$$BA_b + M \longrightarrow MA_m + B$$

where B is the electropositive constituent of the salt having a valence b and M is the reducing metal with a valence m. The reaction ratio of gram atoms of reducing metal M per gram mole of salt used always has a definite value, depending upon the valences of the metals used. An example of this type of reaction is that occurring with silver iodide and sodium.(14)

2. The reduced metal is often very finely divided and may act as an excellent catalyst for the reaction between the reducing metal and the solvent, as illustrated by the following equations.

$$(1)\quad BA_b + M \longrightarrow MA_m + B$$
$$(2)\quad M + m\,NH_3 \longrightarrow M(NH_2)_m + \frac{m}{2} H_2$$

$M(NH_2)_m$ represents the metallic amide of the reducing metal used in the reaction and m represents the valence of the reducing metal. The reaction ratio of gram atoms of alkali or alkaline earth metal per gram mole of salt used will hot have a definite value with this type of reaction. The rate of catalysis varies with the concentrations of the substances used in the reaction and the nature and state of subdivision of the reduced metal. The amount of hydrogen formed is equivalent to the amount of reducing metal used in the second of the reactions listed above. When the total weight of alkali or alkaline earth metal is corrected for this reaction, a corrected ratio closely approaching the theoretical value will be obtained. Similarly the amount of metallic amide present may in many cases be used to obtain the value of the corrected ratio. This type of reaction has been shown to occur between nickel cyanide and sodium.(15) The nickel formed in the reaction is very finely divided and causes any excess sodium to rapidly react with the solvent. The reduced metal, nickel, is pyrophoric when exposed to the air. This pyrophoric nature is possibly due to a layer of adsorbed hydrogen.

3. The reduced metal B may also react with the reducing metal M to form metallic compounds as illustrated by the following equations.

(1) $BA_b + M \longrightarrow MA_m + B$

(2) $M + B \longrightarrow M_b B_m$

$M_b B_m$ is a metallic compound in which the valence of the reducing metal is m and the valence of the reduced metal is b. The valences of the constituents of many of these compounds do not conform to any normal values of valence. Metallic compounds such as NaCd, K_4Pb_9, $NaHg_2$ and K_4Sn_8 have been reported.(16) Metallic compounds of lead, bismuth, mercury, cadmium, zinc, tin and thallium with the alkali and alkaline earth metals have been reported. The reaction ratio for this type will be of a definite value, which will be dependent upon the valences of the metals in the metallic compound formed.

4. Subsequent reduction of the anion of the salt of the alkali or alkaline earth metal may occur, as illustrated below.

$$(1) \quad BA_b + M \longrightarrow MA_m + B$$

$$(2) \quad MA_m + M \longrightarrow MX_m + MY_m$$

X and Y represent anions produced by the decomposition of the anion A. An illustration of this type of reduction is that of the thiocyanate radical, when silver thiocyanate and potassium react.(17) This type of reaction gives an indefinite ratio depending upon the amount of decomposition occurring.

This thesis is a quantitative study of the reduction of inorganic salts by alkali and alkaline earth metals in liquid ammonia. The object of this research was to compare the reducing action of sodium, potassium and calcium solutions in liquid ammonia. This thesis has been divided into nine main parts, namely, I. The Physical and Chemical Nature of Solutions of the Alkali and Alkaline Earth Metals in Liquid Ammonia; II. Apparatus, Experimental Procedure and Materials Used; III. The Reactions between Silver Iodide and the Metals Potassium and Calcium; IV. The Reactions between Silver Cyanide and the Metals Sodium, Potassium and Calcium; V. The Reactions between Silver Cyanate and the Metals Sodium, Potassium and Calcium; VI. The Reaction between Silver Thiocyanate and Calcium; VII. The Reactions between Silver Nitrate Diammonate and the Metals Sodium and Calcium; VIII. The Reactions between Cuprous Iodide and the Metals Sodium, Potassium and Calcium; and IX. The Reaction between Zinc Cyanide and Calcium.

II. APPARATUS, EXPERIMENTAL PROCEDURE AND MATERIALS

A. Apparatus:

There are two general methods for studying reactions in liquid ammonia solution. One requires the use of apparatus capable of withstanding high pressures and is carried out at room temperature. The second method is to work with solutions of liquid ammonia at their boiling point and under atmospheric pressure. The latter method was employed in this research. The apparatus for this type of reaction is illustrated by Figure I.

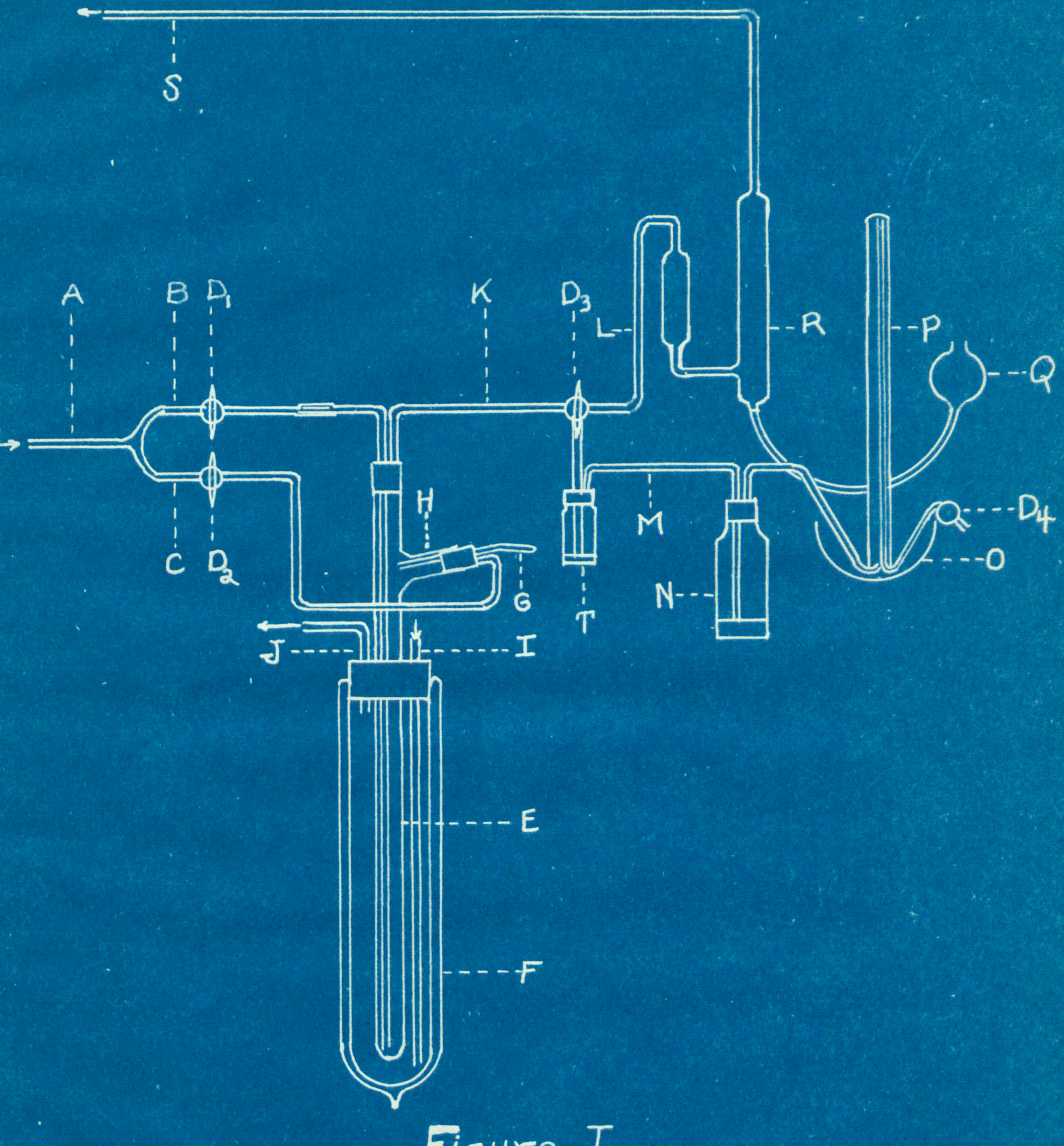


Figure I

APPARATUS FOR THE REDUCTION OF INORGANIC SALTS IN LIQUID AMMONIA

LEGEND FOR FIGURE I

A. Inlet for pure, dry NH_3 gas.

B. Tube carrying NH_3 gas into the reaction tube.

C. Tube carrying NH_3 gas employed in sweeping out side arm.

D. D_1, D_2, D_3 Stop Cocks. D_4 Pinch clamp.

E. Reaction tube.

F. Dewar flask.

G. Tube used for addition of reaction materials.

H. Side arm.

I. Air inlet.

J. Outlet for air and NH_3 vapors.

K. Exit tube for gases from reaction tube.

L. Tube leading to pressure gauge.

M. Connection tube.

N. Ammonia absorption bottle.

O. Water container.

P. Eudiometer.

Q. Pear for mercury.

R. Mercury pressure gauge.

S. Exit for NH_3 vapors.

T. Safety bottle containing 2 cms. of mercury.

B. Experimental Procedure:

To illustrate the use of the apparatus, a typical run using silver cyanide and potassium will be described.

1. A Typical Reaction:

Before each experiment, the reaction tube, E, was thoroughly cleaned with hot cleaning solution and rinsed separately with distilled water, alcohol and ether. The last traces of ether were removed by passing dry, pure nitrogen through the tube for five minutes. The weighed silver cyanide was then placed in the reaction tube which was fastened in position as illustrated by Figure I. An excess of potassium, of known weight, was next placed in tube G, which had been filled with dry nitrogen gas. With stopcocks D_1 and D_2 alternately opened, dry nitrogen was then blown through the assembled apparatus out through the pressure gauge, R, for ten minutes. This was followed by a similar treatment with dry ammonia gas to remove the nitrogen. Then, keeping a pressure of ammonia gas on the system to prevent back pressure from developing, the dewar flask, F, was three-quarters filled with commercial liquid ammonia. The mercury pear, Q, was adjusted so that a pressure of about 10 cms. of mercury would be developed in pressure gauge, R. Then dry air was bubbled through the liquid ammonia in the dewar flask through tube I at such a rate that the temperature of the liquid ammonia was lowered to about -40° C. The ammonia gas entering the reaction tube, E, was under a pressure greater than 1 atmosphere and at a temperature six or seven degrees below its boiling point. About ten minutes was sufficient to condense 50 or 60 ccs. of liquid ammonia in the reaction tube. The air was then shut off at the inlet tube I, and the ammonia in the dewar flask was allowed to warm up to its boiling point, -33.3° C.

With dry ammonia condensed on the soluble silver cyanide the reaction was carried out as follows. Stopcock D_1 was open with stopcock D_2 closed and two way stopcock D_3 turned so that the ammonia gas passed through safety bottle T and absorption bottle N into eudiometer P. The absorption bottle, N, contained 3 cms. of mercury and about 200 ccs. of 6 N. hydrochloric acid. Then tube G was gently tapped to cause the potassium to drop into the solution of silver cyanide. The reduction of the silver salt was quite vigorous and was kept under control by varying the temperature of the outer dewar bath. The completion of the reduction was noted by the appearance of a blue color in the solution and the increase in gas bubbles passing through bottle N. During the subsequent reaction of the excess alkali metal with the solvent ammonia, ammonia gas was passed slowly through side arm H to prevent hydrogen gas from pocketing in tube G. The completion of the reaction was apparent when the blue color of the solution of potassium in liquid ammonia was gone. Ammonia gas was blown through the apparatus for ten minutes after the completion of the reaction to insure the removal of all the hydrogen.

2. Analysis of Products:

The products of the reaction were analyzed in the following manner. The gas collected in eudiometer P was analyzed for hydrogen by the use of an explosion pipette. The grams of potassium equivalent to the ccs. of hydrogen formed were calculated and subtracted from the total of potassium used. This weight of alkali metal was used in calculating the equivalent reaction ratio corrected for hydrogen.

When it was desired to analyze the silver residue it was washed several times with pure liquid ammonia, dried and weighed. The method of analysis consisted of dissolving the residue in nitric acid and precipitating the silver from solution as silver chloride.

C. Materials:

1. Liquid Ammonia:

Synthetic liquid ammonia was obtained from the Mathieson Alkali Works. It contained a small percentage of moisture and non-volatile matter. In order to use this ammonia as a solvent it was transferred *to a small supply* tank with a capacity of about two kilograms. From 2 to 3 grams of sodium were added to each tank to remove the moisture. The sodium immediately reacted with the water to form hydrogen and insoluble sodium hydroxide. Any sodium left reacted with the ammonia to form hydrogen and only slightly soluble sodium amide. This latter reaction was catalyzed by the iron container. The ammonia was distilled from the container and condensed in the reaction tube for each reaction and was free from non-volatile impurities.

2. Sodium:

The sodium used throughout these experiments was Kahlbaum's sodium for analysis. It retained the luster of freshly cut alkali metal throughout the process of weighing.

3. Potassium:

Merck's C. P. potassium was used for this research. It was analyzed by the chloroplatinate method(18) and gave the following results.

Anal. Subs., .0770, .0674: K_2PtCl_6, .4776, .4189.
Calculated for K: K, 1.000. Found: K, .9975, .9995.

The weight of potassium used in all calculations was taken as being 100% pure.

4. Calcium:

Kahlbaum's calcium, used for this research, was analyzed by precipitation as the oxalate and weighing as the oxide.(19) The results of the analysis are recorded below:

Anal. Subs., .2412, .3419: CaO, .3344, .4740. Calculated for Ca: Ca, 1.000. Found: Ca, .9905, .9907.

The purity of 99% calcium was used in all calculations.

5. Silver Iodide:

The silver iodide was prepared by the method suggested by Beekley.(20) To an approximately N/10 solution of strongly ammoniacal potassium iodide was added, slowly with constant stirring, a 1% excess of ammoniacal silver nitrate of the same concentration. The precipitated silver iodide was washed by decantation with dilute ammonium hydroxide until the acidified washings gave no test for silver ions. This was followed by washing with double distilled water until the washings gave no test for ammonia with Nessler's reagent. Then a 5% solution of nitric acid was used until the washings made alkaline gave no test with Nessler's solution. Double distilled water was used to wash the precipitate until all the nitric acid had been removed. The silver iodide was then dried in the electric oven at 120° C. until constant weight was obtained. It was not necessary to protect the salt from light as it was light insensitive.

An analysis of the silver iodide was made as follows:(21) A known amount of silver iodide was added to a small, weighed, porcelain crucible. This was supported in a larger crucible as an air bath. The temperature was raised to 250° C. to 300° C. and pure chlorine gas was passed over the silver iodide for about one hour. The small crucible was then cooled in a dessicator and weighed.

Anal. Subs., .6772: AgCl, .4127. Calculated for AgI: Ag, 45.94. Found Ag, 45.87.

6. Silver Cyanide:

The silver cyanide was prepared from N/10 solutions of Kahlbaum's C. P. potassium cyanide and Mallinckrodt's C. P. silver nitrate. The solution of potassium cyanide was slowly added to the silver nitrate solution with constant stirring. Enough excess potassium cyanide was added to just dissolve the precipitate first formed. The solution was then made slightly acid with nitric acid and gently heated under a hood to remove the hydrogen cyanide formed. The excess acid was neutralized with sodium carbonate and the precipitate was allowed to stand over night. It was next washed by decantation with four or five liters of double distilled water in small portions. The precipitate was then filtered, washed further, and dried in an oven at 110° C. until constant weight was obtained. It was stored over phosphorus pentoxide, in a brown glass dessicator.

The product was analyzed as follows: About .4 to .5 grams of the salt was treated with two hundred ccs. of 1-1 nitric acid and slowly heated over an electric heater in a hood. When all of the hydrogen cyanide and most of the nitric acid had been evaporated, the solution was cooled and diluted to one hundred and fifty ccs. with double distilled water. The resulting solution of silver nitrate was precipitated with dilute hydrochloric acid, filtered and washed thoroughly. It was dried to constant weight in an oven at 110° C.

Anal. Subs., .4751, .4546: AgCl, .5072, .4856. Calculated for AgCN: Ag, 80.57. Found: Ag, 80.35, 80.39.

7. Silver Cyanate:

The silver cyanate was prepared by mixing N/5 solutions of Mallinckrodt's C. P. silver nitrate and Kahlbaum's C. P. potassium cyanate (free from cyanide). The precipitate was washed with several liters of double distilled water until the washings gave only a constant, faint opalescence with dilute hydrochloric acid. The product was filtered and dried in a vacuum dessicator over phosphorus pentoxide.

The silver cyanate was analyzed as follows: About .2 gs. of the product was dissolved in excess concentrated nitric acid and the product evaporated nearly to dryness. The residue was taken up with distilled water and the resulting solution of silver nitrate was precipitated with dilute hydrochloric acid. The precipitate was washed, filtered and dried to constant weight.

Anal. Subs., .2122, .2461: AgCl, .2035, .2364. Calculated for AgCNO: Ag, 71.97. Found: Ag, 72.07, 72.25.

8. Silver Thiocyanate:

The silver thiocyanate was prepared by mixing N/10 solutions of Mallinckrodt's C. P. silver nitrate and Kahlbaum's C. P. potassium thiocyanate. The precipitate was treated in a manner similar to the treatment of the other silver salts. It was stored in a brown glass dessicator over phosphorus pentoxide.

An analysis of the silver thiocyanate was carried out as follows:(22) About .3 to .5 grams of the salt was digested with 50 ccs. of hot, concentrated nitric acid. When the samples had evaporated nearly to dryness, 50 ccs. more of concentrated nitric acid were added and the process was repeated. The silver thiocyanate is decomposed according to the equation,

$$6agSCN + 16HNO_3 + 4H_2O \rightarrow 3ag_2SO_4 + 3(NH_4)_2SO_4 + 6CO_2 + 16NO$$

The silver thiocyanate was oxidized to silver sulphate which was soluble in two hundred ccs. of hot, distilled water. A slight excess of hot, dilute hydrochloric acid was then added and the precipitate set aside over night. The silver chloride was washed by decantation, filtered through a gooch crucible and washed with double distilled water. After drying the crucibles at 110° C. for two hours, they were allowed to cool in a dessicator and weighed.

Anal. Subs., .5509, .4253, .3090: AgCl, .4758, .3665, .2665. Calculated for AgSCN: Ag, 65.01. Found: Ag, 65.00, 64.85, 64.91.

9. Silver Nitrate Diammonate:

Silver nitrate diammonate was prepared by allowing Mallinckrodt's C. P. silver nitrate to dissolve in liquid ammonia and removing the excess ammonia by evaporation. The silver nitrate, crystallized from liquid ammonia, contained two moles of ammonia for each mole of silver nitrate. The crystals of silver nitrate diammonate are stable at 60° C. at which temperature adsorbed ammonia is easily removed.

The product was analyzed for silver by the gravimetric silver chloride method. Analyses of the crystals gave the following results:

Anal. Subs., .6124, .5102, .4218, .4286: AgCl, .4308, .3588, 2963, .3013. Calculated for $AgNO_3.2NH_3$: Ag, 52.89. Found: Ag, 52.92, 52.92, 52.85, 52.92.

The analyses were carried out two at a time, three months apart.

10. Cuprous Iodide:

The cuprous iodide used in this research was a Kahlbaum product. It was dried at 120° C. for three hours.

It was analyzed for copper by converting the cuprous iodide to cupric oxide.(23) The results of the analyses are as follows:

Anal. Subs., .5178, 3718. CuO, .2164, .1552. Calculated for CuI: Cu, 33.38. Found: Cu, 33.41, 33.36.

11. Zinc Cyanide:

Kahlbaum's zinc cyanide was dried at 130° C. for two hours. The compound was not analyzed.

III. THE REACTIONS BETWEEN SILVER IODIDE AND THE METALS POTASSIUM AND CALCIUM

A. The Reaction with Potassium:

Burgess and Smoker(14) studied the reaction between sodium and silver iodide. They found that the ratio of gram atoms sodium used per each gram mole of silver iodide was approximately a 1 to 1 ratio. This result checked with their studies of the sodium-silver chloride reaction and led them to postulate that the reaction was of type I and could be represented by the following equation.

$$AgI + Na \rightarrow Ag + NaI$$

From previous work the writer had found that the reaction between silver iodide and potassium was of type II.(17) These results were obtained by adding silver iodide to the solution of the alkali metal and gave an average reaction ratio of 1.043. Due to difficulties in analyzing the gas obtained, the ratio corrected for hydrogen had an average value of 1.021. The average ratio corrected for amide was 1.000 indicating trouble with gas collection.

The above work was repeated by adding the alkali metal to the solution of the silver salt as described under procedure. The silver precipitate was a definite but poor catalyst and the excess alkali metal was destroyed by adding ammonium bromide to the solution.

The results of these reactions are listed below in Table I.

Table I

Exp. No.	K gms.	AgI gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio Corrected for H_2	Time in Mins.
209	.3639	1.0428	53.8	2.095	1.013	Added NH_4Br after 30 mins.
210	.3344	1.0240	46.4	1.960	1.010	Added NH_4Br after 10 mins.

The column headings have the following meanings reading from left to right. The number of the experiment; the grams of potassium used; the grams of silver iodide used; the ccs. of hydrogen formed at standard temperature and pressure; the ratio of gram atoms of potassium per gram mole of silver iodide; the ratio of gram atoms of potassium, less the amount of potassium used to form hydrogen, per gram mole of silver iodide; and the time in minutes used for the reaction.

The average reaction ratio has no significance as it will depend upon the amount of excess alkali metal used. The corrected reaction ratio has a value of 1.012 which is within experimental error a 1 to 1 ratio. The reaction may be represented by the equations:

(1) $AgI + K \longrightarrow Ag + KI$

(2) $NH_3 + K \longrightarrow KNH_2 + \frac{1}{2}H_2$

The second of the above reactions proceeds very slowly as the silver precipitate is a poor catalyst.

B. The Reaction with Calcium:

There is no reference in the literature of previous study of the reaction between silver iodide and calcium in liquid ammonia.

The results from three experiments are given in the following table.

Table II

Exp. No.	Ca gms.	AgI gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio Corrected for H_2	Time in Mins.
182	.2224	1.2903	62.7	2.020	1.000	26
183	.2709	1.3623	88.3	2.342	.971	33
184	.2126	1.1741	62.5	2.123	1.007	34

The column headings were discussed under table I.

The average corrected reaction ratio is 0.993 gram equivalents of calcium required to reduce one gram mole of silver iodide. This figure is within experimental error a 1 to 1 ratio. The uncorrected reaction ratio may be varied from 1.000 to X, depending upon the amount of excess calcium converted to calcium amide and hydrogen by the active silver catalyst. The reaction may be represented by the following equations:

$$(1)\ 2AgI + Ca \longrightarrow 2Ag + CaI_2$$

$$(2)\ 2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$$

The silver precipitate from this reduction is a much better catalyst for the second of the above reactions than the silver from potassium reductions. It is more finely divided and is difficult to settle from the solution.

Several experiments were made by adding the silver salt to the solution of the alkaline earth metal. The average corrected reaction ratio was 1.136 gram equivalents of calcium required to reduce one gram mole of silver iodide. This ratio was variable and unreliable, as trouble with gas collection was experienced at that time. A loss of three or four cubic centimeters of hydrogen would have caused these high ratios. In no case could the high ratio be interpreted as meaning compound formation between the excess alkaline earth metal and the freshly reduced silver. The ratio of excess calcium to silver was variable and of the order of one to ten.

IV. THE REACTIONS BETWEEN SILVER CYANIDE AND THE METALS SODIUM, POTASSIUM AND CALCIUM

A. The Reaction with Sodium:

Kraus and Kurtz(16) in a preliminary investigation of the reaction between sodium and silver cyanide showed that a ten percent excess of sodium was necessary to complete the reduction. They concluded that there was no compound formed between the freshly precipitated silver and the alkali metal.

In a previous investigation by this writer(17) the average reaction ratio was established to be 1.027 gram atoms of sodium for each gram mole of silver cyanide. These determinations were made by adding the silver salt to the solution of the alkali metal.

To obtain greater accuracy this work was repeated using the method outlined under the procedure. The results of two experiments are shown in the following table.

Table III

The Sodium - Silver Cyanide Reaction

Exp. No.	Na gms.	AgCN gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
205	.2502	.9780	39.9	1.489	1.002	Added NH_4Br after 16 mins.
206	.2432	1.0118	33.1	1.400	1.009	Added NH_4Br after 15 mins.

The column headings were discussed under table I.

The average corrected equivalent ratio is 1.006 gram atoms of sodium required to reduce one gram mole of silver cyanide. This ratio is within experimental error a one to one ratio. The reaction may be represented by the following equation.

$$AgCN + Na \longrightarrow Ag + NaCN$$

The silver residue has negligible value as a catalyst for the reaction of the excess alkali metal with the solvent ammonia. The excess of alkali metal was destroyed by the addition of the ammono acid, ammonium bromide, to the solution.

B. The Reaction with Potassium:

The first recorded use of potassium in reducing silver cyanide was that of this writer.(17) An average corrected reaction ratio of 1.040 gram atoms of potassium per each gram mole of silver cyanide was obtained by adding the silver salt to the solution of the alkali metal. It was also found that the freshly reduced silver was a fair catalyst for the reaction of the excess potassium with the solvent ammonia. In some cases the resulting silver residue was found to heat up on exposure to the air.

The above reaction was repeated using the method of adding the potassium to the solution of the silver salt as described in the procedure. The following table contains the results of three experiments.

Table IV

The Potassium - Silver Cyanide Reaction

Exp. No.	K gms.	AgCN gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
199	.4708	.9967	50.4	1.618	1.012	95
200	.4420	.9837	41.8	1.531	1.031	100
203	.3905	1.0185	25.2	1.313	1.017	74

The column headings were discussed under table I.

The average corrected reaction ratio is 1.020 gram atoms of potassium required to reduce one gram mole of silver cyanide. The ratio is one and a half percent higher than the similar sodium - silver cyanide ratio.

The silver precipitates from experiments numbered 199 and 200 were pyrophoric. They burst into fire when exposed to the air. The precipitates were fair catalysts for the reaction between the excess alkali metal and the solvent liquid ammonia. The activity of the silver precipitate from the reduction of silver cyanide with potassium is noticeably greater than the corresponding precipitate from the silver iodide reduction.

At the completion of experiment number 203, ammonium bromide was added to the solution containing the precipitated silver. This destroyed the pyrophoric nature of the silver.

A marked change in the character of the reduced metal occurs upon the addition of the ammono acid. The metallic precipitate tends to agglomerate into large particles which settle readily to the bottom of the reaction tube.

One experiment was carried out by using a 4% excess of silver salt. The solution never assumed the characteristic blue color of the alkali metal dissolved in liquid ammonia. The residue was inactive in air, indicating that an excess of alkali metal is necessary to obtain pyrophoric silver.

Subsequent work with other metals has shown the pyrophoric nature of freshly precipitated metals, maybe due to adsorbed hydrogen.

The reaction between silver cyanide and potassium may be represented by the equations:

(1) $AgCN + K \longrightarrow Ag + KCN$

(2) $NH_3 + K \longrightarrow KNH_2 + \frac{1}{2}H_2$

C. The Reaction with Calcium:

Kraus and Kurtz(16) in a preliminary investigation of the reaction between silver cyanide and calcium obtained results which led them to postulate the formation of a metallic compound between silver and calcium. They proposed the following equations to represent the reaction.

(1) $2AgCN + Ca \longrightarrow 2Ag + Ca(CN)_2$

(2) $Ag + Ca \longrightarrow AgCa$

The aforementioned writers made no attempt to collect exhaust gases from the reaction tube. The results from the reduction of silver cyanide with potassium have shown that the freshly precipitated silver will catalyze a reaction between excess reducing metal and ammonia. If this type of reaction did occur with calcium and ammonia, it would alter the reaction ratio. In order to test the possibility of the alkaline earth metal reacting with the ammonia, several experiments were made. The following table embodies the results of these experiments.

Table V

The Calcium - Silver Cyanide Reaction

Exp. No.	Ca gms.	AgCN gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
178	.2716	1.1993	48.4	1.514	1.031	11
179	.3254	1.0306	96.6	2.110	.990	21
180	.2934	.7564	100.4	2.593	1.005	23

The column headings were discussed under table I.

The average, corrected, equivalent ratio is 1.009 gram equivalents of calcium required to reduce one gram mole of silver cyanide. This reaction ratio is within experimental error, a 1 to 1 ratio. These results indicate that no compound, CaAg, is formed between the excess alkaline earth metal and the freshly reduced silver. Kraus and Kurtz happened to use amounts of alkaline earth metal and silver cyanide that gave a reaction ratio corresponding to the formation of the metallic compound, CaAg.

The reaction may be represented by the following equations.

(1) $2AgCN + Ca \longrightarrow 2Ag + Ca(CN)_2$

(2) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

The freshly reduced silver is composed of small particles and is an excellent catalyst for the second of the above reactions. The silver is pyrophoric in nature.

After the completion of one experiment, a small piece of sodium, .06 grams, was added to the solution. It was converted to sodium amide and hydrogen in slightly less than fifteen minutes.

From a comparison of amount of silver precipitate, time of reaction, and amount of calcium converted, it is shown that the silver from the cyanide reaction is approximately twice as active as that from the iodide reaction.

V. THE REACTIONS BETWEEN SILVER CYANATE AND THE METALS SODIUM, POTASSIUM AND CALCIUM.

A. The Reaction with Sodium:

There is no evidence in the literature of reductions of inorganic cyanates in liquid ammonia. It was considered of interest to study the stability of the cyanate radical in strong reducing mediums. The results of two experiments are given below.

Table VI

The Sodium - Silver Cyanate Reaction

Exp. No.	Na gms.	AgCNO gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
207	.2491	1.0109	46.3	1.606	1.006	Added NH_4Br after 30 mins.
208	.2433	1.0737	38.9	1.477	0.993	Added NH_4Br after 30 mins.

The table headings were discussed under Table I.

The average corrected equivalent ratio is 1.000 gram equivalent of sodium required to reduce one gram mole of silver cyanate. This indicates that the sodium cyanate formed in the reduction is stable in the presence of the excess alkali metal. The silver precipitate is noticeably agglomerated into particles the size of a pea. The reduction of the slightly soluble silver cyanate requires from ten to fifteen minutes to go to completion. The end of the reduction is noticable by the momentary colorless solution above the agglomerated silver. The solution gradually takes on a bluish tinge which increases in intensity as the excess sodium slowly dissolves.

The reaction may be expressed by the equation:

$$AgCNO + Na \longrightarrow Ag + NaCNO$$

B. The Reaction with Potassium:

The results from two experiments with silver cyanate and potassium are included in the following table.

Table VII

The Potassium - Silver Cyanate Reaction

Exp. No.	K gms.	AgCNO gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
201	.4305	.9951	48.2	1.659	1.010	Added NH_4Br after 30 mins.
202	.4288	1.0023	47.6	1.638	1.004	Added NH_4Br after 34 mins.

The table headings were discussed under Table I.

The average, corrected, equivalent ratio of 1.007 gram atoms of potassium per each gram mole of silver cyanate is approximately a 1 to 1 ratio. The reaction may be expressed by the following equations.

(1) $AgCNO + K \longrightarrow Ag + KCNO$

(2) $NH_3 + K \longrightarrow KNH_2 + \frac{1}{2} H_2$

The silver precipitate is a poor but definite catalyst for the second of the two reactions. It is not pyrophoric in nature.

In each case the residue from the reaction was extracted with distilled water and tested for cyanide. The test was negative indicating no reduction of the cyanate radical by the solution of the potassium.

C. The Reaction with Calcium:

In view of the fact that solutions of calcium in liquid ammonia have given evidence of being better reducing mediums than solutions of sodium and potassium, several experiments between silver cyanate and calcium were made. The results are given in the following table.

Table VIII

The Calcium - Silver Cyanate Reaction

Exp. No.	Ca gms.	AgCNO gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
166	.3498	1.0020	102.4	2.614	1.244	20
167	.4367	1.1983	131.7	2.727	1.255	23
168	.0329	.2413	.9	1.020	.971	4
169	.0213	.1514	.5	1.053	1.004	3
170	.0320	.2275	.5	1.053	1.020	3
171	.0319	.2148	.8	1.112	1.059	3
172	.0458	.2742	2.9	1.250	1.119	3
174	.2752	1.0000	62.9	2.059	1.217	10

The column headings were discussed under Table I.

As shown by the table the corrected equivalent ratio is variable. The value increases with the amount of excess calcium used. In experiment number 168 a two percent excess of calcium was used and the corrected ratio was 2.9% low. Experiments 169 and 170 show an average corrected ratio of 1.012 when a 5.3% excess of calcium was used. In experiments 171, 172, 174, 166 and 167 an 11.2%, a 25%, a 106%, a 161% and a 173% excess was used respectively. In each case the value of the corrected equivalent ratio increased indicating that a secondary reaction using calcium occurs.

The high corrected reaction ratio may be due to one of three possibilities. The finely divided silver precipitate may adsorb hydrogen, it may adsorb calcium or the cyanate radical may be reduced by the excess calcium to form calcium cyanide and calcium oxide.

To investigate the first of the above mentioned possibilities the residue from experiment number 166 was placed in a small tube and heated to 400° C. No hydrogen was obtained. The residue from experiment number 174 was evacuated with a Tőepler pump but no hydrogen was obtained.

The second possibility was examined by adding a mixture of alcohol and ether to the residue from experiment number 167. If adsorbed calcium or hydrogen had been present, hydrogen would have been evolved.(15) No hydrogen was obtained from this experiment.

To test the third possible explanation of the high corrected reaction ratio, the residue from experiment number 174 was extracted with distilled water and tested for the presence of cyanide. The prussian blue test was used and a positive reaction was obtained. Blank tests on the materials used and on the silver cyanate were negative. It was also found that a solution of sodium cyanide of a strength equivalent to the amount of cyanide theoretically present in the residue gave a prussian blue test equal to that from the extracted residue.

The reaction may be represented by the following equations.

(1) $2AgCNO + Ca \longrightarrow 2Ag + Ca(CNO)_2$

(2) $Ca(CNO)_2 + 2Ca \longrightarrow Ca(CN)_2 + 2CaO$

(3) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

Reactions 2 and 3 are catalyzed by the finely divided silver precipitate.

In investigating the reduction of the cyanate radical, ammonia was condensed on dry potassium cyanate and calcium was added to the solution. Potassium cyanate is only slightly soluble in liquid ammonia. The materials were left in contact for one hour and then the excess calcium was reacted with ammonium bromide and the hydrogen was collected and analyzed. The hydrogen collected, corresponded within one-half a cubic centimeter of the hydrogen equivalent to the calcium used. The extracted residue gave no test for cyanide.

The above results might be explained by the following possibilities. The only available cyanate, potassium cyanate, is but slightly soluble in liquid ammonia. The calcium solution consists of two phases, a concentrated and a dilute one. The concentrated phase is in contact with the walls of the reaction tube while the inner dilute phase is available for the reduction. The reaction between such dilute solutions might be negligible. A second explanation is that the finely divided silver precipitate is necessary to catalyze the reduction of the cyanate radical by the calcium.

VI. THE REACTION BETWEEN SILVER THIOCYANATE AND CALCIUM.

No previous work has been done with silver thiocyanate and calcium. The reduction of silver thiocyanate by sodium and potassium gave evidence of partial reduction of the thiocyanate radical.(17) In view of the powerful reducing action shown by calcium solutions in previous work it was considered of interest to extend the work to include the reaction between silver thiocyanate and calcium. The results are given in Table IX.

Table IX

Exp. No.	Ca gms.	AgCNS gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Reaction Ratio corrected for side reactions	Time in Mins.
175	.3949	.9960	15.2	3.284	3.057	1.019	7
176	.5054	.9979	79.6	4.195	3.015	1.005	14
177	.4705	1.0061	58.4	3.893	3.015	1.005	11

The column headings are the same as discussed under Table I, with the exception of the column marked, reaction ratio corrected for the side reactions. This column contains the gram equivalents of calcium required to reduce one mole of silver thiocyanate to metallic silver. The ratio has been corrected for the amount of calcium used in forming calcium amide and hydrogen and the amount of calcium required to completely reduce the thiocyanate radical to calcium sulphide and calcium cyanide.

The average corrected equivalent ratio is 1.010 gram equivalents of calcium required to reduce one gram mole of silver thiocyanate to metallic silver and calcium thiocyanate. The uncorrected reaction ratio varied from 3.284 to 4.195 and would have a value increasing as the amount of excess calcium increases.

The reaction may be represented by the following equations.

(1) $2AgCNS + Ca \longrightarrow 2Ag + Ca(CNS)_2$

(2) $Ca(CNS)_2 + 2Ca \longrightarrow Ca(CN)_2 + 2CaS$

(3) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

It is interesting to note that, whereas the thiocyanate radical is only partially reduced by sodium and potassium, it is completely reduced to sulphide and cyanide by calcium. The extracted residue from these reactions gives strong tests for cyanide and sulphide. The dry reaction product burns when it is exposed to the air.

The silver precipitate from the calcium - silver thiocyanate reaction is very active as indicated by the rapid conversion of excess calcium to calcium amide and hydrogen. It is a better catalyst than the silver obtained from the iodide or cyanide reductions.

VII. THE REACTIONS BETWEEN SILVER NITRATE DIAMMONATE AND THE METALS SODIUM AND POTASSIUM.

A. The Reaction with Sodium:

There is no record of an anion as complex as the nitrate ion having been used in inorganic reductions in liquid ammonia.

Attempts to determine the reaction ratio between silver nitrate and sodium proved unsatisfactory. Two methods of approaching the problem were tried. The first method, that of adding powdered silver nitrate to the solution of sodium in liquid ammonia was not practical. The silver nitrate reacted with ammonia gas and fused to a black pasty mass before it could be added to the solution of the alkali metal. The second method, that of adding metallic sodium to the liquid ammonia solution of silver nitrate was unsatisfactory, due to a coating or a precipitate forming on the sodium, preventing its solution.

It was found that silver nitrate, dissolved in liquid ammonia, crystallized out of solution containing 2 moles of ammonia for each mole of silver nitrate. The preparation and stability of this compound was discussed under the section of the thesis entitled, "Materials".

The results obtained from one experiment are given in Table X. The experiment was carried out by adding the powdered silver nitrate diammonate, slowly, to the solution of the alkali metal, until the blue color disappeared.

Table X

The Sodium - Silver Nitrate Diammonate Reaction

Exp. No.	Na gms.	$AgNO_3.2NH_3$ gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
135	.4184	.6746	6.7	5.50	5.42	22

The column headings were discussed under Table I.

The corrected equivalent ratio is 5.42 gram atoms of sodium per mole of silver nitrate - diammonate. An explanation of this reaction will be discussed after the presentation of the other nitrate reductions.

The dry reaction product was black. The greater part of it burst into flame after exposure to the air. The pieces of the black substance not burning dissolved readily in water. The white product, formed by combustion of the black material, was insoluble in water and ammonium hydroxide but dissolved readily in dilute nitric acid. The acid solution gave a white precipitate with hydrochloric acid.

It is interesting to note that this reaction is the first of the sodium reductions to yield a good catalyst for the reaction of the sodium and the ammonia. The precipitate consists of very small particles, as noted by the difficulty with which the precipitate settles from the solution.

B. The Reaction with Potassium:

The following table contains the results of four experiments using potassium and silver nitrate diammonate. The powdered silver salt was added to the solution of the alkali metal.

Table XI

The Potassium - Silver Nitrate Diammonate Reaction.

Exp. No.	K gms.	$AgNO_3.2NH_3$ gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
121	.2309	.2560	1.5	4.70	4.60	15
122	.1758	.1918	- -	4.78	- -	19
126	.7086	.7022	12.1	4.94	4.65	130
130	.5132	.5633	4.8	4.75	4.60	52

The column headings are the same as those in Table I.

The average corrected ratio is 4.62 gram atoms of potassium required to reduce one gram mole of silver nitrate diammonate. This ratio is .8 of a gram atom of alkali metal less than that obtained with the corresponding sodium reaction.

In order to study the reduction of the nitrate radical without the complication of the presence of the silver precipitate, several experiments were made with alkali nitrates and nitrites.

C. Other Nitrate and Nitrite Reactions:

1. The Sodium - Sodium Nitrate Reaction:

The study of nitrate reductions was extended to sodium nitrate and sodium to attempt to determine the mechanism of the reductions.

The results of two experiments are recorded in Table XII. The sodium salt was added to the solution of the alkali metal.

Table XII

The Sodium - Sodium Nitrate Reaction

Exp. No.	Na gms.	$NaNO_3$ gms.	Reaction Ratio	Time in Mins.
133	.5210	.5486	3.51	20
134	.2213	.2372	3.45	13

The column headings were discussed under Table I.

The average reaction ratio is 3.48 gram atoms of sodium required to reduce one gram mole of sodium nitrate. This is approximately 2 moles less than that of the sodium silver nitrate diammonate reaction.

No hydrogen was evolved in these experiments. The dry reaction product, yellow in color, from experiment number 133 exploded when exposed to the air. Sodium metal was spattered over the inside walls of the reaction tube. The product from experiment 134 was not explosive, however, it flashed when dropped into water. The water solution evolved ammonia and when acidified had the odor of oxides of nitrogen.

2. The Potassium - Potassium Nitrate Reaction:

The following table contains the results of two experiments. The potassium salt was added to the solution of potassium in liquid ammonia.

Table XIII

The Potassium - Potassium Nitrate Reaction.

Exp. No.	K gms.	KNO_3 gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
125	.2461	.1761	8.5	3.61	3.18	161
129	.4043	.3323	1.2	3.15	3.11	59

The column headings were discussed under Table I.

The average corrected reaction ratio is 3.15 gram atoms of potassium required to reduce one gram mole of potassium nitrate. This is approximately 1.5 gram atoms of potassium less than was required to reduce silver nitrate diammonate.

The reaction product was yellow in color. It was stable when kept dry and was not explosive, as was the residue from the sodium reduction.

3. The Potassium - Ammonium Nitrate Reaction:

Two experiments are recorded in the following table. The ammono - acid was added to the solution of the alkali metal.

Table XIV

The Potassium - Ammonium Nitrate Reaction

Exp. No.	K gms.	NH_4NO_3 gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
131	.2835	.1820	- -	3.19	- -	27
132	.5060	.3354	1.0	3.09	3.07	15

The table headings were discussed under Table I.

The corrected reaction ratio of 3.07 gram atoms of potassium required to reduce one mole of ammonium nitrate is approximately the same as that for the potassium - potassium nitrate reaction.

It is of interest to note that ammonium nitrate, a strong ammono - acid, does not react as an acid in this reaction.

4. The Potassium - Potassium Nitrite Reaction:

In order to obtain more information about the nitrate reductions, two experiments between potassium and potassium nitrite were made. The alkali nitrite was added to the solution of potassium in liquid ammonia. The results are embodied in Table XV.

Table XV

The Potassium - Potassium Nitrite Reaction.

Exp. No.	K gms.	KNO_2 gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
127	.2664	.4267	- -	1.36	- -	52
128	.3380	.5427	2.3	1.35	1.32	65

The column headings were discussed under Table I.

The corrected equivalent ratio of 1.32 gram atoms of potassium nitrite shows that approximately 1.8 gram atoms of potassium less are required for the nitrite reaction than for the nitrate reaction. This may mean that the oxygen of the nitrate radical is removed in steps and that the successive steps, having different reaction rates, are not all completed.

A yellow precipitate resembling that obtained from the potassium nitrate and the ammonium nitrate reaction was formed.

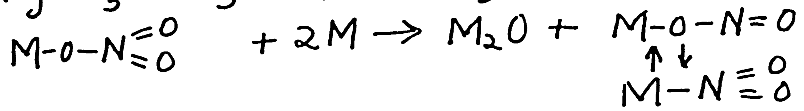
D..Conclusions:

The formulation of an equation in accord with the data offers serious difficulties. The difference between the reaction ratios of potassium nitrate and potassium nitrite is approximately 1.8 gram atoms of potassium. If it is assumed that the excess alkali metal is equivalent to the oxygen atom extra in the potassium nitrate, a compound,

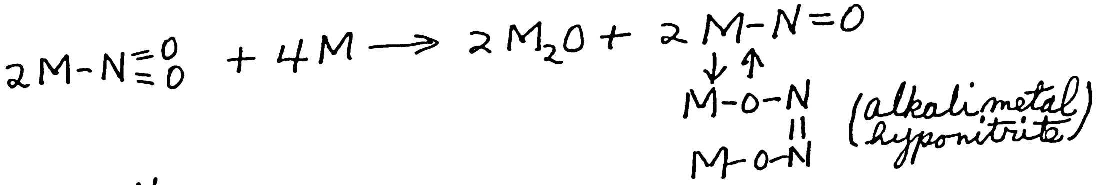
K_9O_5, would be the result. It is more probable that the reduction occurs in a series of reactions having different reaction rates. The reaction products may include oxides, nitrides, amides, imides and hydrazides. Browne(24) has reported the formation of metallic imides from inorganic reactions in liquid ammonia.

The following series of reactions are postulated for the reduction of silver nitrate diammonate by alkali metals.

(1) $AgNO_3 \cdot 2NH_3 + M \longrightarrow Ag + MNO_3 + 2NH_3$

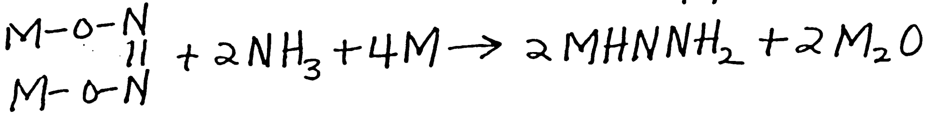
(2) 

$$\mathrm{M{-}O{-}N}\begin{smallmatrix}=O\\=O\end{smallmatrix} + 2M \rightarrow M_2O + \begin{array}{c}\mathrm{M{-}O{-}N{=}O}\\ \uparrow\downarrow \\ \mathrm{M{-}N}\begin{smallmatrix}=O\\=O\end{smallmatrix}\end{array}$$

(3) 

$$2\,\mathrm{M{-}N}\begin{smallmatrix}=O\\=O\end{smallmatrix} + 4M \longrightarrow 2M_2O + 2\begin{array}{c}\mathrm{M{-}N{=}O}\\ \downarrow\uparrow \\ \mathrm{M{-}O{-}N}\\ \| \\ \mathrm{M{-}O{-}N}\end{array}$$

(alkali metal hyponitrite)

(4) 

$$\begin{array}{c}\mathrm{M{-}O{-}N}\\ \| \\ \mathrm{M{-}O{-}N}\end{array} + 2NH_3 + 4M \rightarrow 2MHNNH_2 + 2M_2O$$

The extent to which these reactions occur depends upon reaction rates and solubility relationships.

This mechanism is substantiated by the following facts:

(a) The reduction of $NaNO_3$ by NaHg occurs in similar steps.(25)

(b) In the entire series of reductions the generalization may be made that the reaction rate is higher for the reactions requiring more time for completion.

(c) Explosive or pyrophoric compounds are obtained with the sodium reactions. The ratios for the sodium reactions are all higher than the corresponding potassium reactions. This may be explained by the extent to which reaction 4 is realized. The hydrazides are violently explosive products and have been only casually examined by several investigators.(26)

(d) Tests of the water soluble extract from the sodium nitrate - sodium reaction show the presence of a strong reducing substance, possibly either a nitrite or hyponitrite.

(e) The presence of nitrides, which are all black solids, are improbable because of the color of the reaction products. Sodium hyponitrite has been recorded as having a yellow color by several investigators.(25)

VIII. THE REACTIONS BETWEEN CUPROUS IODIDE AND THE METALS SODIUM, POTASSIUM AND CALCIUM.

A. The Reaction with Sodium:

No previous study has been made of the reduction of copper salts in liquid ammonia

In all of the experiments with cuprous iodide the reducing metal was added to the liquid ammonia solution of the copper salt. The results of two experiments with sodium and cuprous iodide are included in the following table.

Table XVI

The Sodium - Cuprous Iodide Reaction

Exp. No.	Na gms.	CuI gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
197	.1729	.5263	54.1	2.731	0.971	Added NH_4Br after 30 mins.
198	.1855	.5243	61.4	2.932	0.939	Added NH_4Br after 90 mins.

The table headings were discussed under Table I.

The corrected equivalent ratio averages to be 0.950 gram atoms of sodium required to reduce one gram mole of cuprous iodide. The copper precipitate agglomerates into one large piece and is a very poor catalyst for the reaction of the alkali metal with the solvent ammonia. The dry copper precipitate is brownish black but has some bluish precipitate on its surface. This indicates that some of the cuprous iodide does not have a chance to react or that the ammonium bromide dissolves a portion of the copper precipitate yielding hydrogen and copper bromide.

The reduction may be represented by the equation:

$$CuI + Na \longrightarrow Cu + NaI$$

B. The Reaction with Potassium:

The results of two experiments are given in Table XVII.

Table XVII

The Potassium - Cuprous Iodide Reaction.

Exp. No.	K gms.	CuI gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
189	.3476	.5257	40.6	2.295	0.980	Added NH_4Br after 57 mins.
190	.3712	.5616	44.2	2.344	1.014	Added NH_4Br

The column headings were discussed under Table I.

The average corrected reaction ratio has a value of 0.997 gram atoms of potassium required to reduce one gram mole of cuprous iodide. This is approximately a one to one ratio. The copper is a definite but poor catalyst for the conversion of the excess potassium to potassium amide and hydrogen. The precipitate differed from that obtained from the sodium reduction. It consisted of smaller particles and did not have as much of a bluish tinge.

The reaction may be represented by the following equations.

$$(1) \quad CuI + K \longrightarrow Cu + KI$$

$$(2) \quad NH_3 + K \longrightarrow KNH_2 + \frac{1}{2}H_2$$

The second reaction is very slow due to the slight activity of the catalyst.

C. The Reaction with Calcium:

Table XVIII contains the results of several experiments.

Table XVIII

The Calcium - Cuprous Iodide Reaction.

Exp. No.	Ca gms.	CuI gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
186	.1320	.5245	40.2	2.394	1.092	2
187	.1365	.5330	43.0	2.435	1.064	2
188	.2451	1.0416	73.9	2.239	1.030	2
192	.1324	.5180	41.5	2.431	1.068	2
193	.1127	.5153	33.6	2.080	1.078	2
194	.1379	.5259	44.3	2.494	1.060	3
195	.1496	.5106	52.2	2.787	1.049	3
216	.1505	.5455	52.6	2.624	0.982	3
217	.1510	.5017	53.3	2.863	1.054	4
218	.1438	.5253	50.9	2.604	0.954	3

The column headings were discussed under Table I.

The average corrected ratio for all experiments, except numbers 216 and 218, was 1.062 gram equivalents of calcium required to reduce one gram mole of cuprous iodide. After the completion of experiments 216 and 218, ammonium bromide was added to the residue and all evolved gas was collected and analyzed.

In each experiment where no ammonium salt was added, the brown black copper precipitate was pyrophoric. In these cases the high ratios corresponded to a deficit of from 1.8 to 2.2 ccs. of hydrogen. The very finely divided copper was very reactive as a catalyst for the reaction between the excess alkaline earth metal and the solvent as shown by the time required to complete the reaction.

After the completion of experiment number 217 the reaction tube containing the dry residue was attached to a Töepler pump and heated to about 300° C. with bunsen burner. Over ten cubic centimeters of hydrogen were obtained. This indicated a reaction between the metallic copper and the calcium amide. Bergstrom(27) has reported that all metals more electronegative than lead will react with potassium amide. It is probable that the copper reacted with calcium amide to form calcium ammono copperate according to the equation,

$$Cu + 2\,Ca(NH_2)_2 \longrightarrow Cu(NCa)_2 + H_2 + 2NH_3$$

This theory has been confirmed by some unpublished observations of Eastes.(28) He has found that the same reaction occurs with nickel salts. Upon washing out all the residual amide he was able to obtain theoretical hydrogen from the residue of metallic nickel, whereas the presence of amide in the heated material gave a large excess of hydrogen.

The reaction between calcium and cuprous iodide may be represented by the following equations.

(1) $2CuI + Ca \longrightarrow 2Cu + CaI_2$

(2) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

The second reaction proceeds vigorously as it is catalyzed by the finely divided copper.

In those experiments in which an ammono - acid was added to the copper residue a low ratio was obtained. This indicates that the copper liberates hydrogen and forms a copper salt. This may be caused by the presence of adsorbed oxygen on the ammonium salt. No attempt was made to remove the adsorbed air from the salt.

IX. THE REACTION BETWEEN ZINC CYANIDE AND CALCIUM

Burgess and Rose(29) studied the reaction of zinc cyanide and metallic sodium and found that a metallic compound was formed between the zinc and the excess sodium metal. They expressed the reaction by the following equation.

$$4Zn(CN)_2 + 9Na \longrightarrow NaZn_4 + 8NaCN$$

They also found that the sodium - zinc compound was unstable in the presence of excess zinc cyanide and reacted as follows:

$$2NaZn_4 + Zn(CN)_2 \longrightarrow 2NaCN + 9Zn$$

Their results confirmed the preliminary findings of Kraus and Kurtz.(16)

Burgess and Rose also studied the reaction between zinc cyanide and calcium. They obtained a variable reaction ratio having a value of from 3 to 5 gram atoms of calcium per gram mole of zinc cyanide.

Kraus and Kurtz assigned the following equation to the reaction.

$$8Ca + Zn(CN)_2 \longrightarrow Ca(CN)_2 + Ca_7Zn$$

All of the above experiments were carried out by adding the zinc salt to the solution of the alkaline earth metal. The exhaust gases were not examined.

The results of two experiments performed in this research by the method discussed under the procedure are given in Table XIX. The alkaline earth metal was added to the solution of the zinc salt.

Table XIX

The Calcium - Zinc Cyanide Reaction

Exp. No.	Ca gms.	$Zn(CN)_2$ gms.	H_2 collected ccs. S.T.P.	Reaction Ratio	Reaction Ratio corrected for H_2	Time in Mins.
212	.3020	.6190	49.2	1.430	1.013	4
215	.3260	.5015	82.9	1.905	1.039	11

The column headings were discussed under Table I.

The average corrected ratio is 1.026 gram equivalents of calcium required to reduce one gram mole of zinc cyanide. This is very nearly a one to one ratio and indicates that no compound is formed between calcium and zinc, when the alkaline earth metal is added to the solution of the zinc salt.

The reaction may be represented by the following equations.

(1) $Zn(CN)_2 + Ca \rightarrow Zn + Ca(CN)_2$

(2) $2NH_3 + Ca \rightarrow Ca(NH_2)_2 + H_2$

The freshly precipitated zinc is a fine catalyst for the second of the above reactions.

Attempts to determine the reaction between zinc cyanide and calcium by adding the zinc salt to the solution of the alkaline earth metal were unsuccessful. The zinc cyanide in the addition tube absorbs ammonia and sticks in the tube. It is possible that the reaction carried out in this manner might present a different ratio. Burgess and Rose found that the compound, $NaZn_4$, was unstable in the presence of an excess of zinc cyanide.

Future work on this problem will be conducted by attempting to prepare a stable ammonate of zinc cyanide.

X. CONCLUSIONS:

1. The reactions between sodium and the silver salts, whose anions are halogens or simple radicals, occur according to the following equation.

$$AgX + Na \longrightarrow Ag + NaX$$

There is no evidence of any appreciable side reaction and the results agree with those obtained by Burgess and Smoker.(14)

2. The results from the reduction of silver salts with potassium, in each case, show that there is an appreciable reaction between the solvent ammonia and the potassium. This reaction is catalyzed by the freshly reduced silver precipitate. The catalytic value of the silver precipitate from different salts is not the same. The particle size of the precipitate is apparently the major factor in the effectiveness of the silver as a catalyst. The reactions between potassium and silver salts, whose anions are halogens or simple radicals, may be summarized by the following equations.

(a) $AgX + K \longrightarrow Ag + KX$

(b) $NH_3 + K \longrightarrow KNH_2 + \frac{1}{2} H_2$

The silver precipitate from the reduction of silver cyanide with potassium is pyrophoric.

3. The reduction of silver salts with calcium indicates that the reaction is similar to that postulated for potassium and silver salts and may be represented by the

equations.

(a) $2AgX + Ca \rightarrow 2Ag + CaX_2$

(b) $2NH_3 + Ca \rightarrow Ca(NH_2)_2 + H_2$

The silver precipitate is in a very fine state of division and serves as an excellent catalyst for the second of the above reactions. The precipitate is pyrophoric in nature.

There is no evidence of the formation of the compound, CaAg, reported by Kraus and Kurtz.(16)

4. The cyanate radical which is stable in solutions of sodium and potassium is partially decomposed by calcium to form calcium oxide and calcium cyanide. The reaction between silver cyanate and calcium may be represented by the following equations.

(a) $2AgCNO + Ca \rightarrow 2Ag + Ca(CNO)_2$

(b) $Ca(CNO)_2 + 2Ca \rightarrow Ca(CN)_2 + 2CaO$

(c) $2NH_3 + Ca \rightarrow Ca(NH_2)_2 + H_2$

The reaction represented by the second of the above equations is not complete. The extent of this reaction varies with the amount of excess calcium used. The finely divided silver precipitate rapidly catalyzes the reaction represented by the third equation.

5. Solutions of calcium in liquid ammonia completely reduce the thiocyanate radical to calcium cyanide and calcium sulphide. This result is in accord with the reported

partial reduction of the thiocyanate radical by sodium and potassium.(17) The reduction of silver thiocyanate by calcium is represented by the following equations.

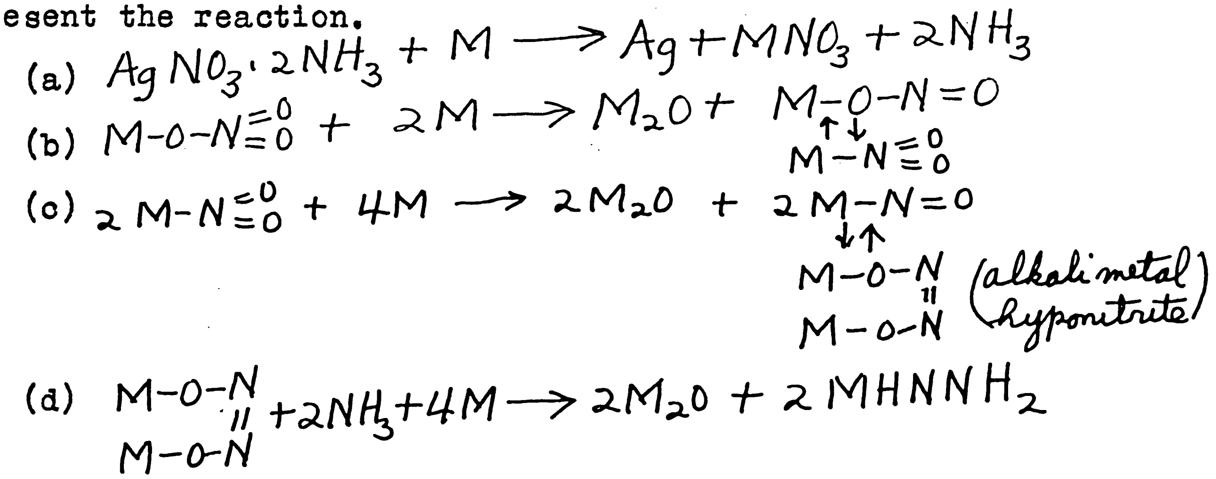
(a) $2AgCNS + Ca \longrightarrow 2Ag + Ca(CNS)_2$

(b) $Ca(CNS)_2 + 2Ca \longrightarrow Ca(CN)_2 + 2CaS$

(c) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

The finely divided precipitate catalyzes the reaction represented by the third of the above equations. The dried reaction product burns when exposed to the air.

6. The reduction of the nitrate radical occurs in steps and the following equations have been offered to represent the reaction.



(a) $AgNO_3 \cdot 2NH_3 + M \longrightarrow Ag + MNO_3 + 2NH_3$

(b) $M{-}O{-}N\overset{=O}{\underset{=O}{}} + 2M \longrightarrow M_2O + \begin{array}{c} M{-}O{-}N{=}O \\ \uparrow\downarrow \\ M{-}N\overset{=O}{\underset{=O}{}} \end{array}$

(c) $2\,M{-}N\overset{=O}{\underset{=O}{}} + 4M \longrightarrow 2M_2O + 2\,\begin{array}{c} M{-}N{=}O \\ \downarrow\uparrow \\ M{-}O{-}N \\ \parallel \\ M{-}O{-}N \end{array}$ (alkali metal hyponitrite)

(d) $\begin{array}{c} M{-}O{-}N \\ \parallel \\ M{-}O{-}N \end{array} + 2NH_3 + 4M \longrightarrow 2M_2O + 2MHNNH_2$

These results are in accordance with the views of other workers, who have studied the reduction of the nitrate radical by sodium amalgam.(25)

7. The reduction of cuprous iodide with sodium may be represented by the equation,

$CuI + Na \longrightarrow Cu + NaI$

There is no evidence of any appreciable side reaction.

8. Cuprous iodide is reduced by potassium as represented by the following equations.

(a) $CuI + K \longrightarrow Cu + KI$

(b) $NH_3 + K \longrightarrow KNH_2 + \frac{1}{2}H_2$

The copper precipitate is a poor but definite catalyst for the second of the above reactions.

9. The reaction between calcium and cuprous iodide may be represented by the following equations.

(a) $2CuI + Ca \longrightarrow 2Cu + CaI_2$

(b) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

The copper precipitate is an excellent catalyst for the reaction between the solvent ammonia and the excess alkaline earth metal. The residue is pyrophoric and contains a small amount of adsorbed hydrogen.

10. When calcium is added to a liquid ammonia solution of zinc cyanide, no metallic compound is formed between the freshly reduced zinc and the alkaline earth metal. The reaction may be represented by the following equations.

(a) $Zn(CN)_2 + Ca \longrightarrow Zn + Ca(CN)_2$

(b) $2NH_3 + Ca \longrightarrow Ca(NH_2)_2 + H_2$

The metallic zinc is pyrophoric. It is an excellent catalyst for the second of the above reactions.

The compound, Ca_7Zn, reported by Kraus and Kurtz(16) is not formed. They did not collect exhaust gases and take the reaction of the alkaline earth metal with ammonia into account.

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