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I hereby recommend that the thesis prepared under my supervision by John Wesley Eastes

entitled Reduction of Nickel Compounds with Alkali Metals in Liquid Ammonia Solution.

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

Approved by:

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REDUCTION OF NICKEL COMPOUNDS WITH ALKALI METALS IN LIQUID AMMONIA SOLUTION.

A dissertation submitted to the

Graduate School

of the University of Cincinnati

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requirements for the degree of

DOCTOR OF PHILOSOPHY.

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by

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To Dr. W. M. Burgess, who suggested this topic and under whose direction this research was carried out, the writer wishes to express deep appreciation for having had the use of a well equipped laboratory and for advice so willingly given upon its solicitation.

CONTENTS.

I. INTRODUCTION..... 1

II. APPARATUS AND ITS MANIPULATION.....16

A. LIQUID AMMONIA APPARATUS.....16

B. VACUUM APPARATUS.....25

III. MATERIALS USED.....31

A. METHODS OF PREPARATION.....33

B. 1. Liquid Ammonia.....33
2. Sodium and Potassium.....33
3. Known Nickel Ammine Salts.....34
4. Hexammine Nickel Acetate.....35
5. Triammine Nickel Cyanide.....35

B. METHODS OF ANALYSIS AND COMPOSITION OF REAGENTS.....36

1. Analysis of Metallic Sodium.....38
2. Analysis of Metallic Potassium.....39
3. Analysis of Known Nickel Ammine Salts....39
4. Analysis of Hexammine Nickel Acetate, a New Compound.....41
5. Analysis of Triammine Nickel Cyanide, a New Compound.....42

IV. REACTION OF SIMPLE NICKEL SALTS WITH SODIUM AND POTASSIUM IN LIQUID AMMONIA.....44

A. HEXAMMINE NICKEL BROMIDE WITH SODIUM.....44

B. HEXAMMINE NICKEL BROMIDE WITH POTASSIUM.....54

C. HEXAMMINE NICKEL IODIDE AND HEXAMMINE NICKEL ACETATE WITH POTASSIUM.....58

D. HEXAMMINE NICKEL CHLORIDE AND HEXAMMINE NICKEL IODIDE WITH SODIUM.....59

CONTENTS.
(continued)

E. TRIAMMINE NICKEL CYANIDE WITH SODIUM AND POTASSIUM.....61

F. TETRAMMINE NICKEL THIOCYANATE WITH SODIUM AND POTASSIUM.....62

G. HEXAMMINE NICKEL NITRATE WITH SODIUM AND POTASSIUM.....64

V. PYROPHORIC PROPERTY OF NICKEL.....66

VI. SUMMARY.....76

VII. REFERENCES.....78

I.

INTRODUCTION.

Although ammonium compounds and ammonia gas (volatile alkali) were known to the ancients, the isolation, liquifaction and determination of the properties of ammonia in its different conditions of state, are events that belong in fairly recent history.

In 1799, M. van Marum (1), while testing Boyle's Law, tried the effect of pressure on ammonia and found that drops of liquid ammonia were produced at three atmospheres pressure. A. F. de Fourchroy and L. N. Vaquelin (2) subjected ammonia to a low temperature and claimed to have liquified the gas at -40. L. B. Guyton de Morveau (3) also cooled the gas to -43.25 and obtained liquid ammonia. In all these cases, considering that the vapor pressure of liquid ammonia at ordinary temperature is near nine atmospheres, it is doubtful if the gas used was dried sufficiently to justify the inference that the drops of liquid formed on the surface of the containing vessels were really those of liquid ammonia, so that it is generally conceded that M. Faraday (4) was the first to liquefy ammonia.

Faraday heated silver ammino chloride in one leg of a sealed $\wedge$-tube and cooled the other leg in a freezing mixture. He thus obtained colorless, transparent liquid ammonia and in 1845, by means of a mixture of solid carbon

dioxide and ether he also obtained ammonia as a white, translucent, crystalline solid. This method of liquifying ammonia was used by most of the early investigators, probably because it afforded, thru the use of various ammoniated salts, a convenient source of liquid ammonia when there was no ready supply, as such, at hand. After Faraday enunciated this method, a number of other men studied liquid ammonia. Faraday (5), Bunsen (6), Regnault (7), and others (8) liquified ammonia, measured its vapor pressure and other properties, but no one up to the time of the German chemist Weyl (9), in 1864, made any recorded attempt to study the action of liquid ammonia on other materials.

Weyl obtained his liquid ammonia from silver ammino chloride by means of the sealed tube method used by Faraday, but instead of leaving the cooled end of the tube, where the liquid ammonia collects, empty, Weyl placed in it the material on which he wished the liquid ammonia to act. Using metallic potassium in this way he found that the silvery metal first turned brown, then, as more ammonia condensed, it changed thru various color shades to blue; all further additions of ammonia after this only decreased the intensity of the blue color. His explanation of this was that the brown material was a compound, potassium ammonium (KNH_3), and that the blue material

was a solution of potassium ammonium in liquid ammonia. These metal ammonium compounds were held to be analogous to the ammonium radical (NH_4^+). i.e. the ammonium radical having one hydrogen replaced by a metal. The metal ammoniums, having no negative radicals to go along with them, were thought to be free radicals. This explanation of the observed phenomena was disputed, however, by the very next person, Seeley (10), who studied the action of liquid ammonia on potassium in the year 1870.

Seeley claimed that no such compound as potassium ammonium was formed, but that the potassium merely went into solution in the liquid ammonia as potassium metal, the observed solor changes being due to different concentrations of potassium in the liquid ammonia solution. This explanation was vigorously opposed by Joannis (11), a Frenchman, who began the study of liquid ammonia in 1889 and continued it for some twenty years, during which time he always adhered to the metal ammonium compound theory which had been proposed by Weyl to explain the blue color produced by alkali metals in liquid ammonia. Joannis and his associates held to this metal ammonium theory even after it was definitely proven that Seeley's explanation was the correct one, by Kraus (12), who applied the phase rule interpretation to vapor pressure measurements on liquid ammonia containing alkali metals.

Kraus is one of the three Americans, who may be regarded as the founders of liquid ammonia chemistry as a definite branch of study.

Cady, Franklin, and Kraus (13) took up the study of liquid ammonia chemistry at the University of Kansas in the years 1897-8. These three men along with their students have continued this study and are responsible for a large portion of the advance made in this field. Thru their efforts, the properties of liquid ammonia have been determined and a system of chemistry based upon liquid ammonia as a solvent has been developed which is comparable to the chemistry of aqueous solutions.

That liquid ammonia, as well as water, is a good solvent for many diverse substances, first became evident thru the work of Gore (14), a British chemist and physicist, who, in 1872, using the Faraday sealed tube procedure, carried out qualitative investigations on the solubility of about three hundred and fifty substances in liquid ammonia. Extension of the knowledge of solubilities, electrolysis experiments, and the measurement of physical constants, as boiling point rise and freezing point lowering, etc., in liquid ammonia solutions show that such solutions are similar to aqueous solutions and that liquid ammonia is a solvent nearly comparable to water in solvent powers. A comparison of solution behavior, solvent powers and physical constants

(see the following table, #1) for liquid ammonia and water shows that just as water may be regarded as an "abnormal" solvent, so may liquid ammonia.

Table #1.

Physical Constants. (15)

Name.	Liquid ammonia:	Water.
Melting point	-77.7	0.0
Boiling point (760 mm.)	-33.35	100.
Specific heat	1.13	1.0
Specific gravity at 20 C.	0.607	0.9982
Critical temperature	131.	365.
Critical pressure (atm.)	112.	195.
Dielectric constant	22.	81.7
Molal freezing point constant	0.98	1.858
Molal boiling point constant	0.34	0.52
Heat of vaporization (at B.P.)	337.	536.
Heat of fusion	108.-11	79.5-8
Specific conductivity (mhos) -33 & 18 C.	5x10	4x10

Franklin (16), having in mind the analogies between water and liquid ammonia solutions, formulated a complete system or classification of nitrogen compounds based upon the solvent liquid ammonia as the parent substance. Since this system was formulated by analogy from the aquo or oxygen system of compounds based upon the solvent water, it might be well to define exactly what we mean by the oxygen system before taking up the nitrogen system of compounds.

Using HOH as the structural formula of water and regarding water as the parent substance from which all oxygen containing compounds are derived, a definition may be given to each class of oxygen compound according to its relation to the

structure HOH of water. Thus any aquo base, as potassium hydroxide (KOH), is a substance that is formed by the replacement of an H in HOH by a metal. An oxide, as potassium oxide (K_2O), results when both of the H's in HOH are replaced by a metal. Any aquo acid, as hypochlorous acid (HOCl), is a substance formed by replacing an H of HOH by a non-metal. Replacement of both H's by a non-metal produces an acid anhydride, as chlorine monoxide (Cl_2O). When an aquo acid reacts with an aquo base there is produced a salt and the solvent, water.

$$KOH + HOCl \longrightarrow KOCl + HOH$$

Amphoteric acids (or bases) are the result of one of the H's in HOH being replaced by an element that may act as a metal and a non-metal. For the sake of brevity only the definitions of acids, bases and salts have been given as examples, but from these it follows how we may define all of the oxygen compounds as being structrual derivatives of water when water is considered as being HOH. Carrying these same ideas over to liquid ammonia solutions we may look upon all compounds containing trivalent nitrogen as being derivatives of ammonia, when ammonia is considered structuraly as being NH_3, and define classes of compounds on this basis.

An ammono base is then, a compound formed by replacing one of the H's in NH_3 by a metal. Potassium amide (KNH_2) is

a strong ammono base, effecting indicators and reacting with acids in liquid ammonia solutions as does potassium hydroxide in water. Replacing a second H in NH_3 by a metal gives an imide, as potassium imide (K_2NH), which is also an ammono base. Replacing all of the H's in NH_3 by a metal gives a nitride, as potassium nitride (K_3N), which is analogous to an oxide in the aquo system. It is seen from this that in the nitrogen system of compounds there is a new class of compounds due to the third valence of nitrogen which has no analog in the aquo system, oxygen being only divalent. An ammono acid is the result of replacing one of the H's in NH_3 by a non-metal. Thus chloramine (H_2NCl) is ammono hypochlorous acid. Introduction of another chlorine atom into NH_3 gives us chlorimid ($HNCl_2$), which is also an ammono acid. Introduction of three chlorine atoms into NH_3 gives nitrogen trichloride (NCl_3), which is an ammono acid anhydride. The reaction of an ammono acid with an ammono base produces a salt and ammonia, the solvent.

$$KNH_2 + H_2NCl \longrightarrow KNHCl + NH_3$$

A consideration of the above definitions of acids, bases, and salts will show that they may be made general and apply to any system of compounds, the solvent being considered as the parent substance from which all of the compounds in the system are derived.

Franklin (17) has made this extension of his aquo and ammono systems of compounds, so that we may now say that in general, a base is a substance formed by replacing one of the H's in the parent (solvent) substance by a metal, an acid is a substance formed by replacing one of the H's in the parent (solvent) substance by a non-metal, and a salt is a substance produced along with the solvent when an acid reacts with a base. The following table, #2, is given to illustrate the application of these generalized definitions.

Table #2.

Systems of Acids, Bases, and Salts.

System	Solvent	Acid	Base	Salt
Water	H-OH	H-OCl	K-OH	K-OCl
Hydrogen sulfide	H-SH	H-SCl	K-SH	K-SCl
Ammonia	$H-NH_2$	H-NHCl	$K-NH_2$	K-NHCl
Hydrogen floride	$H-F_2H$	$H-F_3$	$K-F_2H$	$K-F_3$
Methane	$H-CH_3$	$H-CH_2Cl$	$K-CH_3$	$K-CH_2Cl$

The extension of the original ideas of the aquo system to nitrogen and then generalizing the definitions so that they might embrace any solvent system brings up the question of how to classify a compound that contains two elements, say oxygen and nitrogen, either of which may be used as a basis for classification, such compounds, an example of which is hydroxylamine (NH_2OH), are to be regarded as a mixed type

of compound. Hydroxyl ammine then is an aquo-ammono compound. From this it is seen that we may have any assortment of mixed systems, as well as the simple systems of compounds.

These systems of compounds have been defined upon structrual relations of compounds to a given parent substance and not upon any general property relationships. Thus potassium amide is not an ammono base merely because it turns phenolphthalein pink in liquid ammonia, but because it may be regarded as derived from ammonia by the replacement of a hydrogen atom by an atom of the metal potassium. Potassium hydroxide dissolves in liquid ammonia, turns phenolphthalein pink and reacts with acids in liquid ammonia, but it is not an ammono base. All that we may say about potassium hydroxide in liquid ammonia is that it exhibits reaction properties similar to those of an ammono base. A further illustration of this point is found in the behavoir of ammonium salts, such as ammonium chloride.

In water, ammonium chloride forms a solution that is nearly neutral to indicators, while in liquid ammonia it gives a solution that is very strongly acidic, yet ammonium chloride is neither a true aquo salt nor an ammono acid. In general ammonium salts behave (18) as acids in liquid ammonia. To account for this behavoir the ammonium salt is regarded as an ammoniated hydride, which when in solution has the ammonia associated with the hydrogen ion.

$$NH_3 \cdot HCl \longrightarrow H \cdot (\overset{+}{NH_3}) + \overset{-}{Cl}$$

Thus solid ammonium chloride is monammine hydrogen chloride ($HCl \cdot NH_3$), just as hexammine calcium chloride ($CaCl_2 \cdot 6NH_3$) is ammoniated calcium chloride or calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) is hydrated calcium chloride. In speaking of ammonium chloride as ammoniated hydrogen chloride it is interesting to note that when a solution of ammonium chloride in liquid ammonia is evaporated, the solid phase that separates out is triammine ammonium chloride ($NH_4Cl \cdot 3NH_3$) (19), which may be regarded as tetrammine hydrogen chloride, another ammoniate of hydrogen cholride. This ammine is unstable under ordinary conditions and became known only thru the use of liquid ammonia as a solvent, as have numerous other compounds, which can not exist or be formed in water, were unknown, unpredicted and some of which were not thought to be possible.

A few such compounds which were discovered by the use of liquid ammonia are, ammonium oxide ($(NH_4)_2O$) and ammonium hydroxide (NH_4OH) (20), ammonium methylate NH_4OCH_3) (21), disodium nitrite (Na_2NO_2) (22), potassium tetrazide ($K_2C_2N_4$) (23), disodium aniline ($C_6H_5NNa_2$) and several other new reduction products of nitrobenzene (24). If these few compounds are not enough to convince, an examination of the literature on liquid ammonia work will show that

liquid ammonia as a reaction medium is not to be considered as an interesting curiosity, but as a useful research tool that often brings definite results that are impossible to obtain in any other known way. As an example of everyday practical usefulness of liquid ammonia as a reaction medium, the quantitative determination of halogens in organic compounds (25) thru the use of solutions of alkali metals in liquid ammonia may be cited.

These solutions of alkali metals in liquid ammonia have excited the curiosity of investigators since the time of their discovery by Weyl in 1864. Kraus, after having proved that the blue solutions are in reality solutions of alkali metals in liquid ammonia, showed by the same use of the phase rule that the alkaline earth metals form compounds (12) of the type represented by calcium hexammine ($Ca \cdot 6NH_3$) as well as true solutions of the metal. It is to be noted that calcium hexammine is an ammoniate of calcium and not a metal ammonium compound like postulated by Weyl. Solutions of alkali and alkaline earth metals when concentrated conduct an electric current in the same fashion as does the pure metal in the absence of liquid ammonia, but as the solutions are diluted with liquid ammonia the character of the conduction changes gradualy until at dilute solution the behavoir (26) is that of true electrolytic conductance, which is characteristic of solutions of acids, bases and salts. The theory (27) that

is generally accepted to account for the properties of these solutions of metals is that there exists in the solution an equilibrium between neutral atoms, positively charged metal ions, and free electrons which are ammoniated; the relative amounts of each depending upon the dilution of the solution in question. This equilibrium in solution is represented in the following manner, using the metal potassium for an example.

$$K \rightarrow K^{+} + e^{\bullet}(NH_3)_x$$

To this free electron in solution is attributed the ability of such solutions to quantitativly remove halogen and sulfur (28) from organic compounds, to precipitate metals (29) from their salts and to bring about other reactions that demand violent reducing power.

Some typical examples of reactions between these liquid ammonia solutions of alkali and alkaline earth metals and inorganic salts are as follows.

1. Precipitation of a free metal.

$$AgCl + Na \longrightarrow Ag + NaCl \qquad (29)$$

$$AuI + Na \longrightarrow Au + NaI \qquad (30)$$

1a. Reaction between the precipitated metal and alkali metal.

$$Au + Na \longrightarrow AuNa \qquad (30)$$

(The alkali metal may react directly with the salt without the intermediate formation of the metal precipitate to give the products formed by the occurance of both 1 and 1a.)

1b. Reaction between precipitated metal and alkali amide formed by catalysis of the excess alkali metal.

$$Zn + 2KNH_2 \longrightarrow Zn(NHK)_2 + H_2 \quad (16)$$

$$10Sn + 6NaNH_2 \longrightarrow 2Sn(NH_2)_2 \cdot NaNH_2 + Na_4Sn_8 \quad (31)$$

2. The negative radical of the salt is attacked by the alkali metal.

$$NaNO_2 + Na \longrightarrow Na_2NO_2 \quad (22)$$

$$NaSCN + 2Na \longrightarrow Na_2S + NaCN \quad (32)$$

In addition to the main reaction between alkali metal and the inorganic salt, there may occur side reactions such as;

1. Ammonolysis of the inorganic salt.

$$HgCl_2 + 2NH_3 \longrightarrow HgNH_2Cl + NH_4Cl \quad (33)$$

$$SiCl_4 + 8NH_3 \longrightarrow Si(NH_2)_4 + 4NH_4Cl \quad (16)$$

2. Reaction between the salt and the alkali amide formed by catalysis of the excess alkali metal.

$$2KNH_2 + Ni(SCN)_2 \longrightarrow 2KSCN + Ni(NH_2)_2 \quad (34)$$

The carrying out of the above reactions or any reaction in liquid ammonia solution is not without its difficulties. For instance very small traces of moisture or air (oxygen) in apparatus have been observed to effect some reactions in liquid ammonia to a marked degree. Often products are formed which are unstable at ordinary temperatures (23), in the absence of liquid ammonia or in the absence of an atmosphere of gaseous ammonia (19). Considerable difficulties have been

experienced with some reaction products (23) in making the transfer from the liquid ammonia to the water system for the purpose of analysis, because of instability in the presence of water. In addition to these difficulties, which may be regarded as incidental to some cases, the liquid ammonia, due to its physical properties, requires special apparatus and technique for using it as a solvent medium for chemical reactions.

For carrying out reactions in liquid ammonia two different techniques have been developed, one for working with liquid ammonia at toom temperatures and the other for working at the boiling point of liquid ammonia. A few (35) reactions have been carried out at higher than room remperatures. Working with liquid ammonia solutions at room temperature as discribed by Franklin(36) and others involves the manipulation of solutions in glass or other apparatus under the vapor pressure of liquid ammonia and since the vapor pressure of liquid ammonia at 24 C. is 9.594 atmospheres(37), there is the danger of explosion of glass apparatus. Working with liquid ammonia at its boiling point requires, essentially, some contrivance which will prevent the liquid ammonia from boiling too vigorously and which will take care of the ammonia gas that is boiled-off. While in some cases where it is desired merely to carry out a reaction in liquid ammonia, an ordinary Dewar flask and a

fume hood satisfy these requirements, an apparatus suitable for maintaining complete anhydrous conditions and for investigating the course of a reaction is necessarily more elaborate. Such an apparatus and the procedure used in working with boiling liquid ammonia will be taken up in some detail in the next section of this thesis, because this has been the method used here at the University of Cincinnati, where investigations carried out in liquid ammonia solutions have been focused upon reactions brought about by solutions of alkali and alkaline earth metals.

In harmony with this line of investigation pursued at the University of Cincinnati, the experimental part of this thesis deals with the reactions occurring between nickel compounds and solutions of alkali and alkaline earth metals in liquid ammonia at its boiling point.

II.

APPARATUS AND ITS MANIPULATION.

The apparatus described herein consists of two separate setups, each of which was constructed in the laboratory by the use of a blast lamp and a hand-torch. One setup was that used for working with liquid ammonia at its boiling point and the other for subjecting material to high vacuum treatment.

A. LIQUID AMMONIA APPARATUS.

The liquid ammonia apparatus used in this work was in general like that which had been used here by other workers (32), but modified in its various parts to suit our own notions. The entire apparatus was held securely on an especially built wooden frame (5ft.x 5ft.) in which was mounted strong iron rods. This rack might be regarded as a de luxe model ringstand since it supported the apparatus by means of the ordinary varity of laboratory clamps, rings, etc. The apparatus, most of which was left permenantly clamped to the rack, consisted essentially of a cooling bath, reaction tube, gas collection train and a gas exit train. The general setup of the liquid ammonia apparatus is illustrated in Figure I., and in Figure II., certain details of the apparatus are shown.

Figure I

LIQUID AMMONIA APPARATUS

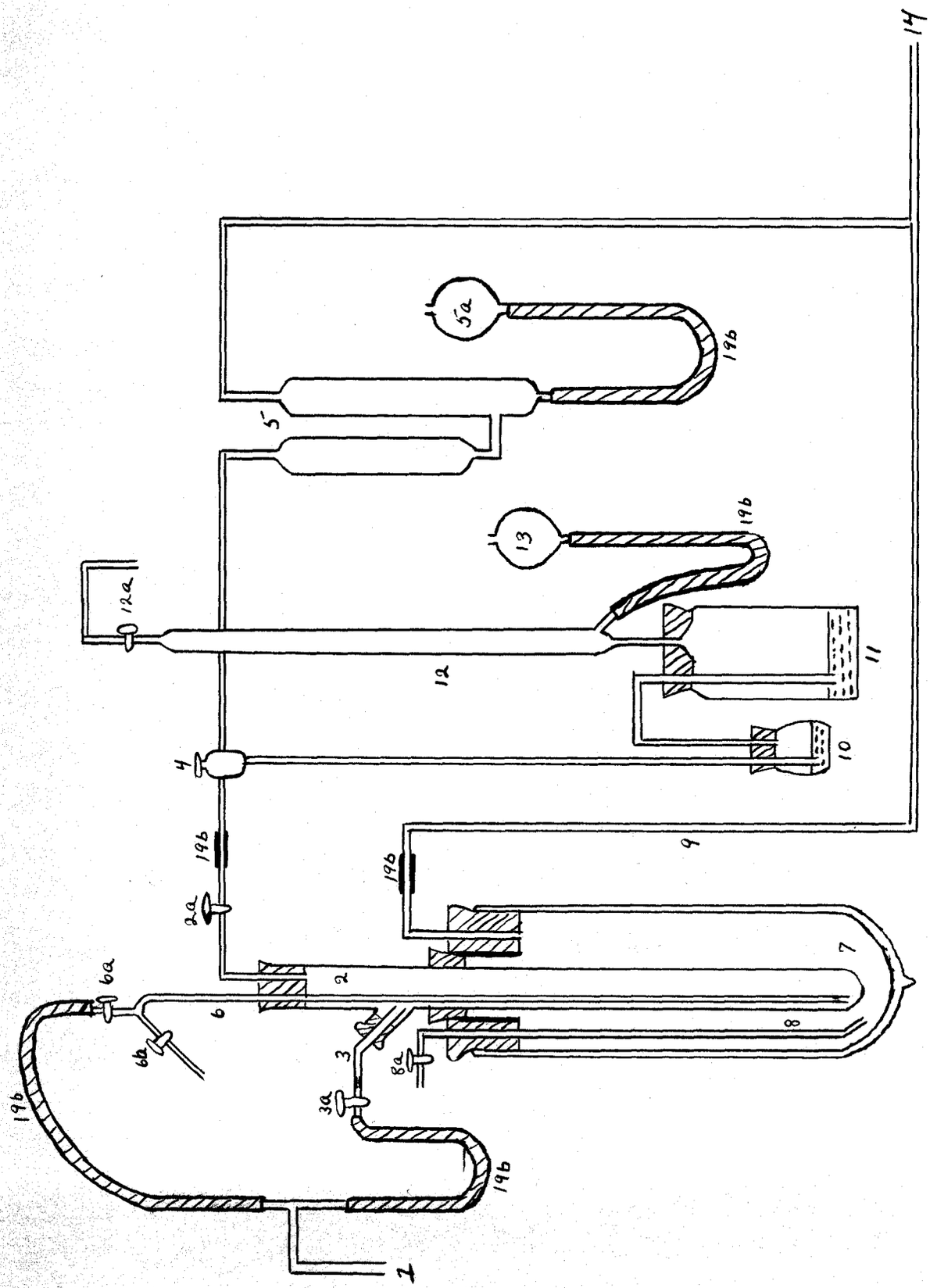
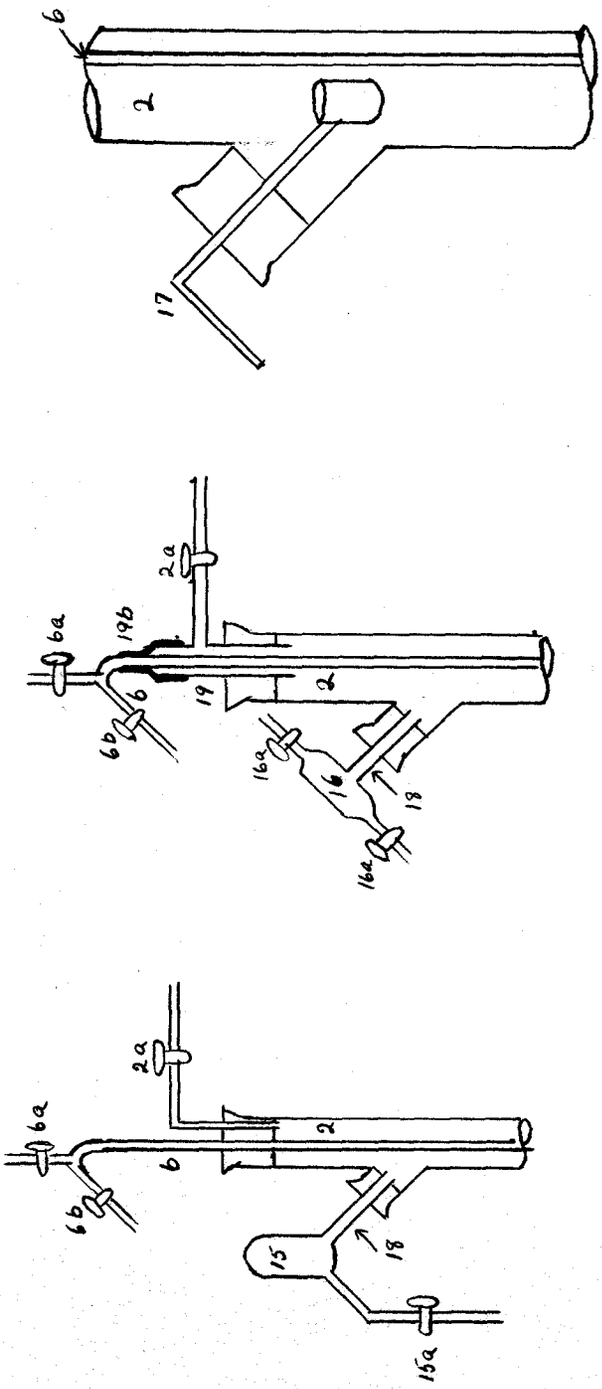


Figure II

REACTION AND SAMPLE TUBE DETAILS



LEGEND FOR FIGURE I AND II.

1. To an iron tank fitted with a needle valve. The tank holds 4.5 lbs. of liquid ammonia.
2. Reaction tube, 22 mm. inside diameter.
3. Bent tube used for addition of alkali metal, etc.
4. Three way stopcock.
5. Mercury pressure gage.
6. Tube delivering anhydrous ammonia gas to the reaction tube and also wash solution delivery tube.
7. Dewar flask, unsilvered, one liter.
8. Tube for blowing dry compressed air thru Dewar flask.
9. Exit tube for compressed air and evaporated ammonia.
10. 100 cc. safety bottle containing 2 cm. of Hg.
11. 500 cc. absorption bottle containing 2 cm. Hg, and 6M HCl.
12. 100 cc. gas burette, containing 6M HCl.
13. Leveling bulb for gas burette, contains 6M HCl.
14. Leads to a ten liter safety bottle which leads to another ten liter bottle filled two-thirds full of water to absorb ammonia that escapes from the apparatus.
15. Pyrex sample tube used for samples that are to be used on the vacuum apparatus, Figure III, #15.
16. Sample tube made with very small stopcocks so that the whole thing is light (Wt. approx. 30 gms.) and may be weighed on an analytical balance.

LEGEND FOR FIGURE I AND II.

17. Bent glass rod fused on to a small glass cup, used in place of #3, Figure I, to introduce samples of nickel salts into reaction tube.

18. Point at which sample tubes are sealed off from the reaction tube.

19. Arrangement of top of reaction tube that facilitates the washing of precipitates with liquid ammonia.

19b. Pressure tubing, rubber.

(2,3,6,8,12,16,19)a and 6b. Two-way stopcocks.

The manipulation of this liquid ammonia apparatus will now be explained by describing the carrying out of an experiment. First, the two reactants, weighed amounts of alkali metal and nickel salt, are placed in the apparatus, the nickel salt in the reaction tube,2, and the alkali metal in the addition tube, 3, the alkali metal being protected from the air by a stream of ammonia gas passing from the tank, 1, thru 3 and 6, out of the reaction tube to stopcock 4, which directs it thru the pressure gage,5. The pressure gage is kept at a pressure of ten to fifteen centimeters of of mercury. The ammonia gas goes from the gage to the absorption bottles,14. Having the reagents in place, a slow stream of ammonia gas is kept flowing thru the apparatus while the Dewar flask, 7, is filled with commercial liquid ammonia. The commercial liquid ammonia is introduced into the Dewar flask thru a glass tube in rubber stopper 7a. This glass tube, not shown in the diagram, is closed with a rubber stopper at all times except when liquid ammonia is being introduced into the Dewar flask. Compressed air is blown thru the commercial liquid ammonia in the Dewar by means of tube 8, The compressed air together with the evaporated ammonia leave the Dewar thru tube 9 and go to the absorption bottles, 14. This evaporation of the commercial liquid am ammonia by the use of compressed air lowers the temperature of the whole cooling bath several degrees below the boiling

point of liquid ammonia, hence the anhydrous ammonia gas coming from tank 1 will condense in the reaction tube, 2.

When sufficient liquid ammonia, about ten centimeters depth, has condensed in the reaction tube, the stopcock 4 is adjusted so that the gas leaving the reaction tube will pass thru the safety bottle 10 and to the bottle 11, where all the ammonia will be absorbed and all gas not soluble in hydrochloric acid will pass up into the graduated gas burette, 12. When stopcock 4 is so changed the stream of ammonia gas coming from the tank 1 is adjusted so that ammonia just does bubble thru the safety bottle 10. At this time the addition tube 3 is gently tapped with the fingers so that the material contained in it will fall into the reaction tube, 2, and react with the material in the liquid ammonia solution. When the reaction occurs it is usually necessary to adjust the stream of ammonia gas coming from 1 so that the flow of gas thru 10 and 11 is not too violent. When the reaction is over the compressed air is turned off and all parts of the system in front of the gas burette is flushed well with ammonia gas so that all the gaseous reaction products which are not soluble in liquid ammonia or hydrochloric acid will be swept into the gas burette 12, where such gases may be kept pending their analysis. After having collected all the gaseous reaction products, attention is turned to the solid and liquid products that may be present. These are separated

into those which are and are not soluble in liquid ammonia by washing them with liquid ammonia.

The method used in washing precipitates with liquid ammonia at its boiling point amounts to "washing by decantation" and is carried out in the following manner. After the reaction is over, stopcock 4 is set so that the ammonia stream flows thru 5. Tube 6 is raised so that its end is above the surface of the liquid ammonia in the reaction tube 2. When the precipitate has settled to the bottom of the reaction tube, 3a is opened and 6a is closed. Then with a brisk stream of ammonia gas passing out thru 5 under a pressure of ten to fifteen centimeters of mercury, 6b is opened and 6 gradually lowered until all of the liquid ammonia above the precipitate has been forced out thru 6. The liquid ammonia, so delivered thru 6, is caught in a Dewar flask of suitable size. When all the liquid ammonia is removed from above the precipitate, 6a is opened, 3a and 6b closed and fresh liquid ammonia is condensed on the precipitate in the same way that the first liquid ammonia was condensed in the reaction tube, 2. This alternate condensing and forcing off of liquid ammonia is continued until the precipitate is washed free of soluble material, after which the cooling bath of liquid ammonia, 7, is removed and all the remaining liquid ammonia allowed to evaporate out of the reaction tube, 2, the ammonia gas passing out thru the gage 5

to the absorption bottles, 14. This treatment isolates the insoluble reaction products in the reaction tube in an atmosphere of dry ammonia gas so that it may be further considered as a part, separate from the soluble products.

If the insoluble reaction product is unstable in air it is removed from the reaction tube for analysis in the following manner. Addition tube 3 is replaced by a sample tube such as illustrated in Figure II, #15 and #16, care being taken that a brisk stream of ammonia is passing thru the apparatus so that no air will enter the reaction tube during the change, and that the sample tube itself will be flushed out, leaving an atmosphere of ammonia in it. For this flushing out, the stopcocks of the sample tube are left open a short time. When the sample tube is in place and its stopcocks closed after flushing with ammonia, 6a and 2a are closed and the reaction tube is taken loose from the rest of the apparatus so that the precipitate may be shaken into the sample tube. The sample tube is then sealed off,using a hand torch, at some convenient point such as 18.

Since the tube to be sealed off had the reaction product shaken thru it, there was always some slight trace of the product on the inside surface of the glass. For this reason there was always a slight discoloration running thru the glass at the point where it was sealed off. This type of seal was all right for ordinary purposes but would leak

under the high vacuum to which it was found desirable to subject some of the reaction products in this work on nickel salts. In order to make such a seal vacuum tight a bead of clear glass from a glass rod was deposited on the discolored end of the sealed off tube immediately after it was sealed off so that the end of the tube was covered with a cap of clear glass.

When experiments were made in which the only object was to obtain the washed reaction product, the reaction tube was arranged as shown in Figure II,#19. This made the raising and lowering of the tube 6 much easier. When the reaction tube 2 was used as shown in Figure I, the hole in the stopper thru which 6 passed was bored large and sealed gas tight with DeKhotinsky cement. Care had to be taken that none of this cement was rubbed into the reaction tube by the raising and lowering of the tube 6. When it was desired to introduce a sample of nickel salt all at once into the reaction tube, the arrangement shown in Figure II, #17, was used.

In order to test this liquid ammonia apparatus for its efficiency in the collection of gases given off by reactions, weighed amounts of sodium were reacted with an excess of ammonium bromide and the hydrogen gas given off collected. The gas was analysed by the explosion method. The following table, #3, contains the results of the four test experiments. All gas volumes are reported calculated to standard conditions.

Table #3.

Gas Collection Test.

Na used grams.	H_2, cc. theoretical.	H_2, cc. found.	error, percent.
0.0774	37.7	37.5	0.53
0.0926	45.1	44.6	0.89
0.0948	46.2	46.6	0.85
0.1017	49.6	50.0	0.80

This data shows that the apparatus collects all hydrogen liberated within about 0.8%, when the volume of gas is around 50 cc. This much error is to be expected since the gas was analysed using a 100 cc. water jacketed burette. The smallest graduation of the burette was 0.2 cc. Twenty cubic centimeters is the largest sample that can be used in a 100 cc. gas burette, hence the total volume change on explosion is 30 cc. An error in reading of 0.2 cc. in 30 cc. is approximately an error of 0.7%. An error of 0.8% when the volume of gas is around 50 cc. is an error of 0.4 cc., which is equivalent to 0. 0005 grams of sodium and 0.0008 grams of potassium. Thus data obtained from this apparatus will be in error by an amount corresponding to that produced by these amounts of sodium and potassium.

B. VACUUM APPARATUS.

The vacuum apparatus, which was constructed entirely of pyrex glass, consisted of a Toepler pump and a mercury vapor pump supported by a Hi-vac oil pump as sources of vacuum, a McCleod gage, and an arrangement for attaching

samples on to the system for their evacuation. The mercury vapor pump was made at the Corning Glass Works after the design of C. A. Kraus (38). This mercury vapor pump, supported by the Hi-vac oil pump, would pump the system out to pressures less than 10^{-5} mm. of Hg, this being the lowest pressure readable on the McCleod gage. After being pumped out to 10^{-5} mm. of Hg, the pressure in the system would rise to about 10^{-3} mm. of Hg, after standing for fifteen hours without further pumping. Approximately four-fifths of the twenty one and a half ohms resistance were required in the circuit to maintain the mercury vapor pump at the right temperature. The volume of the Toepler pump (500 cc.) was approximately twice that of the system not including the mercury vapor pump, so that each stroke of the Toepler pump reduced the pressure to about one-third of its previous value. All connections in the vacuum system were glass to glass seals. These seals as well as the rest of the system were tested under vacuum for leaks by use of a high voltage induction coil. The vacuum apparatus is illustrated in Figure III.

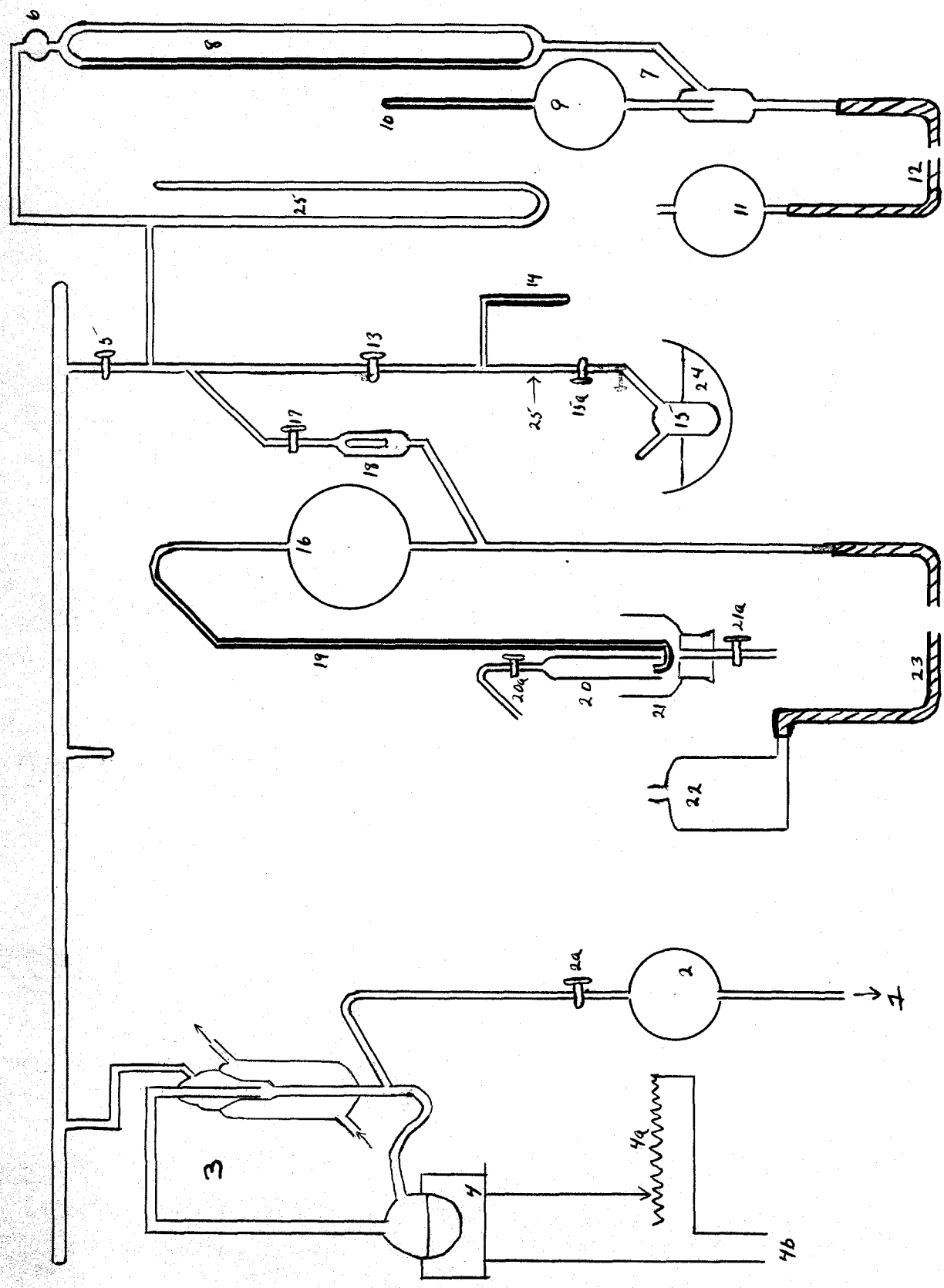


Figure III
VACUUM APPARATUS

LEGEND FOR FIGURE III.

1. To Cenco-Hi-Vac Pump.
2. Safety trap, 200 cc.
3. Mercury vapor pump, cooled with a water cooled condenser.
4. Electric heater, 110 volts, 250 watts.
4a. Slide wire resistance, 21.5 ohms, 2.5 amperes.
4b. Alternating current source, 110 volts.
6. Safety trap for McCleod gage.
7. McCleod gage.
8. Open side of NcCleod gage. One tube is of 6 mm. bore and the other is a 1 mm. capillary tube.
9. McCleod gage bulb of known volume.
10. Capillary tube of known bore. (approx. 1 mm.)
11. Leveling bulb for McCleod gage.
14. Capillary tube, used for making final seal under vacuum.
15. Container for sample that is being evacuated.
16. Toepler pump bulb, approx. 500 cc.
18. Toepler pump valve, consisting of a hollow glass plug which is so ground on the top end that when it is lifted by the rising mercury it prevents the mercury from going past the valve.
19. Capillary tubing.
20. Gas receiver for gases delivered by the Toepler pump.
21. Container for mercury coming from the Toepler pump.
22. Leveling bulb for the Toepler pump.

LEGEND FOR FIGURE III.

23 and 12. Pressure tubing, rubber.

24. Metal bath used for heating sample tube.

5, 13, 17, and (2, 15, 20, 21)a. Two-way diagonal stopcocks.

25. Manometer, mercury filled, 6 mm. tubing.

The vacuum system was used in the following way. Samples, contained in sample tube 15, to be evacuated were sealed on at point 25. This seal was made by blowing thru the capillary tube 14, a calcium chloride tube being used to exclude moisture from the system. After this seal 25 was made the capillary tube 14 was sealed by heating its end until it sealed itself under vacuum. After this capillary was sealed, the gas in the system between stopcock 13 and 15a was pumped out by the mercury vapor pump until the whole system above the stopcock 15a was down to a pressure of 10^{-5} mm. of Hg or less. so that the only free gas in the whole system was that in the sample tube 15. When the gases that were given off by a sample under vacuum were to be collected, stopcock 5 was closed and the sample evacuated with the Toepler pump. If these gases were not wanted, the sample was evacuated by means of the mercury vapor pump.

III.

MATERIALS USED.

As implied by the title of this thesis, the materials necessary for use were liquid ammonia, alkali matals and nickel compounds. The liquid ammonia used was obtained from the Mathieson Alkali Works in cylinders that contained one hundred pounds of anhydrous liquid ammonia. The alkali metals used were Kahlbaum products. All of the nickel compounds used were prepared in the laboratory from appropriate reagents. Since there are numerous nickel compounds which might have been used it was necessary to decide with which one or ones to start.

The use of anhydrous and anammoniated salts in liquid ammonia work offers several disadvantages. First, it is hard to prepare pure anhydrous and anammoniated samples of salts that form hydrates and ammoniates. Next, it is difficult to weigh and handle such salts on account of their picking up moisture. Also when brought into contact with ammonia gas or liquid ammonia the salts at once form ammoniates, with consequent caking-up and sticking of the salts onto parts of apparatus where they are wanted least. In order to avoid these mentioned difficulties it was decided that since practically all nickel salts form hydrates and ammoniates, it would be best to prepare the ammoniates in the first place and weigh them as such. This was found to be of particular advantage in the case of nickel salts because formation of

ammoniates offers the most simple and efficient way of eliminating cobalt impurities from the desired nickel compounds and also because the ammoniates of nickel salts are stable. Since no extensive information about the solubility of nickel compounds in liquid ammonia was available it was necessary to make several salts and try them out.

The known compounds, hexammine nickel chloride, bromide, iodide, nitrate and tetrammine nickel thiocyanate, ($NiCl_2 \cdot 6NH_3$, $NiBr_2 \cdot 6NH_3$, $NiI_2 \cdot 6NH_3$, $Ni(NO_3)_2 6NH_3$, and $Ni(SCN)_2 \cdot 4NH_3$), were prepared and it was found that only the nitrate (18) and the thiocyanate (34) were appreciably soluble in liquid ammonia. Next the compounds, hexammine nickel acetate and triammine nickel cyanide ($Ni(C_2H_3O_2)_2 \cdot 6NH_3$, and $Ni(CN)_2 \cdot 3NH_3$), were prepared and found to be practically insoluble in liquid ammonia. A search of the literature has not revealed any mention of the existance of these ammines of nickel acetate and nickel cyanide, so it is believed that this thesis contains the first knolwedge of these two compounds.

All of these prepared compounds as well as other reagents upon which quantitative results depended in this work were analysed to ascertain their purity. So that there will be no question as to the purity of material used or the reliability of analytical methods, the methods of preparation used, the methods of analysis and the analytical results found in dealing with reagents will now be given in the order named.

A. METHODS OF PREPARATION.

1. Liquid Ammonia.

In order to make the commercial liquid ammonia completely anhydrous for reaction purposes it was distilled into small steel tanks which hold 4.5 pounds of liquid ammonia. A quantity of metallic sodium, sufficient to be in excess of the amount needed to react with the water in the liquid ammonia, was placed in the small tanks before filling them with liquid ammonia. The excess sodium was catalized to amide and hydrogen by the iron tank. Opening the tank's needle valve for a short time let the hydrogen out along with the escaping ammonia gas. Before being used for reaction purposes, each tank was tested for dryness by distilling some ammonia into the liquid ammonia apparatus as described on page 20, and then observing whether or not any hydrogen was given off when a piece of sodium was dropped into it.

2. Sodium and Potassium.

Sodium and potassium, stored under petroleum ether, were used in the following manner. A ten centimeter crystallizing dish was poured two-thirds full of petroleum ether and a large piece of sodium or a ball of potassium placed in the dish, a pair of nickel tweezers being used to handle the alkali metal. With a razor blade, a suitable piece of the alkali metal was cut from the large piece, taking care to pare off all of the oxide film and to leave only

bright pure metal. This piece of metal was transfered to a weighing bottle quickly enough so that the petroleum ether did not evaporate off the metal. The petroleum ether was blown off the metal and out of the weighing bottle by a stream of dry nitrogen. When the petroleum ether was completly removed the weighing bottle was stoppered and weighed. After weighing, the alkali metal was transfered to the liquid ammonia apparatus. When handled in this way the bright surface of the alkali metal became only slightly tarnished. The experiments described on page 25 and the analysis of the metal, page 39 , handled in the same way show the metal to be pure and that no appreciable film of oxide was formed during the handling of the metal.

3. Known Nickel Ammine Salts.

Hexammine nickel chloride, bromide, iodide, and nitrate were made by precipitating the ammine from a solution of its nickel salt by adding strong ammonium hydroxide and cooling in an ice bath. The procedure used was that given by Biltz and Biltz (39). Tetrammine nickel thiocyanate was prepared by mixing equivalent quantities of solutions of nickel sulfate and barium thiocyanate, filtering off the barium sulfate, adding strong ammonium hydroxide, and crystallizing (34) out the tetrammine nickel thiocyanate. The above nickel ammine salts were filtered from their solutions by suction, washed with alcohol, then with ether and air drawn thru for a short time to remove the ether. They were then stored in a

vacuum desiccator, the drying agent of which was a mixture of calcium oxide and ammonium chloride, This gave an atmosphere of dry ammonia gas.

4. Hexammine Nickel Acetate.

Hexammine nickel acetate was prepared by washing nickel acetate three times with anhydrous liquid ammonia in the same manner as described on page 22 for the washing of precipitates. The liquid ammonia caused the bright green nickel acetate to turn to a light violet color which is the color of the hexammine of nickel acetate. After being washed with liquid ammonia, the hexammine nickel acetate, while wet with liquid ammonia, was placed in a vacuum dessicator over a mixture of calcium oxide and ammonium chloride. The excess ammonia was removed from the desiccator by evacuation with a water pump. Hexammine nickel acetate is stable in an atmosphere of ammonia or dry air but is very unstable in ordinary (moist) air, being quickly turned to a green sticky mass smelling strongly of ammonia. The nickel acetate used was prepared by dissolving freshly precipitated nickel hydroxide in an excess of hot glacial acetic acid. The excess of acetic acid was removed by evaporating the solution to dryness. This product was recrystallized from water three times and used as described.

5. Triammine Nickel Cyanide.

Triammine nickel cyanide was prepared from Kahlbaum's pure dry nickel cyanide in exactly the same way that

hexammine nickel acetate was prepared from nickel acetate. Triammine nickel cyanide is light violet in color and is stable.

B. METHODS OF ANALYSIS AND COMPOSITION OF REAGENTS.

Standard methods of gravimetric and volumetric analysis were used but sometimes with modifications to suit the particular case at hand. Gooch crucibles were used in all gravimetric determinations and when the filtrate from one determination was to be used for the determination of another constituent, a bell-jar, with a beaker for receiving the filtrate, was used instead of the usual suction flask. The strength of all volumetric solutions was based upon exactly one-tenth molar hydrochloric acid which was itself prepared from constant boiling hydrochloric acid and checked against sodium carbonate using methyl orange as indicator. The constant boiling hydrochloric acid was prepared according to Foulk and Hollingsworth (40). For analysis, as for use in liquid ammonia reactions, ammoniated nickel salts were stored in weighing bottles placed in a vacuum desiccator over a mixture of calcium oxide and ammonium chloride. The Weight of a sample of nickel salt was determined by the difference in weight of the weighing bottle before and after removing the sample. In general the following standard methods of analysis were used for each constituent mentioned. Any variation of the method will be mentioned under the compound Where it wasnnecessary to employ a change. 1. Nickel was

determined by precipitation as nickel dimethyl glyoxime according to the directions given by Fahles (41). Since no iron, aluminium, etc., were present in any of the solutions to be analysed, the addition of citric acid was omitted. The precipitate is 20.32% nickel. 2. Ammonia was determined in two ways: (a) By dissolving the nickel ammine salts in an excess of standard hydrochloric acid and then titrating the the excess acid with standard sodium hydroxide using methyl red indicator. (b) By dissolving the ammonia containing material in an excess of acid, adding strong sodium hydroxide and distilling the ammonia out into standard hydrochloric acid as in a regular Kjeldahl determination of ammonia. The first method may be regarded as a direct titration of the ammonia in the ammine salts and the second as a Kjeldahl determination of ammonia. 3. Halogens, cyanide and thiocyanate were determined gravimetrically as silver salts and volumetrically by the Mohr method(chloride only) and by the Volhard method. In using the Volhard method the practice of filtering off the silver halide or cyanide precipitate was employed until it was found that the use of nitrobenzene as a coagulating agent, as suggested by Caldwell and Moyer (42), gave equally good results. 4. Potassium was determined by precipitation as $K_2NaCo(NO_2)_6 \cdot H_2O$ as described by Hamid (43). The precipitate is 17.21% potassium. An excess of ten times the calculated amount of sodium cobalti nitrite reagent was used. 5. Sodium was weighed assodium chloride.

Sodium chloride is 39.34% sodium.

1. Analysis of Metallic Sodium.

The sodium metal was weighed out as described on page 33 and then placed in a 150 cc. beaker which contained enough anhydrous diethyl ether to cover the metal. 95% ethyl alcohol was added, little by little, to the ether until all of the alkali metal had reacted. Water was added to decompose the alcholate and then an excess of concentrated hydrochloric acid was added. After the ether had evaporated at room temperature, the solution of sodium chloride was evaporated to dryness on the water bath. Then the beaker was ignited with a bunsen burner to remove all excess acid and moisture. After cooling in a desiccator the beaker was weighed and was washed free of its sodium chloride content. After which the empty beaker was dried in the oven at 110 C., cooled in a desiccator and weighed. The difference in the two weighings was considered as being due to sodium chloride. Four different pieces of sodium gave the following results, given in Table #4, which not only show the metal to be of high purity, but also that no appreciable film of oxide was formed in weighing the metal.

Table #4.

Metallic Sodium Analysis.

Sodium, grams used.	Sodium chloride, grams found.	Sodium, percent.
0.2062	0.5261	100.3
0.2237	0.5719	100.5
0.1701	0.4350	100.6
0.2815	0.7207	100.7

2. Analysis of Metallic Potassium.

Metallic potassium was treated in the same way for analysis as was metallic sodium except that instead of weighing as potassium chloride the potassium chloride was dissolved in a small amount of water and sodium cobalti nitrite reagent added. Four different potassium balls gave the following results, Table #5, which show the metal to be pure potassium.

Table #5.

Metallic Potassium Analysis.

Potassium, grams used.	$K_2NaCo(NO_2)_6 \cdot H_2O$ grams found.	Potassium, percent.
0.1799	1.0475	99.78
0.1997	1.1645	100.4
0.1850	1.0793	100.4
0.1618	0.9483	100.8

3. Analysis of Known Nickel Ammine Salts.

Two samples of each nickel ammine salt were used, one for the negative ion determination and the other for both ammonia and nickel determination. The ammonia was determined by direct titration and then the nickel precipitated out of

this solution. Table #6 contains the analyses of the known nickel ammine salts.

Table #6.

Known Nickel Ammine Salt Analysis.

	Percent, theoretical.	Percent, found.	Method.
	Hexammine Nickel Chloride	(231.8)	
Ni	25.31	25.28	
NH_3	44.10	43.95	direct
Cl	30.59	30.59	Mohr
	Hexammine Nickel Bromide	(320.7)	
Ni	18.29	18.35	
NH_3	31.89	31.74	direct
Br	49.87	49.75	grav. AgBr
	Hexammine Nickel Iodide	(414.7)	
Ni	14.16	14.11	
NH_3	24.69	24.38	direct
I	61.19	61.15	Volhard
	Hexammine Nickel Nitrate	(284.9)	
Ni	20.60	20.70	
NH_3	35.68	35.77	direct
		35.93	Kjeldahl
	Tetrammine Nickel Thiocyanate	(243.0)	
Ni	24.14	23.99	
NH_3	28.09	27.78	direct
SCN	47.77	47.73	Volhard

From the above results it is seen that the nickel salts were in such a high state of purity that they could by weighed out as such and used in reactions in the capacity of a "primary standard".

4. Analysis of Hexammine Nickel Acetate, a New Compound.

Hexammine nickel acetate was analysed for only nickel and ammonia. As with the rest of the nickel salts the weight of the sample was determined by the difference in weight of the weighing bottle before and after removal of the sample, but in this case the sample was transfered, in a desiccator, to a second weighing bottle. This second weighing bottle was then opened under the surface of a solution containing dilute sulfuric acid in excess of that needed to react with the ammonia in the nickel salt. This procedure was employed because the hexammine loses ammonia when exposed to the air and because the presence of the acetate ion does not allow the direct titration of the ammonia present to be carried out with any accuracy. The end point could only be guessed in a direct titration of the ammonia as the color change of methyl red was gradual. Nickel hydroxide precipitated out before the basic end point of phenolphthalein occurred. Table #7 summarizes the analyses of this compound.

Table #7.

Hexammine Nickel Acetate Analysis.
$Ni(C_2H_3O_2)_2 \cdot 6NH_3$ (278.9)

Nickel, percent. (21.04)	Ammonia, percent. (36.65)	Method. (calculated)
21.38	35.95	direct
21.15	35.14	direct
21.20	36.42	Kjeldahl
21.17	36.38	Kjeldahl

These analyses show, without question, that the violet compound formed when nickel acetate is treated with liquid ammonia is hexammine nickel acetate. Taft and Barham(51) used nickel acetate in liquid ammonia but made no mention of the formation of ammine. A search of the literature has not revealed any other mention of the use of nickel acetate in liquid ammonia or of the formation of ammines between nickel acetate and ammonia, so that it is believed that this thesis contains the first knowledge of the existance, isolation and analysis of the compound, hexammine nickel acetate.

5. Analysis of Triammine Nickel Cyanide, a New Compound.

This compound could not be directly titrated for its ammonia content because it would not give up all of its ammonia to dilute acids (nickel cyanide is insoluble in water). Kjeldahl analysis always gave results that were one to three percent high due to hydrolysis of the cyanide present. No further attempt was made to get an accurate analysis of the ammonia content of this compound.

For nickel and cyanide analysis use was made of the fact that ammonicial silver nitrate solutions decompose nickel cyanides. Small amounts of the nickel triammine cyanide dissolve fairly rapidly in ammonicial silver nitrate with stirring. One-tenth gram or less of the compound was stirred into 100 cc. of one-tenth molar silver nitrate solution which contained 10 cc. of concentrated ammonium hydroxide. When the sample had dissolved the solution was

at once made acid with nitric acid. The precipitated silver cyanide was allowed to coagulate in the cold solution and then filtered off, washed with cold water and weighed. Nickel was determined out of the filtrate from the silver cyanide precipitation. As an alternate method nickel was determined in separate samples by decomposing them with hot concentrated sulfuric acid and then determining the nickel out of this solution. Table #8 contains the results of analyses made on this compound.

Table #8.

Triammine Nickel Cyanide Analysis.
$Ni(CN)_2 \cdot 3NH_3$ (161.8)

Nickel, percent. (36.27)	Cyanide, percent. (32.16)	Ammonia, percent. (31.57)	Method. (Calculated)
36.37	32.25	32.95	Kjeldahl
36.30	32.37		
36.45	32.33		

These analyses demonstrate that the stable violet compound formed when nickel cyanide is treated with liquid ammonia is triammine nickel cyanide. Hovey (52) used nickel cyanide in liquid ammonia but made no mention of its forming any ammine compounds. A search of the literature has revealed no mention of this particular ammine of nickel cyanide so it is believed that this thesis contains the first knowledge of of the existance, isolation and analysis of the compound, triammine nickel cyanide.

IV.

REACTION OF SIMPLE NICKEL SALTS WITH SODIUM AND POTASSIUM IN LIQUID AMMONIA.

A. HEXAMMINE NICKEL BROMIDE WITH SODIUM.

Hexammine nickel bromide was the first compound to be prepared for use in liquid ammonia, and although it was found to be practically insoluble, it was tried out with sodium in liquid ammonia. Since it was practically insoluble it was ground up so finely that with a little stirring it would remain suspended in liquid ammonia so that all of the salt present might have a chance to react with the sodium. Since, when such a suspension was tried out with sodium, it gave a very vigorous reaction, further experiments and observations were made to determine the nature of the reaction.

The vigorous reaction that occurs when sodium is added to hexammine nickel bromide or the hexammine nickel bromide added to sodium in liquid ammonia is denoted by the immediate formation of a black precipitate and by the giving off of a gas. If enough sodium is present the solution turns to the blue color that is characteristic of solutions of sodium in liquid ammonia, but this blue color disappears in a short time, its fading out being accompanied by the giving off of gas. The evolution of gas stops at the same time that the blue color disappears. Some gas is given off whether the alkali metal is present in sufficient amount to give a blue solution or not. If after the blue color disappears, more

sodium is added the solution turns blue and gives off gas until the blue color again disappears. All further additions of sodium produce the same result and apparently any amount of sodium can be added and used up in this fashion by the reaction. Since the reaction that occurs is evidenced by the formation of a black precipitate and the giving off of a gas, the identification of these two reaction products was taken up in order to get a clue to what was taking place when the reaction occurred.

As a first guess it was thought that the black precipitate formed must be metallic nickel and that the gas given off must be hydrogen produced by the catalysis of sodium to sodium amide and hydrogen. This guess is a logical one in the light of the facts that almost any amount of sodium may be used by the reaction and that finely divided metals are good catalysts for the conversion of alkali metals to amides and hydrogen in liquid ammonia. When the gas given off by the reaction was collected as described on page 21 and analysed by the explosion method it was found to be practically pure hydrogen. The following table, #9, contains typical examples of analyses of gas given off by reactions and shows the gas to be practically pure hydrogen.

Table #9.

Analysis of Gaseous Reaction Products.

Gas collected, cc.	Hydrogen found, cc.	Hydrogen, percent.
68.2	66.5	97.6
112.9	111.8	99.1
138.7	137.2	98.9
25.6	25.3	98.9

(All gas volumes reported in this thesis are given calculated to standard conditions.)

In order to analyse the black precipitate formed by the reaction it was washed with liquid ammonia several times to remove all soluble material from it. After being washed and dried the black precipitate, now appearing as a black powder, was found to occasionally have mixed with it a small amount of red material. The presence or absence of the red material seemed to depend upon the way the reaction was carried out. Thus if a small enough amount of sodium was added to a suspension of the nickel salt in liquid ammonia so that the solution did not turn blue, the red material was always found to be present and also some of the nickel salt was left unreacted. If this was repeated with the exception that after the first addition of alkali metal had reacted, enough more sodium was added to turn the solution blue and this allowed to react, the washed black precipitate when dried was seen to be composed of the black precipitate and the red substance (no unreacted nickel salt present). If a small amount of the

hexammine nickel bromide was added in one addition to an excess of alkali metal in order that the nickel salt might react all at one time there were no red particles to be observed mixed with the black precipitate. If this last were repeated with the exception that after the sodium had all reacted, a further quantity of nickel salt was added, the solution took on a red color and then formed a red precipitate which remained with the black precipitate in spite of washing with liquid ammonia. Thus the presence of the red material along with the black precipitate was due to a reaction between hexammine nickelbromide and a reaction product produced by the formation of the black precipitate and hydrogen.

Since nickelamide is bright red in color (34), this red substance was thought to be nickel amide produced by the reaction of hexammine nickel bromide and sodium amide as shown by the following equation.

$$NiBr_2 \cdot 6NH_3 + 2NaNH_2 \longrightarrow Ni(NH_2)_2 + 2NaBr + 6NH_3$$

To see if this was the case hexammine nickel bromide, chloride, iodide and acetate were reacted with sodium and potassium amides in liquid ammonia, the resulting red precipitates washed, dried and analysed. The analyses only approximated the formula for nickel amides as no product was obtained which was free from unreacted nickel salt. Bohardt (34) experienced the same difficulty in trying to prepare nickel amide from hexammine nickel iodide in liquid ammonia at room temperature.

The above observations are in line with the view that the red material, which sometimes occurs in the reaction between hexammine nickel bromide and sodium, is nickel amide formed by the interaction of sodium amide and hexammine nickel bromide.

In order to avoid the formation of nickelamides during the reaction of hexammine nickel bromide and sodium, small samples of the nickel salt were used and the addition of them to the sodium or the addition of the sodium to them in liquid ammonia was carried out so that the hexammine nickel bromide would all react completely at one time and offer no chance for nickel amide to form. After having in this way regulated the reaction procedure so that the formation of this insoluble red material was eliminated and the black precipitate was the only insoluble material produced by the reaction, the black precipitate was analysed and found to be 90-95% metallic nickel. This black precipitate is pyrophoric in air, reacts vigorously with dilute acids and has other properties along with its pyrophoric nature which made it desirable to give it special attention in an attempt to find out why it was pyrophoric. Since a special study of the composition and pyrophoric property of this black, finely divided, pyrophoric precipitate was made, all that will be said of it here is that it was found to be mainly metallic nickel, the analyses supporting this statement being found on page 68.

After finding that, as suspected, the gas given off was hydrogen and that the black precipitate was metallic nickel, the next step taken was to investigate the relation between the amounts of hexammine nickel bromide and sodium used and the amount of hydrogen produced. According to the original assumption of the sodium reacting with the hexammine nickel bromide to produce metallic nickel and then the rest of the sodium present reacting with ammonia to form sodium amide liberate hydrogen, the relation between the amounts of sodium and hexammine nickel bromide used and the amounts of hydrogen produced should be represented by the following two equations.

$$NiBr_2 \cdot 6NH_3 + 2Na \longrightarrow Ni + 2NaBr + 6NH_3$$

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2}H_2$$

Since, by these equations, the evolved hydrogen is equivalent to the sodium converted to amide, the measurement of the hydrogen given off gives the quantity of sodium present in excess of that demanded for the formation of nickel in the first equation. Subtraction of this amount of sodium, which formed hydrogen, from the total amount of sodium used gives the amount used for the reduction of the hexammine nickel bromide to metallic nickel. This so calculated amount of sodium, when expressed as atomic weights of sodium, should give a number that is equal to twice the number of molecular weights of hexammine nickel bromide used, i.e. the ratio between the number of gram atoms of sodium and gram molecular

weights of hexammine nickel bromide should be 2/1, when a correction is made for the amount of hydrogen gas given off. This ratio may be termed the "ratio corrected for hydrogen" or simply the "corrected ratio (1)". From what has just been said it is seen that this "ratio corrected for hydrogen" being 2/1 may be used as a criteria to verify the equations proposed to represent the reaction, consequently weighed amounts of sodium and hexammine nickel bromide were reacted, the evolved hydrogen measured and the "corrected ratio (1)" calculated. This "corrected ratio (1)", as shown in Table #10, column IV, was found to be always greater than 2/1.

Table #10.

Corrected Reaction Ratio (1).

I $NiBr_2 \cdot 6NH_3$ grams.	II Sodium, grams.	III H_2, cc. found.	IV Corrected ratio (1).
0.8558	0.2129	33.8	2.33
0.5793	0.2000	50.2	2.33
0.9974	0.2494	36.5	2.37
0.9791	0.2598	41.2	2.33
0.7509	0.2039	37.6	2.35
0.9761	0.2915	61.6	2.38

The "corrected ratio (1)" being greater than 2/1 indicates that more sodium is being used than is required for the formation of metallic nickel. But since metallic nickel was formed and in so active (pyrophoric) a state and nickel is known to be a good absorbant for hydrogen, it was thought that possibly the high "corrected ratio (1)" might be due to some of the liberated hydrogen being held back by the

precipitated nickel for such a holding back of hydrogen would make it appear in the calculations as though more sodium were being used than required for the production of metallic nickel. In order to see if the nickel precipitate did have any hydrogen associated with it, it was washed with liquid ammonia, dried and then evacuated, while in the reaction tube, with the Toepler pump.

Some hydrogen was obtained from such nickel samples by pumping them at room temperature, but only in trifling amounts compared to that necessary to change the "corrected ratio" to a value of 2/1. Heating the samples while evacuating them caused excessively large amounts (30-40 cc.) of hydrogen and some incombustable gas, probably nitrogen, to be given off and also caused the inside of the pyrex reaction tube to become badly etched. This excessive liberation of hydrogen was thought to be due to sodium amide reacting (44) with the glass, it being impossible to remove much of the sodium amide from the black precipitate by washing because of the low solubility of sodium amide in liquid ammonia. In order to eliminate the presence of sodium amide from the nickel it was decided to add an excess of ammonium bromide to the reaction solution. This would convert the sodium amide to sodium bromide which is soluble and should be washed out of the nickel precipitate.

When ammonium bromide was added to the solution

containing the nickel precipitate and sodium amide it was found that a small amount of hydrogen was given off. The following table, #11, shows, in column VI, "corrected ratio (2)" obtained by including this amount of hydrogen in correcting the reaction ratio for hydrogen.

Table #11.

Corrected Reaction Ratio (2).

I $NiBr_2 \cdot 6NH_3$ grams.	II Sodium grams.	III H_2, cc. found.	IV Corrected ratio (1).	V H_2, cc. (by NH_4Br)	VI Corrected ratio (2).
0.4324	0.1512	39.3	2.27	2.0	2.14
1.0174	0.3098	71.4	2.26	3.8	2.15
1.8389	0.4563	80.3	2.21	5.2	2.13

Since this amount of hydrogen given by the addition of ammonium bromide (column V, Table #11) was never in any case enough to bring the "corrected ratio (2)" to a value of 2/1 or less, the idea that this hydrogen was due to chemical reaction between the ammonium bromide and the precipitated nickel was discarded in favor of the idea that the ammonium bromide merely loosened up some, but not all of the hydrogen that the nickel was holding back. Consequently in the experiments shown in the following table, #12, the ammonium bromide was added, the hydrogen evolved at this addition collected and combined with the first hydrogen given off and then the nickel precipitate was washed well with liquid ammonia, dried and pumped with the Toepler pump. The nickel precipitate was heated while being pumped.

Table #12.

Corrected Reaction Ratio (3)

I $NiBr_2 \cdot 6NH_3$ grams.	II Sodium, grams.	III H_2, cc. found.	IV Corrected ratio (2).	V H_2, cc. found.	VI Corrected ratio (3).
0.6943	0.1988	49.7	2.21	4.9	2.01
1.2641	0.4117	105.0	2.16	5.1	2.04
1.2513	0.2611	35.0	2.11	6.0	1.97
1.0340	0.2360	38.4	2.12	5.6	1.98

In Table #12, column III gives the hydrogen obtained by the addition of ammonium bromide plus that given off by the reaction at first, while in column IV there is the "corrected ratio (2)" calculated with this amount of hydrogen. Column V shows the amount of hydrogen obtained by the use of the Toepler pump and column VI shows the "corrected ratio (3)" calculated with this amount of hydrogen added to that given in column III.

It is seen from column VI, Table #12, that the total amount of hydrogen obtained is just enough to make the "corrected ratio (3)" 2/1, within the limits of experimental error. No experiment gave more than enough hydrogen than necessary to give the 2/1 ratio. The obtaining of hydrogen from the nickel precipitates by evacuation with the Toepler pump shows that nickel has hydrogen associated with it. So if the only action of the ammonium bromide was to make the nickel precipitate give up part of the hydrogen that was associated with it, the experiments prove that the original "corrected ratio (1)" was high due to the nickel holding

back part of the hydrogen that was associated with it, and that the reactions that occur may be represented by the following equations.

$$NiBr_2 \cdot 6NH_3 + 2Na \longrightarrow Ni + 2NaBr + 6NH_3$$

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2}H_2$$

The same reaction occurs in liquid ammonia when the sodium is added to the hexammine nickel bromide as when the hexammine nickel bromide is added to the sodium.

Since the ammonium bromide was added on account of the inability to wash out the insoluble sodium amide and since potassium amide is very soluble in liquid ammonia, it was decided to investigate the reaction between potassium and hexammine nickel bromide, for it should be possible to wash potassium amide completely out of a nickel precipitate without the use of ammonium bromide and then to recover all of the hydrogen that is associated with the nickel precipitate by evacuation with the Toepler pump.

B. HEXAMMINE NICKEL BROMIDE WITH POTASSIUM.

The addition of potassium to a suspension of hexammine nickel bromide in liquid ammonia or the addition of hexammine nickel bromide to a solution of potassium in liquid ammonia gave the same type of reaction as did sodium and hexammine nickel bromide. i.e. hydrogen gas was given off and a black precipitate of pyrophoric metallic nickel was formed.

Since the purpose of studying the reaction between potassium and hexammine nickel bromide was to avoid the use of ammonium bromide in obtaining the hydrogen that is associated with the nickel precipitate and to obtain this hydrogen by use of the Toepler pump, the experiments were carried out in the following way.

Known amounts (see table #13 for data) of hexammine nickel bromide (column I) andpotassium (column II) were reacted and the hydrogen (column III) given off by the reaction collected. From this amount of hydrogen a "corrected ratio (1)" was calculated. This "corrected ratio (1)" (found in column IV) was always found to be greater than 2/1 as was the case in the sodium reaction. The precipitate nickel was washed with liquid ammonia, dried, and evacuated while in the reaction tube by use of the Toepler pump. This amount of hydrogen given off by the nickel while heated under vacuum is shown in column V and in column VI is shown the "corrected ratio ($)" between potassium and hexammine nickel bromide calculated using this additional amount of hydrogen obtained with the Toepler pump, no ammonium bromide having been added.

Table #13.

Corrected Reaction Ratio (4).

I $NiBr_2.6NH_3$ grams.	II Potassium, grams.	III H_2, cc. found.	IV Corrected ratio (1).	V H_2, cc. found	VI Corrected ratio (4)
0.2999	0.1732	25.7	2.28	2.7	2.02
0.2439	0.1838	30.9	2.56	4.0	2.08
0.2777	0.2192	41.0	2.25	2.8	1.96
0.2224	0.1803	34.9	2.16 (2)	0.7	2.07 (3)

In these experiments the samples of nickel were evacuated while in the reaction tube and while being heated with a bunsen burner. Continueous evacuation while heating just below the softening point of pyrex did not in any case yield more than the necessary amount of hydrogen to bring the "corrected ratio (4)" to a value of 2/1. The results of these experiments on potassium were taken as proof that:

1. the precipitated nickel has hydrogen associated with it.
2. this hydrogen may be removed from the nickel by heat and vacuum.
3. this hydrogen is the cause of the "corrected ratio (1)" being high when it is calculated using the hydrogen collected during the reaction.
4. the reaction between potassium and hexammine nickel bromide in liquid ammonia is represented by the equation,

$$NiBr_2 \cdot 6NH_3 + 2K \longrightarrow Ni + 2KBr + 6NH_3$$

while the excess potassium is used up according to the equation,

$$K + NH_3 \longrightarrow KNH_2 + \tfrac{1}{2}H_2$$

After having established this reaction ratio without using ammonium bromide to obtain the missing hydrogen, the effect of ammonium bromide on the black precipitate produced in the potassium reaction was tried out and found to be the same as found in the case of the sodium reaction. i.e. the ammonium bromide caused the liberation of part, but

not all of the hydrogen held back by the nickel precipitate and the remaining hydrogen on the nickel would be obtained with the Toepler pump as was the case in the sodium reaction. This is illustrated by the experiment marked with an @ in Table #13. For this experiment, column III shows the hydrogen obtained by the reaction plus that liberated by the addition of ammonium bromide, column IV shows the "corrected ratio (2)" calculated from this amount of hydrogen, column V the amount of hydrogen obtained with the Toepler pump and column VI shows the "corrected ratio (3)" using this additional amount of hydrogen.

Having found that the practically insoluble hexammine nickel bromide would react quantitatively with alkali metals and having found what the reaction was, the reactions of sodium and potassium with all of the simple nickel salts on hand were carried out regardless of whether or not they were soluble in liquid ammonia. The results of these reactions will occupy the next few pages.

Before taking up these reactions, however, it should be pointed out that if, in carrying out the above reactions between sodium, potassium and hexammine nickel bromide or in carrying out any similar reactions, the right small amount of nickel amide had been formed or the right small amount of nickel salt had not reacted, the "corrected ratio (1)" which was calculated from the amount of hydrogen given off during

the reaction, would have been 2/1 in spite of hydrogen being held back by the precipitated nickel, because the formation of nickel amide or the failure of nickel salt to react has an effect on the so calculated "corrected ration(1)" that is opposite to that produced by hydrogen being held back. For this reason it was of capital importance that the presence of nickel amide with some precipitates of nickel was noticed and its formation eliminated before attempting to establish the quantitative reaction ratio between alkali metals and nickel salts, because other-wise the ratio might have accidently came out very near 2/1 and then the fact that the nickel precipitate had hydrogen associated with it would have gone unnoticed.

C. HEXAMMINE NICKEL IODIDE AND HEXAMMINE NICKEL ACETATE WITH POTASSIUM.

These two nickel salts reacted with potassium in exactly the same way that hexammine nickel bromide did, giving off hydrogen gas and forming a black precipitate of pyrophoric nickel that held back some of the liberated hydrogen. Table #14 shows the results of experiments on hexammine nickel iodide and acetate with potassium, The columns have the same meaning as in Table #13.

Table #14.

Corrected Reaction Ratio (4).

I $NiI_2 \cdot 6NH_3$ grams.	II Potassium, grams.	III H_2, cc. found.	IV Corrected ratio (1).	V H_2, cc. found.	VI Corrected ratio (4).
0.3495	0.1474	20.4	2.31	2.6	2.03
0.5289	0.2412	37.4	2.25	4.7	1.91
0.6284	0.2958	47.5	2.21	3.1	2.02
0.5617	0.2858	50.9	2.04 (2)	1.2	1.97 (3)
$Ni(C_2H_3O_2)_2 \cdot 6NH_3$					
0.1673	0.1892	36.3	2.65	4.1	2.09

From these experiments it was taken that hexammine nickel iodide and acetate react with potassium in accordance with the following equations.

$$NiI_2 \cdot 6NH_3 + 2K \longrightarrow Ni + 2KI + 6NH_3$$

$$Ni(C_2H_3O_2)_2 \cdot 6NH_3 + 2K \longrightarrow Ni + 2KC_2H_3O_2 + 6NH_3$$

$$K + NH_3 \longrightarrow KNH_2 + \tfrac{1}{2}H_2$$

Since acetic acid can be reduced to acetaldehyde, and ethyl alcohol one would not have been surprised if potassium had reacted with the acetate ion, but in the above experiments there is no evidence of any appreciable amount of potassium being used by the acetate group.

D. HEXAMMINE NICKEL CHLORIDE AND HEXAMMINE NICKEL IODIDE WITH SODIUM.

These two salts reacted with sodium in liquid ammonia in the same way that hexammine nickel bromide did, giving off hydrogen and forming a black precipitate of pyrophoric nickel, which had associated with it some of the liberated hydrogen.

Table #15 contains the results of experiments on hexammine nickel chloride and iodide with sodium. The columns have the same meaning as in Table #12.

Table #15.

Corrected Reaction Ratio (3).

I $NiCl_2 \cdot 6NH_3$ grams.	II Sodium, grams.	III H_2, cc. found.	IV Corrected ratio (2).	V H_2, cc. found.	VI Corrected ratio (3).
0.1697	0.1361	50.4	1.96	none	1.96
$NiI_2 \cdot 6NH_3$					
0.6251	0.2446	85.4	2.03	none	2.03

From these experiments it was taken that hexammine nickel chloride and iodide react with sodium in accordance with the following equations.

$$NiCl_2 \cdot 6NH_3 + 2Na \longrightarrow Ni + 2NaCl + 6NH_3$$

$$NiI_2 . \underline{6}NH_3 + 2Na \longrightarrow Ni + 2NaI + 6NH_3$$

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2}H_2$$

The black pyrophoric precipitates formed from these two nickel salts were relatively slow catalysts for the conversion of sodium to amide. In the experiment with hexammine nickel chloride it took twenty minutes and with hexammine nickel iodide twelve minutes, while in experiments with other nickel salts it usually took only one or two minutes to convert the excess sodium to amide. Also it is to be noted that the hydrogen which was liberated by the ammonium bromide was the total amount associated with the nickel as

none was obtained with the Toepler pump. Others (32) have obtained correct "corrected ratios" by the use of only ammonium bromide on slow metallic catalyst precipitated from salts other than nickel salts.

E. TRIAMMINE NICKEL CYANIDE WITH SODIUM AND POTASSIUM.

When sodium or potassium was added to a suspension of triammine nickel cyanide in liquid ammonia, the solution turned red for a brief instant before it became black with precipitated metallic nickel. Hydrogen gas was given off during the reaction. When triammine nickel cyanide was added to a solution of sodium or potassium in liquid ammonia, this red coloration was never visible, because the solution was intensly blue until the reaction was over. However, regardless of the order of addition the washed black precipitate of pyrophoric nickel was, upon careful inspection found to contain very small amounts of red material which when the precipitate was treated with water caused the water to form a cherry red solution.

Although this red material was formed along with the metallic nickel the "corrected ratio" when calculated using the hydrogen obtained from the pyrophoric nickel with the Toepler pump was found to be practically 2/1 as demanded for the formation of only metallic nickel. Doubtless the metallic nickel was formed in accordance with the equation,

$$Ni(CN)_2 \cdot 3NH_3 + 2K \text{ (or Na)} \rightarrow Ni + 3NH_3 + 2KCN \text{ (or NaCN)}$$

but the "corrected ratio" being found to be 2/1 must also include the formation of the red material along with the nickel. Later the compounds responsible for the formation of this red solution with water were investigated and found to be of importance in both the liquid ammonia and the aqueous solution chemistry of nickel.

F. TETRAMMINE NICKEL THIOCYANATE WITH SODIUM AND WITH POTASSIUM.

Nickel thiocyanate is very soluble in liquid ammonia, giving violet to purple colored solutions, the depth of color depending upon the concentration of the solutions. When, to such solutionsm sodium or potassium was added, a finely divided black precipitate formed which consisted mostly of metallic nickel. This precipitate was so very finely divided that it did not settle out of solution very well and when the liquid ammonia was evaporated off, the precipitate stuck very tenaciously to the sides of the reaction tube. When formed using excess alkali metal over the nickel salt present, the black precipitate was pyrophoric. No hydrogen was given off at all during the reaction until the solution turned blue and then the liberation of hydrogen was slow, this black precipitate being a poor catalyst compared to nickel precipitated from other salts. When the "corrected ratio" was calculated using the hydrogen obtained by use of the Toepler pump it was found to be

materially greater than 2/1. I.e. values of 2.3-2.5. Analogous to the findings of Holden (32) for the reaction between silver thiocyanate and sodium, potassium and calcium this high "corrected ratio" was due to some alkali metal being used in the breaking down of the thiocyanate group.

That the thiocyanate group was broken down into sulfide and cyanide was shown by evaporating the liquid ammonia washings of the black precipitate to dryness, dissolving them in water and obtaining positive qualitative tests for both sulfide and cyanide radicals in the water solution. Also when the washed black precipitate was treated with water it gave weak-coffee colored solutions, which behaved like colloidal nickel sulfide solutions. Dilute hydrochloric acid cleared up such solutions with the liberation of hydrogen sulfide. Also treatment of the dry black precipitate with dilute hydrochloric acid caused hydrogen sulfide to be given off.

From the above observations it was concluded that when liquid ammonia solutions of nickel thiocyanate are reacted with sodium or potassium, the formation of metallic nickel is accompanied by side reactions involving the break down of the thiocyanate group, nickel sulfide being formed along with alkali sulfide and cyanide. Nickel is no doubt formed according to the following equation.

$$Ni(SCN)_2 + 2K \text{ (or Na)} \longrightarrow Ni + 2KSCN \text{ (or NaSCN)}$$

G?. HEXAMMINE NICKEL NITRATE WITH SODIUM AND POTASSIUM.

Hexammine nickel nitrate is soluble enough in liquid ammonia to give pale violet colored solutions, but since the nitrate group is known to be attacked by alkali metals (32) in liquid ammonia, nothing more was done with this compound than to react it with sodium and potassium and to observe that hydrogen was given off and that a black precipitate of pyrophoric nickel was formed. The formation of metallic nickel is explained by the equation.

$$Ni(NO_3)_2 + 2K \text{ (or Na)} \longrightarrow Ni + 2KNO_3 \text{ (or } NaNO_3)$$

In this work blue liquid ammonia solutions of sodium and potassium have been reacted with the simple nickel salts, hexammine nickel chloride, bromide, iodide, acetate and nitrate, and triammine nickel cyanide and tetrammine thiocyanate. In each reaction there was produced a precipitate of black finely divided pyrophoric metallic nickel and hydrogen gas. The precipitated nickel was shown to have hydrogen associated with it and that one gram mol of nickel salt was reduced by the using up of two gram atoms of sodium or potassium. The hydrogen liberated during the reaction was explained by the excess alkali metal over that necessary to reduce the nickel salt being converted to amide and hydrogen under the catalytic influence of the precipitated nickel.

For the readers convenience the experimental data given in tables, #10, 11, 12, 13, 14, 15, has been collected into Table #18, wherein the columns have the same meaning as in the respective individual tables.

Table #16.

Collective Table of Reaction Ratios for Simple Nickel Salts.

# table	I grams Ni salt used.	II grams alk. metal used.	III H_2, cc, found.	IV Corrected ratio ( ).	V H_2, cc. found.	VI Corrected ratio ( ).
12.	$NiBr_2 \cdot 6NH_3$ with Sodium.					
	0.8558	0.2129	33.3	2.33		
	0.5793	0.2000	30.2	2.33		
	0.9974	0.2494	36.5	2.37		
	0.9701	0.2598	41.2	2.33		
	0.7509	0.2039	37.6	2.35		
	0.9761	0.2915	61.6	2.38		
13.	Use of Ammonium Bromide.					
	0.4324	0.1521	39.3	2.27	2.0	2.14
	1.0174	0.3098	71.4	2.26	3.8	2.15
	1.8389	0.4563	80.3	2.21	5.2	2.13
14.	Use of Ammonium Bromide and the Toepler Pump.					
	0.6943	0.1988	49.7	2.21	4.9	2.01
	1.2641	0.4117	105.0	2.16	5.1	2.04
	1.2513	0.2611	35.0	2.11	6.0	1.97
	1.0340	0.2367	38.4	2.12	5.6	1.98
15.	$NiBr_2 \cdot 6NH_3$ and Potassium.					
	0.2999	0.1732	25.7	2.28	2.7	2.02
	0.2439	0.1838	30.9	2.56	4.0	2.08
	0.2777	0.2192	41.0	2.25	2.8	1.96
	@0.2224	0.1803	34.9	2.16 (2)	0.7	2.07 (3)
16.	$NiI_2 \cdot 6NH_3$ and Potassium;					
	0.3495	0.1474	20.4	2.31	2.6	2.03
	0.5289	0.2412	37.4	2.25	4.7	1.91
	0.6284	0.2958	47.5	2.21	5.1	2.02
	@0.5617	0.2858	50.9	2.04 (2)	1.2	1.97 (3)
	$Ni(C_2H_3O_2)_2 \cdot 6NH_3$ and Potassium.					
	0.1673	0.1892	36.3	2.65	4.1	2.09
17.	$NiCl_2 \cdot 6NH_3$ and Sodium.					
	0.1659	0.1361	50.4	1.96	none	1.96
	$NiI_2 \cdot 6NH_3$ and Sodium.					
	0.6251	0.2446	85.4	2.03	none	2.03

V.

PYROPHORIC PROPERTY OF NICKEL.

Simple nickel salts such as the hexammine nickel halides react with alkali metals, sodium and potassium, in liquid ammonia solution to produce hydrogen gas and also a finely divided intensly black precipitate which settles to the bottom of the reaction tube readily, taking only one or two minutes to leave a clear colorless solution above. Evaporation of the liquid ammonia off the black, washed or unwashed, precipitate leaves an intensly black powder some of which now clings together in small clumps, If this dried precipitate is shaken out of the reaction tube into the air, the small powder like bits burst into flame. i.e. they become red hot and appear as sparks while falling thru the air. The larger clumps will fall to the floor or table top and in four or five seconds they also will become red hot and glow like a live coal. In other words the nickel is pyrophoric in the presence of air. That the black precipitate was pyrophoric in air because of the oxygen in the air, was shown by the fact that pure oxygen causes so violent a reaction that an explosion sometimes results. The black precipitate could be left in an atmosphere of dry nitrogen indefinitely and still remain pyrophoric. In general these preparations are unusually reactive. With dilute hydrochloric acid (M/10) a vigorous evolution of hydrogen is accompanied with emmision of light and violence if care is not taken in the introduction

of the hydrochloric acid into the tube containing the pyrophoric precipitate. Water alone caused the liberation of hydrogen. These pyrophoric preparations are the best catalyst known to this laboratory for the conversion of alkali and alkaline earth metals to amide and hydrogen, being far superior to platinium black, iron oxide or copper, silver, gold, zinc or cadmium precipitated from their salts in liquid ammonia solution. Since it was known that some products formed in liquid ammonia, as metallic compounds like Zn_4Na (45), are pyrophoric and highly reactive and that metallic hydrides as NiH_2 are highly reactive (46) the first step in determining the cause of the pyrophoricity of these black precipitates prepared from nickel salts in liquid ammonia was to determine their composition.

For analysis of these black precipitated reaction products, samples were prepared by the action of excess potassium on hexammine nickel iodide, because both potassium amide and potassium iodide are soluble in liquid ammonia. The precipitate was washed with liquid ammonia, sealed off in a sample tube like illustrated in Figure II,#16, and weighed with an atmosphere of nitrogen in the sample tube. Then the sample tube was slightly evacuated with a water pump and dilute hydroghloric acid (6M) carefully drawn into the tube. The sample always dissolved completly, after which the solution of the sample was washed out of the tube into

a 250 cc. volumetric flask, made up to volume and analysed. The results of analyses are given in Table #17. Sample number three was evacuated at the softening point of pyrex glass with the mercury vapor pump before analysis. The samples were all of approximately one-tenth gram size, because attempts to prepare larger quantities, five-tenths grams, of these precipitates from salts insoluble in liquid ammonia resulted in products that contained unreacted nickel salt and nickel amides. Samples prepared from the soluble salt, nickel thiocyanate, always contained sulfides, thought to be nickel sulfide.

Table #17.

Analysis of Insoluble Reaction Product.

#	Nickel, percent.	Ammonia, percent,	Potassium, percent.	Total, percent.
1	92.41	----	----	------
2	94.63	----	----	------
3	95.40	----	----	------
4	93.30	4.02	3.05	100.37
5	91.27	6.16	2.77	100.20

A consideration of these analyses bring out the following points concerning the black reaction products:

1. It is not, by any stretch of the imagination, a pure metallic compound of nickel and potassium with ammonia adsorbed on it.

2. If its pyrophoricity is due to a nickel-potassium compound the compound must be present only in very small amounts.

3. Since the ammonia is always present in amounts greater than required for the potassium to be present as potassium amide, the potassium may be there as potassium amide.

4. If its pyrophoricity is due to nickel hydride it is caused by only a trace on nickel hydride, since hydrogen is known to be associated (see section IV) with the precipitate in amounts which would effect the mass composition by less than 0.5%.

There are no doubt other "might and might not be" speculations which may be drawn from these analyses, but from the ones given it is clear that no answer as to why the black precipitates are pyrophoric can be furnished by the precipitate's chemical analysis alone. From these analyses, however, it may be said that the precipitate is mainly metallic nickel, which contains absorbed ammonia (see vacuum experiments on page 72) and that the precipitate contains potassium probably as potassium amide. Since the black precipitates are mainly metallic nickel, have hydrogen associated with them and are in a very fine state of division it was thought that the pyrophoricity might be due to the fine state of division (47) of the metallic nickel or to the associated hydrogen. For this reason it was decided to carry out experiments for the purpose of demonstrating first that the associated hydrogen either did or did not cause the pyrophoricity of the black precipitates.

In carrying out liquid ammonia reactions certain observations were made which seemed to have a bearing upon the question of whether hydrogen was responsible for the pyrophoric nature of the nickel precipitates. These observations were:

1. Treatment of highly active pyrophoric nickel with ammonium bromide in liquid ammonia caused some hydrogen but not all of the hydrogen associated with the nickel to be liberated. The nickel was still pyrophoric after treatment with ammonium bromide. The addition of ammonium bromide seemed to make the finely divided nickel agglomerate into larger particles and clumps.

2. Nickel prepared from a reaction where there was an excess of nickel thiocyanate present was not pyrophoric. No hydrogen is given off at all by such a reaction. (In the reactions with nickel compounds which were practically insoluble the hydrogen started coming off as soon as the black precipitate was formed and the precipitate was always pyrophoric regardless of whether the alkali metal was present in excess or not.)

3. Nickel prepared from excess alkali metal and nickel thiocyanate was pyrophoric. Hydrogen was given off in this kind of a reaction, but only after the nickel thiocyanate had all reacted and the solution had turned blue with the excess of alkali metal.

4. Nickel prepared from excess nickel thiocyanate, washed well with liquid ammonia and then treated with alkali metal, the alkali metal being allowed to be catalysed to amide and liberate hydrogen, was pyrophoric. (all samples prepared from nickel thiocyanate contained small amounts of sulfides, NiS) These experiments with nickel thiocyanate indicate that hydrogen is necessary for the nickel to be pyrophoric, and for this reason the vacuum system illustrated in Figure III was constructed for use with the nickel precipitates.

It was the original plan to remove all of the hydrogen from a nickel sample by means of the vacuum system, this removal being indicated by the pressure of the system being down to 10^{-5} mm. of Hg, the lowest pressure capable of being detected on the McCleod gage, and remaining near this pressure for the same length of time as would the vacuum system without the nickel sample, and then observing whether or not the nickel was still pyrophoric. This complete removal of hydrogen from pyrophoric nickel was never accomplished when the evacuation was carried out at a temperature below 360°C. One sample was heated under vacuum at $320 \pm 10^{\circ}$C. for 135 hrs. and at the end of this time the pressure would rise when the evacuation was discontinued with the temperature being kept at 320°C. When the temperature was lowered to room temperature and then the evacuation stopped the pressure did

not raise after standing eight hours at room temperature. It is to be noted that the presence of potassium, probably as potassium amide, on the pyrophoric nickel caused the origin of pressure raises at low pressures and high temperatures to be subject to question, for the pressure increase might be due to decomposition of the potassium amide. The several different and varied vacuum experiments carried out on different samples of nickel prepared in liquid ammonia, resulted in the making of the following list of observations which seem to have to do with the relation of hydrogen to the pyrophoric nature of the nickel preparations.

1. Definite but small amounts of hydrogen and considerable amounts of ammonia can be removed from pyrophoric nickel with a Toepler pump working at room temperature. Thus the nickel does have hydrogen associated with it.

2. Only a small fraction of the hydrogen that is on the nickel, along with considerable ammonia, can be obtained in a reasonable length of time, two weeks, by evacuation at room temperature. However the pressure in the system always raised again as soom as the evacuation was stopped.

3. After a sample of nickel had been pumped for a long time while atroom temperature, heating it caused a marked raise in pressure due to liberation of both hydrogen and ammonia.

4. Pyrophoric nickel may be heated for any length of time under vacuum and still remain pyrophoric so long as the

temperature is kept below 360°C. The sample that was heated for 135 hours at 320°C was pyrophoric when exposed to air.

5. Heating to or above 360°C under vacuum caused the intense black color of the pyrophoric nickel to change to grey after which change it was no longer pyrophoric. Replacing the vacuum with an atmosphere of hydrogen, heating to 360°C and letting the nickel cool in the atmosphere of hydrogen neither changes the grey color nor restores the pyrophoric nature of the sample.

6. Heating for one hour under vacuum at 360-80°C is ample time to destroy pyrophoricity.

7. After heating for one hour at 360°C to destroy pyrophoricity continued heating at the softening point of pyrex yields more hydrogen but in very small amounts compared to that yielded by the first one hour of heating and evacuation at 360°C.

8. Nickel (non-pyrophoric) prepared from excess nickel thiocyanate and potassium contains only a slight amount of hydrogen compared to the amount obtained by pyrophoric nickel prepared from nickel thiocyanate and an excess of potassium. Such unpyrophoric nickel, when heated under vacuum with a bunsen burner, readily fuses to a button of metallic nickel while a pyrophoric sample made with excess potassium will not fuse to a button before the pyrex container starts to collapse from heating. Pyrophoric nickel prepared from potassium and nickelhhalides also will not fuse to a button of metallic nickel before pyrex softens.

While the above observations are not of such character as to warrant any decisive decision to be made from them, it seems that they do point toward the conclusion that the pyrophoric property of the nickel preparations is due to the hydrogen that is associated with the nickel, because no sample of pyrophoric nickel was ever found that did not have hydrogen associated with it, heating under vacuum at or above 360°C removes most of the hydrogen from the nickel and simultaneously destroys its pyrophoric nature, and because the samples of non-pyrophoric nickel prepared from excess nickel thiocyanate were found to contain next to no hydrogen. (Sulfur compounds are known to "poison" nickel catalyst (48) which are used in hydrogenations so that they are rendered useless as hydrogenation catalyst because the "poisoning" effect is that of rendering the nickel unable to adsorb hydrogen.) The above observations are concordant with the findings of Tamman and Nikitin (49) in their work on pyrophoric nickel prepared by reducing nickel oxide, formate, etc., with hydrogen at high temperatures. They found that nickel prepared by reduction at temperatures above 360°C was not pyrophoric, while that prepared by reduction at temperatures below 360°C was pyrophoric, this difference being attributed to the different kinds of nickel, magnetic and non-magnetic, that exists below and above 360°C. (50).

The opinion is offered that so long as samples of pyrophoric nickel or any other metal can not be prepared

one hundred percent pure by liquid ammonia reactions because of adsorption of salts, amides, etc., high vacuum experiments designed to determine the presence or absence of hydrogen on the pyrophoric metals by pressure measurements, involving very low pressures (10^{-5} mm. of Hg) and high temperatures (300°C.) are not capable of furnishing a decisive answer to the question of whether or not nickel is pyrophoric on account of hydrogen. It seems that the proper approach to the cause of nickel's pyrophoricity lies in the use of experiments similar to those done with the soluble salt, nickel thiocyanate, with excess and insufficient amounts of potassium wherein it was found that the non-pyrophoric preparations had relative little hydrogen associated with them compared to the amounts associated with the pyrophoric preparations. The fact that the thiocyanate radical is attacked by the alkali metal and causes sulfides to be present on the nickel detracts from the results in this particular case. Since there has been found no other salts of nickel that are soluble and whose negative radical is not attacked by alkali metal in liquid ammonia, it was impossible to carry this idea further with nickel. Therefore, for further study, the cause of the pyrophoric nature of nickel should be extended to the pyrophoric nature of other metals which form salts soluble in liquid ammonia so that experiments like those with nickel thiocyanate, may be performed with these metals.

VI.

SUMMARY.

1. The advantages, in liquid ammonia work, of the use of ammoniated over anhydrated compounds has been pointed out and found to be of special advantage in the case of nickel compounds.

2. In a search for compounds soluble in liquid ammonia two new ammoniates were prepared, namely hexammine nickel acetate and triammine nickel cyanide.

3. Hexammine nickel chloride, bromide, iodide, acetate and triammine nickel cyanide are practically insoluble in liquid ammonia. Hexammine nickel nitrate is soluble enough to give a pale violet solution. Tetrammine nickel thiocyanate is very soluble in liquid ammonia, the color of its solutions ranging form pale violet for dilute solutions to purple for concentrated solutions.

4. Simple nickel salts as the ammoniates of nickel halides react with excess alkali metals, sodium and potassium, to produce finely divided pyrophoric nickel and then under the catalytic effect of the precipitated nickel the excess alkali metal is converted to amide and hydrogen. The precipitated nickel has some of the liberated hydrogen associated with it. This hydrogen can be removed with high vacuum treatment. Ammonium bromide in liquid ammonia causes liberation of some of the hydrogen associated with the precipitated nickel.

4a. For the precipitation of the nickel out of one gram mol of nickel compound, two gram atoms of alkali metal are used.

4b. In the reaction between nickel thiocyanate and alkali metals the thiocyanate group is partially broken down in addition to the main reaction in which metallic nickel is produced.

4c. In the reaction between triammine nickel cyanide and alkali metals there is a side reaction in addition to the production of metallic nickel.

5. Evidence has been produced which points toward the pyrophoricity of nickel precipitated in liquid ammonia being due to the hydrogen that is associated with the nickel.

VII.

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