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A STUDY OF THE REACTION BETWEEN
SODIUM AND SILVER IODIDE
AND
SODIUM AND MANGANESE IODIDE
IN LIQUID AMMONIA

A Dissertation submitted in partial
fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the Graduate School of the
University of Cincinnati

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by

Edward H. Smoker

B.S. Franklin and Marshall College 1926

M.A. University of Cincinnati 1927

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INTRODUCTION

Liquid ammonia is the liquid whose physical properties and solvent power bear the closest resemblance to those of water.[1] Accordingly much research has been carried out using liquid ammonia as a solvent and reacting medium. But in one respect, namely a much smaller tendency to react with dissolved substances, liquid ammonia is far superior to water as a solvent. Thus the alkali and alkaline earth metals dissolve in it without appreciable reaction to form solutions with most interesting properties. Investigation has shown that such solutions react vigorously with many salts, giving rise to a variety of products. In some cases compounds consisting solely of metals such as NaCd, $NaZn_4$, Na_3Tl_2, etc., have been postulated.[2] The properties and valence relationships in such compounds are abnormal to say the least, and as yet they have been obtained under no other conditions. In other cases, however, metallic compounds are not formed, but the less electropositive metal is precipitated from solution often in an activated form. Secondary reactions may then occur such as the formation of metallic amides through interaction with the solvent. A thorough study of such reactions occurring between soluble salts and dissolved alkali and alkaline earth metals has never been made. Here lies a field which offers unusual opportunities for the formation and study of new metallic compounds and the preparation of free metals

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in an activated form.

This research is a quantitative study of the reaction between silver iodide and sodium, and manganous iodide and sodium in liquid ammonia solution. A silver salt was studied because preliminary work by Kraus and Kurtz[2] indicated that it reacted in the simplest possible manner, according to the equation

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

If this be true, the reaction between silver iodide and sodium could be used as a check on the utility of any particular method for carrying out reactions of this sort, and as a means of discovering errors inherent in the apparatus or procedure. No previous work has been done using manganese salts. The possibility of obtaining metallic compounds between sodium and a metal as electropositive as manganese led to the choice of manganous iodide. While this possibility has not been realized, the reaction itself is of a most interesting nature.

This thesis may be conveniently divided into four main parts: I. The Physical and Chemical Properties of a Solution of Sodium in Liquid Ammonia; II. A Description of the Apparatus and Experimental Procedure; III. The Action of Sodium upon Silver Iodide; and IV. The Action of Sodium upon Manganous Iodide.

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I. THE PHYSICAL AND CHEMICAL PROPERTIES OF A SOLUTION OF SODIUM IN LIQUID AMMONIA.

A large portion of the research done using liquid ammonia as a solvent has been dependent on the fact that the alkali and alkaline earth metals dissolve in this medium without reaction. Sodium has been used to the greatest extent, and properties of a liquid ammonia solution of this metal have been studied by many investigators. The literature concerned with both the physical and chemical properties is summarized in order to give a compact survey of this important branch of liquid ammonia chemistry.

PHYSICAL PROPERTIES. Ammonia was liquified by Faraday[3] in 1823, but it was not until 1864 that Weyl[4] first used it as a solvent. He discovered, among other things, the solubility of sodium, but mistook the solution for a compound of sodium with ammonia $NaNH_3$, which he appropriately named "sodammonium." Seeley[5] condensed gaseous ammonia on sodium, and saw no discontinuity of physical properties as solid sodium disappeared and liquid appeared. He concluded that the resulting phase was a true solution of sodium in liquid ammonia.

The first quantitative measurements were made by Joannis,[6] who determined vapor tensions at various temperatures and boiling points of differently concentrated solutions. From his results he concluded that the compound sodammonium was formed. His work was quite extensive and his ideas were

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dominant for a decade, and are still accepted by some chemists. Ruff and Giesel[7] presented evidence to the effect that Joannis' sodammonium was merely free metal coated with a layer of saturated solution. Kraus[8] applied the phase rule to Joannis' data and proved conclusively the non-existence of sodammonium. His reasoning is briefly as follows. The system sodium and ammonia is a two component one, and therefore invariant when four phases and univariant when three phases are present. According to Joannis, when ammonia gas is removed from an unsaturated solution of sodium in liquid ammonia, the solution first becomes saturated, and further removal of ammonia results in the appearance of the solid compound sodammonium. When all the solution has disappeared and the removal of ammonia continued, this compound then breaks down to ammonia and free sodium. Joannis' data shows that the vapor pressure of the two systems vapor--saturated solution--solid compound and vapor--solid compound--free sodium are the same at several different temperatures. If this be true the four phases vapor, saturated solution, solid compound, and free sodium could co-exist at each of these temperatures. But such a system of four phases is invariant and can exist at only one temperature. Therefore, one phase, obviously sodammonium, must be non-existent.

Sodium dissolves in liquid ammonia to give an intensely blue-colored solution, which darkens and finally changes to a characteristic bronze as the concentration is in-

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creased. The blue color is discernible at a dilution of one part of sodium in about two million of ammonia. The solubility curve has been partially determined through the work of Ruff and Zedner,[9] Kraus,[10] and Kraus and Lucasse.[11] At temperatures between -78°C and -42°C and compositions between one and fourteen per cent. sodium, the solution separates into two liquid phases with an upper consolute temperature. It is odd that two liquid phases should co-exist, the composition of which is never over fourteen per cent. of one component. At the boiling temperature of ammonia, -33°C, about nineteen grams of sodium will dissolve in 100 c.c. of ammonia.

Electrical conductivity measurements have been made by Kraus[12] with interesting results. When a current is passed through a solution of sodium in liquid ammonia, no deposition occurs at either electrode. The only visible effect is a deepening of the blue color around the cathode. The conductivity of dilute solutions is of the same order of magnitude as strong electrolytes of the same formal concentration. With increased concentration of sodium, the conductivity becomes comparable to that of metals such as iron. Kraus explains these results by postulating that sodium ionizes in accordance with the equation

$$Na \rightleftharpoons Na^{+} + E^{-} \qquad (1)$$

where E^{-} is an electron. In dilute solution these electrons are surrounded by an envelope of ammonia, thereby giving them a size comparable to other ions. Consequently these solu-

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tions behave like those of ordinary electrolytes. In concentrated solution the equilibrium represented by the equation

$$E^- + n\ NH_3 \rightleftharpoons E(NH_3)_n^- \qquad (2)$$

furnishes a few electrons free from the solvent envelope. Due to their extremely small size, their speed will be exceedingly high. Consequently these solutions are excellent conductors, and conduction is metallic in nature since most of the current is carried by electrons without transfer of matter.

CHEMICAL PROPERTIES. The presence of free electrons in a solution of sodium in liquid ammonia should make this solution an excellent reducing agent. Many researches have been performed in which numerous types of substances, both organic and inorganic, have been reduced by this solution. In nearly all cases, the reactions were carried out by adding the given reactant, gas, liquid, or solid, until the blue color of the sodium had disappeared. The supernatant ammonia was then allowed to evaporate and necessary analyses made. A brief summary of the results of these researches as recorded in the literature will now be given. It should be stated, however, that some of the earlier results are questionable.

The first reaction considered is that between sodium and ammonia according to the equation

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2}H_2 \qquad (3)$$

Kraus[13] measured the pressure developed by the liberated hydrogen, and showed that the reaction was exceedingly slow. Va-

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rious substances, such as platinum, will increase the speed considerably.

Among organic compounds, halides have been used extensively, the sodium salt of the halogen being formed. Methyl chloride[14] gives methane and methylamine. Chloroform and iodoform[15] yield methane, ethylene, acetylene, and cyanides. Carbon tetrachloride[15] gives methane, nitrogen, and cyanides. Chlorbenzene[16] results in benzene, secondary and tertiary amines, with small quantities of aniline, isocyanides and cyanides. With excess sodium, the sodium salts of diphenylamine and aniline have been isolated. Clifford[17] has shown that the halogen of organic compounds always forms sodium halide, which may be estimated as the silver salt, and suggests this method for halogen determination in preference to the usual Carius fusion.

Saturated hydrocarbons[16] are usually inert, but the sodium salt of tri-alkyl and aryl substituted methanes have been formed. Acetylene[18] gives a precipitate of $C_2Na_2.C_2H_2$. Heat liberates this combined acetylene, and disodium acetylide results. Aniline[19] yields the mono- and di-sodium salts. Nitrobenzene[20] gives $C_6H_5NNaONa$ and $C_6H_5NNa_2$. Amides[21] form sodium salts. Esters[21] of the general formula RCOOR' give RCONHNa and R'ONa. Alcohols[22] including glycol, glycerol, mannitol, erythritol, borneol, and menthol give mono-sodium salts. Phenols and thio-phenols[22] result in corresponding ethers, while naphthols[22] yield tetra-hydronaphthols.

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The action of only a few inorganic compounds of non-metallic elements has been studied. Carbon monoxide[23] gives $Na(CO)_2$, while carbon dioxide[24] yields sodium carbamate. Nitrous oxide[25] reacts with both sodium and ammonia, precipitating sodium azide NaN_3. Nitrogen dioxide[25] forms NaNO. Phosphine[26] yields PH_2Na and PNa_3, depending on the relative quantities of reactants.

Since most elements are insoluble in liquid ammonia, but few reactions between them and sodium are recorded in the literature. Among the non-metals, oxygen[27] forms $Na_2O.NH_3$. Nitrogen[25] is non-reactive, while phosphorus[28] yields Na_3P and $Na_3P_2H_3$. Sulphur, selenium, and tellurium[29] form their normal salts, but when in excess give respectively Na_2S_5, Na_2Se_4, and Na_2Te_3.

Several metallic compounds may be formed by direct union. Lead gives a series NaPb,[30] $NaPb_4$,[31] and Na_4Pb_9.[32] The last seems more stable and its constitution has been verified by electrolysis during which lead is deposited on the anode. According to Joannis, mercury forms $NaHg_8$.[31] Bismuth,[30] arsenic,[33] and antimony[30] yield normal salts, Na_3Bi, Na_3As, and Na_3Sb. When in excess, antimony[34] gives a series of compounds.

When a sodium solution is used to reduce a salt, a variety of products may be obtained--pure metal, metallic compounds or amides. Kraus and Kurtz[2] have discussed the theory of the possible reactions, and also give preliminary

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data on specific cases. Using iodides or cyanides of the metals tested, they have recorded the formation of NaHg, $NaHg_2$, NaCd, $NaZn_4$, Na_4Sn, Na_4Pb, Na_3Tl_2 and Ag. These results were deduced from the quantities of salt necessary to discharge the blue color due to a given weight of sodium, and not by analysis of the precipitates formed.

Reactions of this latter type have been studied more completely in the ammonia laboratory of the University of Cincinnati. Rose[35] has established the constitution of $NaZn_4$ by analysis and studied its reactivity toward air, moisture, and oxygen. A study of the reaction of cuprous iodide is almost finished at this time. As previously mentioned, this thesis will describe fully the reaction between silver iodide and sodium, and manganous iodide and sodium.

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II. APPARATUS AND EXPERIMENTAL PROCEDURE

Liquid ammonia boils at -33° C at atmospheric pressure, while at room temperature it exerts a vapor pressure of about eight atmospheres. These two sets of conditions form the basis for two distinct methods of carrying out reactions. In one, the apparatus is designed to withstand high pressures, while in the other low temperatures must be maintained. In these experiments the latter procedure is used, and the apparatus made to meet the requirements is shown in Figure I.

APPARATUS. The most important part is the reaction tube A, in which all reactions have been carried out. At the top it is fitted with a two-hole rubber stopper C, through which pass a long and a short piece of glass tubing. Both of these are connected by rubber tubing to the tube D, which leads to a source of anhydrous ammonia (not illustrated). The longer tube is also fitted with an outlet E. Any substance contained in the weighing tube F, fitting tightly into a one-hole rubber stopper, may be introduced into the reaction chamber through the side arm G. Gases may leave the reaction tube through the side arm H, and are either caught in the eudiometer I for subsequent analysis, or allowed to escape through the pressure gauge K to a collecting bottle partially filled with water (not shown in the diagram). The safety bottle S is partially filled with mercury to prevent the entrance of any moisture into the reaction tube. The leveling pear R is

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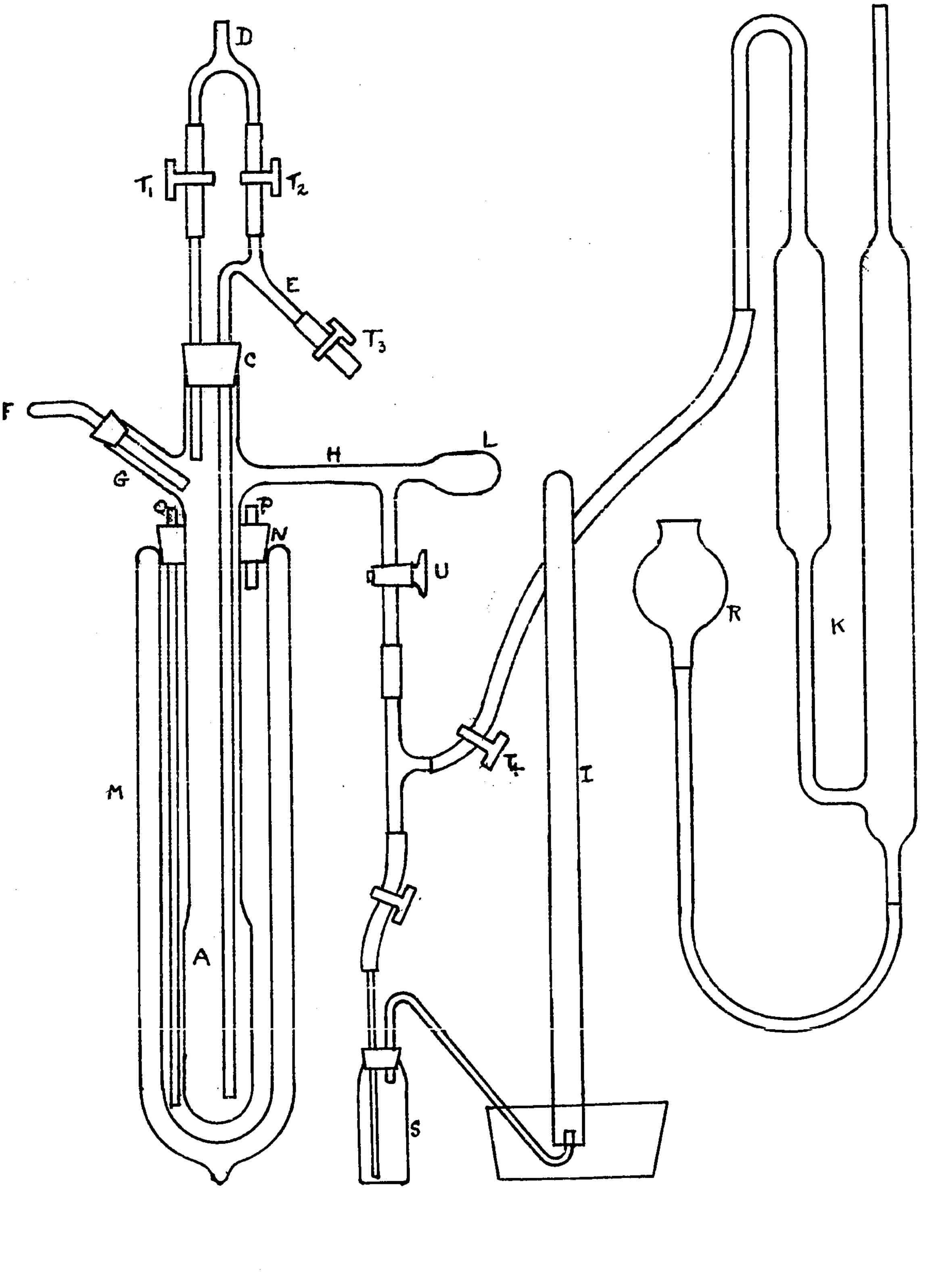

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used to maintain any desired mercury level in the gauge K. The large Dewar tube M is fitted with the rubber stopper N, through which pass the reaction tube A, a long tube O connected to a supply of dry air, and a short tube P through which gases escape to the collecting bottle. Screw clamps T and the stopcock U are used to control gas flow through the apparatus.

PROCEDURE. In order to illustrate the use of the apparatus, a typical run using silver iodide and sodium will be described. The clean reaction tube is rinsed with alcohol and ether and dried by a stream of air previously passed over phosphorus pentoxide. It is then connected as shown in Figure I, and the air swept out by a stream of dry ammonia. Liquid ammonia is next withdrawn from a stock cylinder into a Dewar similar to M. This is then fitted with a two-hole rubber stopper through which pass a short and a long glass tube, the latter reaching to the bottom of the vessel. When one's finger is held over the end of the short tube, the vapor pressure of the ammonia is sufficient to force the liquid out through the other. In this way, with the reaction tube held in a slightly raised position, ammonia is transferred to M until it is about half full. With T_1 or T_2, T_4 and U open, a stream of dry ammonia gas enters through D under a pressure of about 15 cm. of mercury, as registered by the gauge K. At the same time the temperature of the cooling bath in M is con-

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siderably lowered by bubbling dry air through the outer Dewar. Condensation of dry liquid ammonia then occurs so rapidly that 50 c.c. can be obtained in about fifteen minutes.

Sodium, previously cut under petroleum ether, dried quickly and weighed in a weighing bottle filled with ammonia gas or petroleum ether vapors, is introduced into the reaction tube through the side arm G. A calculated quantity of silver iodide is weighed in tube F and placed in the position indicated in figure I. With a slight stream of ammonia passing through T_2, and T_5 and U open, the tube F is gently tapped causing silver iodide to fall into the sodium solution. A vigorous reaction results and any gases, insoluble in water, which may be generated are caught in the eudiometer I. Addition of silver iodide is continued until the blue color just disappears. The tube F is reweighed and the amount of silver iodide necessary to react with the known quantity of sodium may be calculated.

The precipitate is then washed free from soluble sodium iodide in the following manner. The long tube into A is raised so that its lower end is just above the surface of the supernatant liquid. With T_1 and T_3 open and ammonia from the supply tank streaming thru the apparatus, this tube is lowered carefully into the liquid ammonia. The latter is forced up through the tube and out of the apparatus at T_3 into a conveniently placed Dewar. In this way practically all the liquid may be removed from the reaction tube without

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losing any appreciable quantity of the precipitate. Condensation is again carried out, the last portion with ammonia entering through T_2, thereby mixing the precipitate with the fresh ammonia. After settling, the supernatant liquid is again withdrawn. The washing is continued until thewash ammonia is free from iodides, usually four times being sufficient. After the last washing, the remaining liquid ammonia is allowed to evaporate, usually overnight, under a pressure of about 2 cm. of mercury.

The reaction tube is then disconnected from the remainder of the apparatus, care being taken to prevent the entrance of air. By suitable tipping the precipitate is transferred to the collecting tube L, and the latter is then sealed off at H. The resulting small tube containing the precipitate is evacuated and weighed. The sample may then be treated in any desired manner. For analytical purposes, the sample is dissolved according to the method developed by Rose[35].

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III. REACTION BETWEEN SODIUM AND SILVER IODIDE

The only previous research on the reaction between sodium and silver salts in liquid ammonia was done by Kraus and Kurtz[2]. They added either silver cyanide or silver iodide to a sodium solution until the blue color was discharged. A metallic precipitate, inactive toward air and moisture, was formed. Several determinations of the ratio of the sodium (in excess of that necessary to reduce the silver salt to free metal) to total silver gave values of 0.1 and 0.09. While this represents approximately ten per cent. excess sodium, they concluded that no compound of sodium and silver was formed. The high ratio of sodium to silver, together with lack of knowledge concerning the composition of the precipitate, obscures the exact course of the reaction. To secure added information, a complete study of the reaction between sodium and silver iodide has been made.

STARTING MATERIALS. Before presenting experimental results, the substances used will be described. In choosing a silver salt, several factors must be considered: first, the salt must be soluble in liquid ammonia; second, the anion must be stable in the presence of sodium; and, finally, the sodium salt of the anion must be easily soluble. The first requirement is necessary in order that reaction occur readily. Reduction of the anion by sodium would introduce serious complications. The last requirement permits purification by wash-

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ing of any precipitate formed. In view of the solubility data in the literature,[36] silver iodide and cyanide are best suited. Silver iodide was chosen for the research because of the comparative simplicity of its preparation.

Silver iodide was made from Mallinkrodt's C. P. potassium iodide and Merck's C. P. silver nitrate. Equal volumes of approximately .5 N solutions of each were mixed slowly with stirring, and then heated to boiling. The resulting silver iodide, after settling, was washed about six times by decantation, and recovered on a Buchner funnel. It was heated to dryness in an oven at 110°C, pulverized, and kept in a brown bottle.

Commercial liquid ammonia contains a small percentage of water which must be removed before the ammonia can be used as a solvent. This is done by transferring the impure ammonia to a smaller and more easily handled supply tank, which contains small pieces of metallic sodium. The latter immediately reacts with any water present, forming hydrogen and insoluble sodium hydroxide. Any excess sodium then reacts with ammonia, giving hydrogen and difficultly soluble sodium amide. The ammonia gas obtained from this tank is both anhydrous and sodium free.

The sodium used throughout these experiments was obtained from Kahlbaum and a sample analyzed 99.7% pure.

EXPERIMENTAL PROCEDURE. The procedure outlined in Part II. of

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this thesis was employed to carry out numerous reactions between silver iodide and sodium with a few modifications. Several qualitative determinations were sufficient to show that no gas is evolved. Other experiments showed that the precipitate is non-reactive and does not change weight in air. This fact facilitated handling to a large degree. Samples could be removed from the reaction tube at will, and weighed directly on a balance.

ANALYTICAL METHODS. The precipitate was analyzed for heat loss, silver, sodium, iodide and ammonia. A portion of the precipitate was put in the collection tube which was evacuated and weighed. The tube was then partially immersed in a beaker of water, slowly heated to 100°C, and kept at this temperature for about ten minutes. Before discontinuing the heating the tube was again evacuated. After cooling, the tube was reweighed and any change in weight recorded as heat loss.

To determine silver the sample was dissolved in concentrated nitric acid and made up to 100 c.c. Any colloidal precipitate which formed was allowed to remain in the solution. Aliquot parts were treated with dilute hydrochloric acid and heated to boiling. The precipitate was allowed to settle, filtered, washed, and weighed as silver chloride. In several cases, instead of choosing aliquot parts of a single solution to be used as duplicates, two separate portions of the precipitate were employed.

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Another sample was digested well with water and filtered. The filtrate was made up to 100 c.c. and used to determine sodium and iodides. For sodium, an aliquot portion was placed in a weighed evaporating dish, and heated nearly to dryness on a hot plate. Then several c.c. of dilute hydrochloric acid were added, and the dish heated to dryness. To remove any ammonium salts the dish was then heated over an open flame. It was finally cooled in a desiccator and weighed. Usually the weight of the sodium chloride was so exceedingly small compared to the dish (.005 gm. to 25.0 gm.) that the accuracy of the method is questionable.

To determine iodide, an aliquot part of the solution was treated with several drops of 0.1 N silver nitrate solution and heated to boiling. Coagulation of the colloidal solution was aided by adding a small quantity of nitric acid. After settling, the precipitate was filtered, heated at 110°C for an hour, cooled and weighed as silver iodide.

Numerous samples which had been heated to 100°C, and then dissolved in nitric acid for subsequent silver analysis, were tested for ammonia by Nessler's reagent. The amount present in all cases was negligible.

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EXPERIMENTAL RESULTS. The results of all experiments properly carried out are given in Tables I, II, and III. Table IV gives a compact summary of all analytical results scattered throughout Tables I, II, and III.

TABLE I.

Ratio of Reacting Substances

Expt. No.	Na grams	AgI grams	Na m.atoms	AgI m. mols	Ratio Na/AgI
178	.1584	1.5981	6.887	6.806	1.012
179	.1581	1.5833	6.870	6.743	1.019
180	.1543	1.5728	6.709	6.706	1.000
186	.1214	1.1954	5.278	5.091	1.037
192	.5497	5.4077	23.90	23.03	1.038
193	.4213	4.1953	18.32	17.87	1.025
194	.3181	3.2505	13.83	13.86	0.998
195	.2846	2.8812	12.37	12.27	1.008
196	.2620	2.6156	11.39	11.14	1.023
198	.4652	4.7343	20.23	20.16	1.003
202	.3255	3.2386	14.15	13.80	1.025

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TABLE II.

Analyses for Silver and Heat Loss

Expt. No.	Sample grams	Ag aliquot	AgCl grams	% Ag	Heat loss grams	% heat loss
178	.5844	1.	.7847	96.4		
179	.7172	.4834	.1795	97.4		
		.4900	.1816	97.2		
180	.6982	.4850	.1746	97.0	.0050	0.7
		.4950	.1786	97.2		
186	.5376	.2456	.1711	97.5	.0007	0.1
		.2436	.1696	97.5		
192	.9075	1.	1.1624	96.4		
193	1.3529	.2480	.4351	97.6	.0012	0.1
194	.4994	.2436	.1591	98.4	.0013	0.3
		.2466	.1609	98.3		
195	.5088	1.	.6649	98.3		
196	.2045	1.	.2649	97.5		
	.2297	1.	.2988	97.9		
198	.2792	1.	.3660	98.6		
	.4856	1.	.6335	98.2		
202	.9740	1.	1.2627	97.6	.0047	0.5

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TABLE III.

Analyses for Sodium and Iodide

Expt. No.	Sample grams	Na aliquot	NaCl grams	% Na	I aliquot	AgI grams	% I
186	.5376	0.5	.0061	0.9			
192	1.1557	0.5	.0119	0.8			
193	1.3529	0.5	.0090	0.5	0.25	.0049	0.8
194	.4994				1.	.0025	0.3
195	.8218				1.	.0108	0.8
196	.7379				1.	.0000	0.0
198	1.0522				1.	.0241	1.3
202	.9740				1.	.0022	0.1

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TABLE IV.

Summary

Expt. No.	% Ag	% Ag corrected	% Heat loss	% Na	% I	Ratio Na/AgI
178	96.4					1.012
179	97.3					1.019
180	97.1		0.7			1.000
186	97.5		0.1	0.9		1.037
192	96.4			0.8		1.038
193	97.6	97.2	0.1	0.5	0.8	1.025
194	98.4	98.3	0.3		0.3	0.998
195	98.3	97.9			0.8	1.008
196	97.7	97.7			0.0	1.023
198	98.4	97.8			1.3	1.003
202	97.6	97.6			0.1	1.025

The columns of Table I, reading from left to right, represent the number of the experiment, grams of sodium employed, grams of silver iodide employed, milli-atoms of sodium calculated, milli-mols of silver iodide calculated, and the calculated ratio of milli-atoms of sodium to milli-mols of silver iodide. In Table II, the columns are the number of the experiment, grams of sample chosen for analysis, aliquot portions for silver analysis, grams of silver chloride obtained, per cent. silver calculated, grams loss on heating sample, and per cent. heat loss calculated. In Table III,

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the columns are the number of the experiment, grams of sample chosen for analysis, aliquot portion for sodium analysis, grams of sodium chloride obtained, per cent. sodium calculated, aliquot portion for iodide analysis, grams of silver iodide obtained, and per cent. iodide calculated. In Table IV, the columns are the number of the experiment, per cent. silver as shown in Table II, per cent. silver corrected for iodide content, per cent. heat loss, per cent. sodium, per cent. iodide and ratio of sodium to silver iodide.

Several portions of the tables will be explained in more detail. The term "milli-atom" of sodium means .0230 grams, while "milli-mol" of silver iodide means 0.2348 grams. In Table II, experiments 178, 192, 193, 195, and 202 were not analyzed in duplicate for silver. In Table II, column 3, experiment 179, the figure .4834 means that of the 100 c.c. of solution of sample, 48.34 c.c. as measured from a burette were chosen for silver analysis. In experiments 186, 193, 194, and 202, the same sample was analyzed for all constituents. This was done by first getting heat loss, then digesting the sample with water and filtering. The filtrate was then analyzed for sodium and iodide, and the residue for silver in the usual way. Column 3 in Table IV gives the silver per cent. corrected for the presence of iodide (indicated by a faintly yellow colloidal precipitate in the nitric acid solution of the sample.) In analyzing for silver, all the

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iodide present was assumed to be in the form of silver iodide. From the known iodide content was calculated the amount of silver iodide present. This weight deducted from the total weight of silver halide found in the analysis gave the weight of silver chloride. From these data the corrected per cent. of silver was calculated.

DISCUSSION OF RESULTS. An interpretation of the experimental results summarized in Table IV is next presented. It is to be remembered that these are the results of all experiments performed without accident. The average ratio of sodium to silver iodide is 1.017 with a maximum deviation of 2.1 per cent., while the average percentage of silver in the solid residue is 97.4 with a maximum deviation of 1.0 per cent. These facts immediately suggest that sodium reacts with silver iodide according to the equation

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

This agrees with the conclusions drawn by Kraus and Kurtz[2].

The analyses of the solid residue, however, do not indicate that it is composed of pure silver. The heat loss is assumed to be due to the expulsion of adsorbed ammonia gas which is driven off completely by heating to 100°C. Small quantities of sodium and iodides are also present. This may be due either to incomplete washing to remove sodium iodide or to adsorption or occlusion of sodium iodide by the precipitate. Since the latter forms in large lumps, it is most

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probable that some sodium iodide is enclosed mechanically, and cannot be removed by the ordinary washing process. In this connection it is worthy of note that in experiment 194, where the silver per cent. is the highest, the precipitate was much more finely divided than in any other case.

The ratio of sodium to silver iodide is nearly always greater than unity, in spite of the fact that the silver iodide may be added in slight excess due to the method of obtaining an end point for the reaction. It was first thought that this was due to a slight reaction between sodium and ammonia according to the equation

$$Na + NH_3 \rightarrow NaNH_2 + \frac{1}{2}H_2$$

A secondary reaction of this sort could be catalyzed by the glass walls of the container or by freshly reduced silver. This would explain the high ratio since some of the sodium would be used in forming sodium amide, and consequently less silver iodide would be needed to react with the remaining sodium.

In order to check these possibilities, the following experiments were performed. 5.017 milli-atoms of sodium were dissolved in liquid ammonia, the apparatus well sealed with paraffin, and allowed to stand for twenty-four hours. 4.863 milli-mols of silver iodide were then necessary to discharge the sodium color. This corresponds to a ratio of sodium to silver iodide of 1.032, which is quite comparable to those ratios obtained when silver iodide reacts with freshly

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prepared sodium solution. It was concluded that a negligible quantity of sodium formed sodium amide due to the catalyzing action of the walls of the containing vessel.

A second experiment to determine the catalytic effect of freshly reduced silver was performed. 4.004 milli-atoms of sodium were dissolved in liquid ammonia, and 1.652 milli-mols of silver iodide added. The apparatus was again sealed with paraffin and allowed to stand for eight hours. 2.047 milli-mols of silver iodide were then necessary to discharge the blue color. The total quantity of silver iodide used was 3.699 milli-mols. The corresponding ratio is 1.083, which indicates that a slight amount of sodium had reacted with ammonia to form sodium amide. Since it usually requires only about fifteen minutes to perform an experiment, it was concluded that a negligible quantity of sodium formed sodium amide due to the catalyzing action of the silver.

These two experiments disproved the hypothesis of a secondary reaction between sodium and ammonia. It was necessary, therefore, to look for other possibilities whereby the high ratio of sodium to silver iodide may be explained. The ammonia used as the solvent and the silver iodide were shown to be practically anhydrous. The method of weighing the sodium introduces an error due to a slight oxide formation. The silver iodide used may have contained small quantities of the nitrate radical or some silver chloride as impurities.

All these errors are in the same direction resulting in

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a high ratio of sodium to silver iodide. It is believed that the predominating error is due to impurities in the silver iodide.

In the reaction between sodium and silver iodide, the end point can be obtained very accurately. This suggests that a silver salt can be used to "titrate" the sodium content of a solution. Such a process can be applied readily to numerous reactions. It has already been used in determining the catalytic effect of glass and freshly reduced silver. Another simple adaptation would be the determination of errors which would arise from the presence of moisture or air within the apparatus. The results obtained in this study indicate that silver iodide can be used when an error of 3% is permissible.

Since this 3% error is too large for accurate quantitative work, and as doubt has already been thrown on the purity of the silver iodide, another silver salt was tried. At the writer's suggestion, Mr. Hooper Linford, employing the same apparatus and procedure, used silver chloride with remarkable success. In four runs, in which only the ratio of sodium to silver chloride was determined, it was found to be 1 [illegible] .001. This indicates that silver chloride can be used to titrate sodium in liquid ammonia solution with an error of only 0.1%. It also confirms the conclusion previously drawn that impurities in the silver iodide are the most probable

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source of error. Further study and application of this method will be carried out in the ammonia laboratory.

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SUMMARY -- SILVER IODIDE EXPERIMENTS

1. Silver iodide and sodium react in liquid ammonia solution according to the equation

$$Na + AgI \longrightarrow NaI + Ag$$

2. The precipitated silver contains traces of ammonia and sodium iodide. The former may be removed completely by heating to 100°C. The latter is mechanically enclosed.

3. The reaction ratio of sodium to silver iodide averages 1.017 with a maximum deviation of 2% from this value.

4. The catalytic effects of the reaction tube and metallic silver on the reaction

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

are negligible.

5. Impurities in the silver iodide are the most probable cause of the high ratio.

6. Silver iodide may be employed to titrate sodium in liquid ammonia solution when an error of not more than 3% is permissible.

7. Preliminary determinations show that silver chloride may be employed to titrate sodium in liquid ammonia with an error of 0.1%. Further study of this method is advisable.

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IV. REACTION BETWEEN SODIUM AND MANGANOUS IODIDE.

No references to the reducing action of sodium on a manganese salt can be found in the literature. Consequently, no information as to the course of the reaction was available at the beginning of this research.

STARTING MATERIALS. The same reasoning which governed the choice of silver iodide led to the selection of manganous iodide as the manganese salt. A quantity of this compound, obtained from Kahlbaum, analyzed 90.5% of the theoretical manganese content, and a quantity from Coleman and Bell analyzed 83.3%. The appearance of the substance, as well as these results, indicated the presence of considerable water. It was therefore necessary to dehydrate the manganous iodide before use. Since the compound decomposes into its constituent elements at about 50°C, driving off the water by heat is impossible. The method finally adopted was to let the manganese iodide stand over phosphorus pentoxide in an evacuated desiccator for several weeks. After such treatment the results of analyses of various samples indicated between 98 and 99.5% of the theoretical manganese content, and slightly less values for the iodine content. Throughout all the experiments, the manganese iodide probably contained a small quantity of oxides or hydroxides of manganese, and possibly a trace of water which was not removed in the drying process.

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In the face of such facts, it might be inquired why manganese iodide was used rather than some other manganese salt. As previously shown, iodides or cyanides are preferable for this type of work in liquid ammonia. Since the solid cyanide is practically unknown, the iodide was used even though it is exceedingly deliquescent and very likely unobtainable in a strictly pure state.

The ammonia and sodium used in these experiments were the same as that previously employed.

EXPERIMENTAL PROCEDURE. The procedure outlined in part II was changed in several respects. Since manganese iodide absorbs large quantities of ammonia gas, the weight added to the sodium solution cannot be obtained as in the case of silver iodide. After numerous modifications, the reaction was carried out as follows. A quantity of manganous iodide was weighed and transferred to the reaction tube, using all precautions to prevent contact with moisture. The tube was quickly closed and connected to the remainder of the apparatus. Ammonia gas was allowed to stream slowly over the manganese iodide until the reaction, which generates considerable heat, was complete. Then liquid ammonia was placed in the cooling bath and condensation performed as usual.

When ready to carry out the reaction, the side arm G was opened and a weighed piece of sodium placed just inside. The stopper was then replaced and any air present driven out

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by a stream of ammonia. Tapping the side arm caused the sodium to fall into the solution of manganous iodide. The remainder of the procedure is identical with that outlined in part II.

ANALYTICAL METHODS. Analyses for heat loss, manganese, sodium, amide, and hydrogen were made. Heat loss was determined in the same way as in the silver experiments.

After much experimentation the following method for manganese analysis was developed and proven to give excellent results. The sample for analysis was dissolved in hydrochloric acid, according to the method described by Rose,[35] made up to 100 c.c., and aliquot parts chosen for duplicate analyses. After adding one gram of ammonium chloride, ammonium hydroxide was added until a slight permanent precipitate formed. This was dissolved in just sufficient hydrochloric acid, 5 c.c. of 1N ammonium hydrogen phosphate added, and the solution heated to boiling. Then ammonium hydroxide was added dropwise until distinctly alkaline to litmus. A curdy precipitate formed, which, upon continued boiling, soon changed to a crystalline one. After settling this precipitate was filtered, washed, ignited to 300°C on an air bath for a half hour, cooled in a desiccator, and weighed as manganese pyrophosphate. Some earlier manganese analyses were made according to the method described by Scott.[37]

The method of analyzing for sodium differed from

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that employed in the silver experiments, in that the sample was digested with 1N ammonium hydroxide instead of distilled water. This was done to remove as hydroxide any manganese which might be present in the water solution. The sample analyzed for sodium was usually not analyzed for any other constituent.

Aliquot portions of the solution in which manganese was determined were used for amide analysis. Since the amide was present as ammonium chloride, the amount of the latter was estimated by a simplification of the Kjeldall process. In a few cases the ammonia was determined by the sodium hypobromite method.[38]

Gases collected in the eudiometer I during a reaction were analyzed for hydrogen by the common combustion method.[39]

EXPERIMENTAL RESULTS. In carrying out these experiments, numerous qualitative observations proved to be of importance, and consequently are described in some detail. When liquid ammonia is condensed on manganous iodide, the system consists of a colorless solution and a voluminous white residue. Upon the addition of sodium, a vigorous reaction occurs in which gas is evolved, a shiny black precipitate forms, and the white suspension disappears. As long as the piece of sodium is present, the blue color is visible in the immediate neighborhood and the vigorous reaction continues. Ordinarily

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all the sodium disappears within fifteen minutes, but in an extreme case, in which the ratio of sodium to manganese iodide was 30, two hours were required.

In all cases in which the ratio is considerably greater than 2, a secondary reaction is evident after the sodium has disappeared. This reaction is characterized by very slow but steady gas evolution, and requires approximately two days for completion.

When the precipitate settles, the color of the supernatant liquid varies between golden yellow and colorless. The intensity and persistence of the yellow color during subsequent washing increases with increasing ratio of sodium to manganous iodide. In some experiments in which the ratio was less than 2, no yellow color was visible at any time.

The precipitate formed is exceedingly reactive toward air. When suddenly exposed, sparking occurs and the solid changes in color from a shiny black to medium brown and some dark green.

Since the complete reaction occurs in two stages, two distinct types of experiment were performed. In the first, hereafter referred to as Type I, gas collection was discontinued and washing begun immediately after all the sodium had disappeared. In the second, hereafter referred to as Type II, gas was collected and the reacting system not disturbed until the secondary reaction was complete. The quantitative data on the experiments of Type I are given in

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Tables I, II, and III. The quantitative data on the experiments of Type II are given in Tables IV, V, and VI. As in the case of silver iodide, the results of all experiments which have been performed without accident are shown.

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TABLE I.

Ratio of Reacting Substances and Volume of Gas Evolved

Type I

Expt. No.	Na grams	MnI$_2$ grams	Na m.atoms	MnI$_2$ m.mols	Ratio Na/MnI$_2$	H$_2$ c.c. S.T.P.
131	.1545	.6290	6.717	2.038	3.297	35.65
132	.2265	.1781	9.848	.577	17.07	106.8
137	.1645	.6474	7.152	2.097	3.410	39.94
139	.2776	1.1455	12.07	3.711	3.253	71.84
145	.1820	.8770	7.913	2.841	2.785	34.69
146	.2144	1.2837	9.322	4.158	2.242	13.97
147	.3105	.7464	13.50	2.418	5.583	105.9
158	.6359	2.0178	27.65	6.536	4.230	185.1
166	.3203	1.3703	13.93	4.439	3.137	
169	.1750	.7791	7.609	2.524	3.015	
170	.3022	1.3512	13.14	4.377	3.002	
174	.2833	1.4917	12.32	4.832	2.549	
208	.2803	1.4833	12.19	4.805	2.536	
210	.2228	1.3910	9.687	4.506	2.150	
211	.2118	1.5764	9.209	5.107	1.803	0.0
212	.2193	1.4632	9.535	4.740	2.012	10.98
215	.2439	1.6466	10.60	5.334	1.988	20.90
216	.3570	2.3906	15.52	7.744	2.004	4.0

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TABLE II.

Analyses for Sodium

Type I

Expt. No.	Sample grams	Na aliquot	NaCl grams	% Na
145	.1933	.2118	.0119	11.4
		.1745	.0100	11.2
146	.2470	.1791	.0046	4.1
		.1796	.0047	4.1
147	.1728	.1868	.0233	28.4
		.1847	.0230	28.3
158	.0659	.4071	.0100	15.0
		.3948	.0098	15.3
169	.0590	1.	.0084	5.6
170	.0824	.4088	.0052	6.1
		.4157	.0057	6.5
174	.0750	1.	.0105	5.5
208	.0604	1.	.0067	4.4
210	.0754	1.	.0051	2.7
215	.1104	.5	.0011	0.8
216	.1540	1.	.0026	0.6

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TABLE III.

Analyses for Manganese, Heat Loss, and Amide

Type I

Expt. No.	Sample grams	Mn Aliquot	$Mn_2P_2O_7$ grams	% Mn	Heat Loss grams	% Heat Loss	% NH_2
131	.1287	.1412	.0275	58.6	.0037	2.9	18.4 18.0
132	.0975	.3 .3	.0112 .0094	14.8 12.4	.0004	0.4	26.3 27.3
137	.1452	.2 .2	.0507 .0511	67.6 68.1	.0034	2.3	10.7 8.8
139	.2814	.1 .1	.0439 .0442	60.2 60.5			22.3 21.5
145	.1933	.2524	.0910	72.2			
146	.2470	.2 .2	.1206 .1179	94.5 92.4			
147	.1728	.2 .2	.0320 .0327	35.8 36.6			
158	.0830	.2006 .2005	.0241 .0233	56.0 54.2	.0034	4.1	4.4 4.9
166	.0980	.2493 .2470	.0427 .0423	67.6 67.5	.0010	1.0	3.3 3.3
169	.0710	.2446 .2488	.0337 .0337	75.1 73.9	.0006	0.9	6.1
170	.1436	.2063 .2089	.0546 .0549	71.3 70.8	.0015	1.1	4.4 3.5
174	.1290	.2524 .2125	.0580 .0489	69.0 69.2			11.1 11.0
208	.1763	.2477 .2498	.0911 .0916	80.7 80.5	.0013	0.8	6.4 7.1
210	.1758	.2456 .2499	.0943 .0962	84.5 84.7			4.6 4.8

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TABLE III. (Cont'd)

Analyses for Manganese, Heat Loss, and Amide

Type I

Expt. No.	Sample grams	Mn Aliquot	$Mn_2P_2O_7$ grams	% Mn	Heat Loss grams	% Heat Loss	% NH_2
211	.2534	.2430	.1370	86.1			1.9
		.2500	.1421	86.8			1.8
212	.2678	.2479	.1445	84.2			5.9
							5.2
215	.1501	.2455	.0854	89.7			4.1
		.2493	.0863	89.3			4.5
216	.2952	.2447	.1680	90.0			2.7
		.2507	.1709	89.4			2.7

TABLE IV.

Ratio of Reacting Substances and Volume of Gas Evolved

Type II

Expt. No.	Na grams	MnI_2 grams	Na m.atoms	MnI_2 m.mols	Ratio Na/MnI_2	Time run hours	H_2 c.c. S.T.P.
161	.4024	1.8321	17.50	5.935	2.948	48	175.4
162	.3096	1.2205	13.46	3.954	3.405	48	148.0
167	.2954	1.3317	12.84	4.314	2.977	60	139.8

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TABLE V.

Analyses for Sodium

Type II

Expt. No.	Sample grams	Na aliquot	NaCl grams	% Na
161	.1049	.361	.0056	5.8
		.396	.0062	5.9
162	.0766	.2508	.0072	14.5
		.2426	.0077	16.3
167	.0865	.4043	.0412	16.0
		.3804	.0133	15.6

TABLE VI.

Analyses for Manganese, Heat Loss, and Amide

Type II

Expt. No.	Sample grams	Mn aliquot	$Mn_2P_2O_7$ grams	% Mn	Heat Loss grams	% Heat Loss	% NH_2
161	.1930	.2020	.0587	58.3	.0073	3.8	24.8
		.2003	.0576	57.7			25.9
162	.0746	.4496	.0403	46.5			
		.4048	.0352	45.1			
167	.1245	.2022	.0308	47.7	.0156	12.5	17.5
		.2036	.0311	47.5			16.9

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In Table I, reading from left to right, the columns represent the number of the experiment, grams of sodium used, grams of manganese iodide used, milli-atoms of sodium calculated, milli-mols of manganese iodide calculated, ratio of milli-atoms of sodium to milli-mols of manganese iodide, and the c.c. of hydrogen evolved, measured at standard conditions. The columns in Table II are the number of the experiment, grams of sample chosen for analysis, aliquot parts for sodium, grams of sodium chloride obtained, and the per cent. sodium calculated. In Table III the columns are the number of the experiment, grams of sample chosen for analysis, aliquot parts for manganese, grams of manganese pyrophosphate obtained, per cent. manganese calculated, heat loss in grams, per cent. heat loss calculated, and the per cent. amide calculated. In Table IV the first six columns represent the same facts as analogous columns in Table I. Column 7 represents the time in hours required for the reaction to go to completion. Column eight is similar to column seven, Table I. In Tables V and VI, the columns are analgous to similarly placed columns in Tables II and III respectively.

Various parts of the Tables will be explained at greater length. The term "milli-mol" of manganese iodide means .3087 grams. In Table I, the time during which gas was collected corresponded to the time required for complete disappearance of the sodium, varying from seven to sixty minutes. In experiments 145, 146, and 147, the same sample was

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analyzed for both sodium and manganese. This was done by digesting the sample with 1N ammonium hydroxide and filtering. The filtrate was analyzed for sodium and the residue for manganese in the usual manner. In Table III, experiments 131, 132, 137, and 139, the ammonia content of the samples was determined by the sodium hypobromite method. In Table III, experiments 132, 137, 139, 145, and 146, the manganese content of the samples was determined by the method described by Scott. All of these values are believed to be too high and are not considered in the discussion. In Table III, experiment 211, the precipitate was found to contain 6.7% iodide. The method of analysis was identical with the iodide analysis described in the silver experiments.

DISCUSSION OF RESULTS. The qualitative and quantitative results obtained permit no simple interpretation of the course of the reaction between sodium and manganese iodide. The following pertinent facts all emphasize that the reaction is quite complex. First, the blue color of sodium disappears regardless of the amounts of sodium and manganese iodide present. Therefore, no constant reaction ratio is possible. Second, the rate of gas evolution decreases abruptly when the blue color disappears. Third, a slow evolution of gas continues for a considerable length of time. Fourth, analyses of the precipitate show it to contain manganese, sodium, and amide in widely varying proportions.

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As the simplest explanation of these facts, the following theory is proposed. At least three separate reactions are taking place which can most easily be represented by the equations:

$$2Na + MnI_2 \rightarrow 2NaI + Mn \qquad (1)$$

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

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

Equation (1) represents the first step in the reduction of any halide by sodium in liquid ammonia. It occurs rapidly and is complete within thirty seconds. Equation (2) does not occur in the absence of a catalyst. The manganese freshly reduced in (1) acts as the catalytic agent. The time required for the completion of (2) is of the order of magnitude of fifteen minutes and corresponds to the first stage of the reaction. Equation (3) represents a hypothetical reaction which can be considered as the sum of a series of reactions involving manganese, ammonia, and sodium amide. Since the part played by sodium amide is not known, (3) represents the reaction in the simplest, but in all probability not the correct way. Reaction (3) is by far the slowest and extends over a period of days.

The experimental evidence which supports this theory will be discussed under two heads: first, the short experiment previously designated as Type I, and second, the long experiment called Type II.

Three methods for checking the theory present them-

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selves in the reactions of Type I which have been stopped after the first stage. The volume of hydrogen evolved here should be determined by the mass of sodium reacting to (2). The precipitate should consist of free manganese and sodium amide. The per cent. of manganese in the precipitate should increase with decreasing ratio of sodium to manganese iodide.

The relation of the amount of hydrogen obtained to the mass of sodium not required for reaction (1) is brought out in Table VII. The experiments are arranged in order of decreasing quantity of hydrogen obtained according to (2).

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TABLE VII.

Comparison of H_2 Calculated and Obtained.

Type I

Expt. No.	Na m.atoms	MnI_2 m.mols	H_2 calculated m.mols	H_2 obtained m.mols
158	27.65	6.536	7.289	8.263
132	9.848	.577	4.347	4.768
147	13.50	2.418	4.332	4.728
139	12.07	3.711	2.324	3.207
137	7.152	2.097	1.479	1.783
131	6.717	2.038	1.321	1.592
145	7.913	2.841	1.116	1.549
146	9.322	4.158	0.503	0.624
212	9.535	4.740	0.028	0.490
216	15.52	7.744	0.016	0.180
215	10.60	5.334		0.930
211	9.209	5.107		0.000

The columns, reading from left to right, are the number of the experiment, milli-atoms of sodium used, milli-mols of manganese iodide used, the calculated milli-mols of hydrogen equivalent to sodium not required for reaction (1), and the milli-mols of hydrogen obtained. The term "milli-mol" of hydrogen means 22.4 c.c. at standard conditions. Columns two and three are obtained from columns four and five

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of Table I. To illustrate the method of calculating the values in column four, experiment 158 will be used. 6.536 milli-mols of manganese iodide require 13.072 milli-atoms of sodium to react according to (1). The remaining sodium, 14.578 milli-atoms, then reacts according to (2) giving 7.289 milli-mols of hydrogen. This figure is recorded in column four. In experiments 211 and 215 the amounts of sodium employed were less than that required for equation (1).

Table VII shows that the hydrogen not only decreases regularly, but also is nearly equivalent in practically all cases to the hydrogen calculated on the basis of the theory. In every case it is to be noted that the volume of hydrogen is slightly larger than the calculated value. The formation of this excess indicates that reaction (3) is occurring simultaneously with (1) and (2). Some hydrogen, therefore, comes from this source.

That the precipitate contains manganese, sodium and amide is apparent from the analytical data. However, in the eight experiments in which complete analyses were made, (158, 169, 170, 174, 208, 210, 215, and 216), these three constituents account for from 75.0% to 94.6% of the total. The remainder is probably oxides or hydroxides due to the impurities in the manganese iodide or faulty manipulation. The composition of the precipitate tells little about the normal course of the reaction.

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The relation between the per cent. of manganese in the precipitate and decreasing ratio of sodium to manganese iodide is shown in

TABLE VIII.

Relation of Ratio and % Manganese

Type I

Expt. No.	Ratio Na/MnI_2	% Mn
147	5.583	36.2
158	4.230	55.1
131	3.297	58.6
166	3.137	67.5
169	3.015	74.5
170	3.002	71.1
174	2.549	69.9
208	2.536	80.6
210	2.150	84.6
212	2.012	84.2
216	2.004	89.7
215	1.988	89.5

The columns, from left to right, are the number of the experiment, ration of milli-atoms of sodium to milli-mols of manganese iodide, and per cent. of manganese in the precipitate. Column two is obtained from Table I, column six, while the figures in column three are found in Table III, column five.

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Table VIII shows that, with a few exceptions, the per cent. of manganese increases with a decrease in the ratio of sodium to manganese iodide. This agrees with the theory because a high ratio causes increased importance of reaction (2).

The experimental results of Type II will be used chiefly to give further proof of the existence of reaction (3), and the extent to which it occurs. Any hydrogen in excess of that demanded by (2) establishes (3). The amount of the excess hydrogen is a measure of its extent. The total hydrogen obtained from experiments of Type II, and the extent of reaction (3) are given in

TABLE IX.

Total Hydrogen and Extent of Reaction (3)

Expt. No.	H_2 collected m.mols	H_2 from Na m.mols	H_2 from Mn m.mols	Mn m.atoms	% Mn to amide
161	7.831	2.815	5.016	5.935	85
162	6.609	2.776	3.833	3.954	97
167	6.241	2.106	4.135	4.314	96

The columns in Table IX are the number of the experiment, milli-mols of hydrogen collected, millimols of hydrogen calculated from equation (2), milli-mols of hydrogen due to reaction (3) calculated, milli-atoms of manganese used, and per cent. of manganese changed to amide, or extent of reaction (3) calculated. The term "milli-atom" of manganese

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means .05493 grams. Column two is determined directly from column eight, Table IV, by simply changing from c.c. to milli-mols. Column five corresponds to column five, Table IV, since of milli-mol of manganese iodide contains a milli-atom of manganese.

Experiment 161 will be used to show how columns three, four, and six are calsulated. According to Table IV, 17.50 milli-atoms of sodium react with 5.935 milli-mols of manganese iodide. The latter will require 11.870 milli-atoms of sodium to react according to (1). Consequently, 5.63 milli-atoms of sodium can react according to (2), generating 2.815 milli-mols of hydrogen. This figure is placed in column three. The difference between total hydrogen and hydrogen generated by sodium must be formed by manganese according to (3). Hence, the value 5.016 appears in column four. Since 5.016 milli-mols of hydrogen are generated by an equal number of milli-atoms of manganese according to (3), 5.016 milli-atoms of manganese must have formed manganese amide. Therefore, column four divided by column five gives the per cent. of manganese which has formed amide, and is recorded in column six.

Table IX shows, first, that a considerable excess of hydrogen over that required by (2) is evolved thereby definitely establishing reaction (3). It also shows that (3) goes nearly to completion when sufficient time is allowed.

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That reaction (3) also takes place in the experiments of Type I is indicated by two facts. First, as shown in Table VII, more hydrogen is found in these experiments than can be accounted for by equation (2). Second, in experiments of both types, in which the ratio was large, a deep yellow color often persisting after several washings was obtained. According to Bergstrom[40] such a color is obtained when manganese thiocyanate reacts with potassium amide in liquid ammonia. Since the other substances present form colorless solutions, the color described by Bergstrom is probably due to manganese amide. A qualitative analysis of the residue from this yellow solution showed the presence of manganese. These results indicate that reaction (3) occurred in experiments of Type I.

Since freshly reduced manganese catalyzes the reaction between sodium and liquid ammonia, and also reacts slowly in the presence of sodium amide to form manganese amide, the manganese thus prepared possesses unusual properties. In experiments 210, 211, 212, 215, and 216, attempts were made to prepare pure manganese by using a ratio as near as possible to 2 and washing the precipitate immediately after (1) was complete. Since reactions (2) and (3) occurred to some extent, as shown by the formation of a small quantity of hydrogen and a slight yellow color, the precipitate was not pure but consisted of approximately 90% manganese and small

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quantities of sodium and amide (see Tables II and III). The solid, when suddenly exposed to air, sparked vigorously and changed in color from shiny black to medium brown. In the only case measured, the precipitate gained 13% of its original weight on exposure, due to oxide formation. These facts indicate that the solid consists mainly of a pyrophoric variety of manganese. Further research on the properties of manganese so prepared seems advisable.

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SUMMARY

1. Sodium and manganese iodide react in liquid ammonia solution according to the following equations:

$$Na + MnI_2 \rightarrow 2NaI + Mn \qquad (1)$$

$$Na + NH_3 \rightarrow NaNH_2 + \tfrac{1}{2}H_2 \qquad (2)$$

$$Mn + 2NH_3 \rightarrow Mn(NH_2)_2 + H_2 \qquad (3)$$

2. Reaction (1) occurs rapidly and is complete within thirty seconds.

3. Reaction (2) is catalyzed by manganese freshly reduced in (1). It is slower than (1) and requires between seven and sixty minutes for completion, depending on the ratio of sodium to manganese iodide.

4. Reaction (3) is a hypothetical one, and may be considered as the sum of a series of reactions involving sodium amide, manganese, and ammonia. It is by far the slowest, and is nearly complete in two days.

5. These three reactions occur simultaneously at their different speeds.

6. Reaction (3) may be prohibited to a large extent by washing the precipitated with liquid ammonia as soon as reaction (2) is complete.

7. Reactions (2) and (3) may be prohibited to a large extent if the ratio of sodium to manganese iodide is equal to 2.

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8. The precipitate consists of manganese, sodium amide, and manganese amide in varying proportions, depending on the ratio and the time of reaction. This precipitate sparks vigorously when exposed to air. The manganese so prepared is a pyrophoric variety.

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