A STUDY OF THE COMPOUNDS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA.

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by
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A STUDY OF THE COMPOUNDS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA.

INTRODUCTION.

Compounds consisting of metals only and metallic substances in general are of very common occurrence, and of great importance practically. Yet knowledge of the chemical constitution of this class of substances is very meagre. Many systems have been studied from the point of view of the phase rule, and a large number of metallic compounds discovered in this way. But while such studies allow conclusions to be drawn as to the existence and stability of these substances they give no idea of their chemical properties, nor do they indicate the existence of less stable compounds. A study of solutions of metallic substances in liquid ammonia has been more successful in explaining their chemical nature. As a result of an exhaustive investigation of liquid ammonia solutions of this type, Kraus[1] has arrived at the following general conclusions: in dilute solutions the chemical behavior of metallic substances is similar to that of salts; the more electropositive metal is associated with the positive charge, while the less electropositive metal is associated with the negative charge; the property of forming negative ions is quite general among the less electropositive elements; complex anions are often formed in which varying amounts of the less positive metal is present; this property of forming complex ions is very common among all elements in the electronegative condition and accounts for the numerous compounds formed from the same pair of elements; and the forces joining the anion and cation are similar to ordinary valence forces governing salt formation, but the forces joining the constituents of the complex ion are of a different nature, and apparently do not involve valence electrons. The experimental evidence upon which the above conclusions are based will be briefly presented in a later discussion concerning liquid ammonia chemistry.

This same investigation of liquid ammonia solutions indicated the existence of many new compounds. Kraus and Kurtz[*] have shown by reacting liquid ammonia solutions of various alkali or alkaline earth metals on the one hand, with various salts on the other hand, that usually compounds of the two metals are formed. The less electropositive elements present in these compounds are of the most varied nature. Thus they include not only members of the fourth and fifth columns of the periodic table, such as tin, lead, antimony and bismuth, but also representatives of the third, second and even first columns, such as thallium, zinc, mercury and silver. It should be noted at this point that in some cases and under certain conditions a compound is not formed, but instead a precipitate of the less electropositive metal alone appears. None of the products of these reactions were isolated, but the conclusions concerning their composition were drawn from the amounts of metallic salt and sodium interacting. The unusual nature of the results obtained in this way is illustrated by the compounds of sodium and zinc and of calcium and zinc which have the composition $NaZn_4$ and Ca_7Zn, respectively. Such a ratio for the atoms in combination is alone enough to make these compounds worth investigating further. Besides, a number of the compounds are also interesting because of their reactivity. For instance, a few qualitative experiments carried out by Kraus and Kurtz indicated that the above mentioned sodium zinc compound is very reactive towards both water and air. The nature and reactivity of compounds such as $NaZn_4$ indicated that a more definite quantitative study of its properties might very well lead to further conclusions concerning metallic compounds in general. The purpose of this thesis was to carry out such a study, especially in regard to behavior on oxidation and hydrolysis. However, before this could be done, it was necessary to prove more definitely that the formula $NaZn_4$ was correct and establish the reaction

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

In order to make the nature of the investigation somewhat clearer, it is desirable to discuss at some length certain special topics concerning liquid ammonia chemistry. These are first, the properties of liquid ammonia which allow its use as a solvent, second, the energetic reducing action of liquid ammonia solutions of electropositive elements such as sodium, and third, the properties of some of the metallic substances prepared and studied in liquid ammonia. There will then be given a survey of previous work closely related to that done in this investigation, and this in turn followed by the presentation of the details of the investigation. These are nicely divided into three groups, namely, the formation and isolation of sodium zinc, the properties of sodium zinc, and the study of certain other metallic compounds. The final part of the paper will then be devoted to a discussion and correlation of the results obtained.

Pure ammonia is now obtained in large quantities and at low cost by synthesis from hydrogen and nitrogen. The gas is rather easily liquefied at ordinary temperatures, a pressure of ten times that of the atmosphere being required. The liquid is shipped and stored in steel cylinders, from which it can be obtained when needed. Since liquid ammonia boils at -33° C. at atmospheric pressure either of two sets of conditions may be chosen in carrying out experiments with it. First the work may be done at atmospheric pressure, while the liquid ammonia is kept in a cooling bath or Dewar tube at a temperature near its boiling point. Second the work may be done with the ammonia at room temperature, and in this case it is necessary to use sealed tubes. In either case special apparatus and a special technique are necessary, but both of these methods have been successful in work involving the use of liquid ammonia as a solvent.

A large number of substances both organic and inorganic dissolve in liquid ammonia without chemical reaction taking place[3], and a number of interesting properties of these solutions have been discovered.[4] Foremost among these is the fact that in many of these solutions the dissolved substance is ionized to a considerable extent. The work of Franklin and Kraus[5] has shown that such solutions show all the properties to be expected of electrolytes dissolved in a good ionizing solvent. Metathetic reactions take place, and the boiling point elevation, freezing point depression, vapor pressure lowering, and electrical conductivity are all abnormally large.

These properties of the solutions, together with the fact that the ammonia itself is very slightly ionized according to the following scheme

$$NH_3 = NH_2^- + H^+ \quad .$$

led Franklin[6] to develop the ammonia system of acids, bases and salts. These classes of substances are related to the solvent ammonia, in the following way. An acid in the ammonia system, i.e., an ammono acid, is a substance which, when dissolved in ammonia, ionizes to give H^+ (the positive ion of the solvent), for example an acid amide. An ammono base is a substance ionizing to give NH_2^- (the negative ion of the solvent), for example potassium amide (KNH_2). An ammono salt is a substance which ionizes to give ions other than those resulting from the ionization of the solvent ammonia. This relationship between the acids, bases and salts of the ammonia system, and the solvent ammonia, taken along with the other properties of liquid ammonia noted above, indicates a great resemblance to water. Indeed, upon closer examination of the properties of the two substances it is found that the resemblance extends into the physical constants. Thus the specific heat, heat of volatilization, heat of fusion, critical constants, dielectric constant and association constant of both of these substances are all abnormally high.

There are, however, a few very important differences between liquid ammonia and water. Most important among these from the point of view of its use as a solvent is the relatively slight auto-ionization of ammonia, compared with water. The result of this is that the decomposition of substances through reaction with the solvent occurs to a correspondingly smaller extent in ammonia solution. Franklin has named such reactions ammonolysis in analogy to the corresponding term hydrolysis. This property of liquid ammonia has made it possible to prepare and to study substances which are entirely unknown in water solutions. For example, Franklin[7] was able to prepare and study many metallic amides and nitrides, most of which were not known before. This same property makes it possible for solutions of the more electropositive metals in liquid ammonia to exist, and their study is a very interesting chapter in liquid ammonia chemistry.

On adding any one of the alkali or alkaline earth metals to liquid ammonia, solution takes place rapidly with the formation of a blue or a bronze color depending upon the concentration. Concentrated solutions are bronze colored and possess a metallic luster, but on dilution a dull opaque blue is obtained. In very dilute solution this blue becomes transparent, but since it is still distinct in a 0.000025 N sodium solution it can readily be used as a test for the presence of free metal in the solution. The solubility of metals in liquid ammonia was first noticed by Weyl[8] in 1864. Seely[9], Gore,[10] Joannis,[11] Moissan,[12] Ruff,[13] Cady,[14] and others, worked with these interesting substances, but it was Kraus[15] who first made a thorough study of their properties. The earlier investigators of these systems considered that a compound of metal amd ammonia existed in such solutions, and could be separated upon evaporation. These compounds were thought to be derivatives of ammonium (NH_4) in which a hydrogen atom had been replaced by metal. They were called metal-ammoniums. However it has been conclusively shown by Kraus and others that the so-called "metal-ammoniums" do not exist. That the alkali metals do not combine at all with ammonia is shown by an application of the phase rule to the data obtained by vapor pressure measurements. Furthermore direct experiment shows that there is liquid present in a system of a composition such that less ammonia is present than that corresponding to the compound supposed to be formed. If the compound existed at all, such could not be the case. The alkaline earth metals apparently do form compounds with ammonia, such as $Ca(NH_3)_6$. These however are not analogous to "ammonium" in any way.

While the alkali metals do not combine directly with ammonia, they, and also the alkaline earth metals, do undergo a slow reaction with it, which results in the liberation of hydrogen and the formation of the corresponding metal amide. This reaction is catalyzed by many substances, but normally the reaction with potassium is most rapid, while sodium reacts at the slowest rate. Because of its slow reaction with ammonia, and its ready availability, sodium is the metal most commonly used in experimental work. For these reasons the discussion from this point on will be limited to solutions of sodium in liquid ammonia.

It is now necessary to present the results of further work by Kraus[16] on such systems. He concluded that the sodium atoms in a liquid ammonia solution are actually dissociated into positive and negative ions according to the scheme

$$Na = Na^+ + \epsilon^-.$$

The positive ion is the ordinary sodium ion, while the negative ion is the negative electron. The latter is surrounded by an envelope of solvent molecules but the forces of attraction here are not chemical, but of the nature of that observed between any charged particle and uncharged bodies of the medium, such as an electron in a rarefied gas atmosphere. The electrons are solvated, we might say. However there is no doubt that a few electrons are entirely free at any one instant. The experimental data for the above conclusions lie in experiments on the electrolysis and electrical conductivity relations of these systems. All the solutions conduct metallically, that is without polarization effects at the electrodes, and in concentrated solutions the conductivity is of the same order as that of metals, all of which clearly indicates the presence of free electrons. The conductivity function for dilute solutions of the metal is of the same type shown by salts, and in general in dilute solution the metal acts as though it were a salt, the only difference being the peculiar nature of the negative ion. Since negative electrons are so readily available in these solutions, and since the essential nature of reduction is combination with negative electrons, it is to be expected that solutions of sodium in liquid ammonia are energetic reducing agents. The reduction of non-metals takes place readily when they are placed in a sodium solution. For instance when sulfur is added to such a solution, normal sodium sulfide is formed.[17] Ionically this might be formulated:

$$2\ Na^{+} + 2\,\epsilon^{-} + S = 2\ Na^{+} + S^{=} = Na_2S$$

or more simply:

$$2\,\epsilon^{-} + S = S^{=}.$$

The latter is essentially what takes place, and indicates clearly the way in which the reducing agent functions. However if more sulfur is used than is necessary to form Na_2S, further reactions take place. It is worth discussing these briefly at this point, because they are a fruitful source of confusion in any study involving elements in the electronegative condition. In the above case a polysulfide is formed when excess sulfur is used. The reaction may be formulated

$$S^{=} + S = S^{=}.S \text{ or } (S_2)^{=}.$$

This type of reaction is common to all elements in the electronegative condition, and becomes even more pronounced in the metallic elements. Such combinations do not involve ordinary valence electrons, but the forces joining the atoms of such a complex anion are of the kind involved in hydrate or double salt formation, and are little understood. It should be noted that the valence of the anion does not change as the result of such a reaction. Furthermore several anions of varying complexity often exist in equilibrium with one another in solution, so that isolation of a definite compound is difficult. These points should be kept in mind during the following discussion of the reducing action of sodium solution on metals.

Sodium solutions not only reduce elements like sulfur, selenium, tellurium, and the more negative elements, but also arsenic, antimony, bismuth, and even lead and tin.[18] The reduction of tin may be formulated:

$$4\ Na^{+} + 4\ \varepsilon^{-} + Sn = Sn^{==} + 4\ Na^{+} = Na_4Sn$$

Normal sodium stannide, however, is unstable, or in other words, normal stannide ion decomposes with the formation of a complex tin ion, even though free sodium is present. Similarly normal sodium plumbide, Na_4Pb, decomposes to yield finally Na_4Pb_9. In general most of these compounds are soluble in liquid ammonia. Sodium solutions not only reduce free metals in the manner described above, but also reduce metals from their salts. In some experiments in which solutions of sodium and also of calcium were used as reducing agents, Kraus and Kurtz[8] discovered that salts of tin, lead, antimony, and bismuth are reduced, forming sodium and calcium compounds of these elements. Much more interesting however is the fact that salts of the more positive elements, thallium, zinc, cadmium and mercury, are also reduced and compounds with sodium or calcium obtained. In the free state these elements are not reduced by the sodium solutions. These latter compounds are all insoluble in liquid ammonia and appear as metallic precipitates during the reaction. The properties of these have not been investigated but a study was made by Kraus of the solutions of the soluble compounds previously mentioned.

The outstanding property of solutions of these metallic substances in liquid ammonia is that they behave very much like salt solutions. They undergo the usual type of electrolysis and metathesis reactions, and vapor pressure measurements indicate the presence of ions in the solutions. Thus, electrolysis of a solution of the sodium lead compound gives a deposit of lead on the anode. Such deposition can be carried out quantitatively where the experimental conditions are satisfactory and it is in this way that the formula Na_4Pb, was confirmed. When such solutions are treated with the salt of a metal, a metallic precipitate results from metathesis, as shown by the reactions:

$$Na_4Pb_9 + 2\ Cd(NO_3)_2 = 4\ NaNO_3 + Cd_xPb_y$$

$$Na_4Pb_9 + 2\ Pb(NO_3)_2 = 4\ NaNO_3 + Pb_2Pb_9$$

There is no doubt of the salt-like nature of these metallic substances. The study of them is confused by the fact that two compounds of the same two elements often exist in equilibrium with one another in such a solution, or in equilibrium with one or the other free metal. This is due to the tendency of atoms of the less electropositive element to become associated with the anion in varying numbers. As has already been mentioned, the forces causing this association are different from those causing the combination of the cation and anion parts of the molecule. This may best be symbolized by writing the formulae $Na_2S.S_x$ or $Na_4Pb.Pb_8$, etc., thus indicating that some of the atoms in the anion are held in combination in a different manner than others. We should expect a difference in the properties of these two types of atoms, but no investigations along this line have been carried out as yet.

It is also necessary to note another property of these substances and that is their action toward water. While sodium chloride is very slightly hydrolyzed, sodium sulfide is very much hydrolyzed, and the sodium salts of the elements of the fifth, fourth, and other columns of the periodic table are completely hydrolyzed. This accounts for their not being known and studied previously. That they exist in liquid ammonia solution is due to the far smaller tendency for salts to undergo ammonolysis. To summarize the properties of these metallic substances, it may be said, (1) that they are essentially salt-like in properties, (2) that they are hydrolyzed by water, and (3) that they are usually complex in composition due to association of varying amounts of the less electropositive metal with the anion.

This discussion of liquid ammonia solutions, of the reducing action of sodium solutions, and of the formation and properties of certain metallic substances should be concluded by a short review summarizing and correlating previous work involving the reduction of metallic salts by solutions of electropositive elements in liquid ammonia.

The earliest work of this nature which is recorded in the literature is that done by Weyl[8] who added salts of barium, zinc, copper, mercury, and silver to very concentrated solutions of sodium in ammonia. He thought the latter was sodammonium, a derivative of NH_4, with one hydrogen atom replaced by a sodium atom. When the above reactions were carried out he observed that the bronze color changed to blue and that precipitates were formed. He thought the latter were metal-ammoniums, in which the metallic element of the salt had taken the place of the sodium in sodammonium but he had no evidence for such conclusions. Seely[9] repeated and extended Weyl's work, and concluded that the precipitates formed were simply free metals. Much later Cady[14] observed that on addition of sodium to solutions of silver, copper, and barium salts in ammonia a precipitate of the free metal was formed, and that the characteristic blue color of the alkali metal was not produced until all of the less electropositive metal had been precipitated. Kraus[15], in discussing the methods of forming the compound of sodium and lead, noted that it could be prepared by adding lead iodide to sodium solution, provided an excess of lead salt was not used. When ammonium chloride was added to the solution containing this compound, decomposition occurred with evolution of gas. Spongy metallic lead was precipitated when a lead salt was added to the solution. When other metallic salts were used, the resulting precipitate contained both lead and the other metal.

All the above observations were qualitative in nature, and some even merely incidental observations. The recent investigation of Kraus and Kurtz[8] is the only quantitative investigation of reactions of the type being considered. Their experiments were carried out by adding different metallic salts to solutions of sodium or calcium in liquid ammonia, until the blue color was just discharged. From the weight of salt added and the weight of sodium used they determined the reaction which took place. Iodides and cyanides were found to be the most satisfactory salts since they are easily soluble in liquid ammonia. The results showed the formation of the following compounds: NaHg, $NaHg_2$, $NaZn_4$, Na_4Sn, Na_3Tl_2, CaAg, Ca_7Zn, Ca_3Hg_2, Ca_2Pb_3, Ca_3Sn. Evidence was also obtained of the existence of compounds of cadmium, antimony, and bismuth with sodium but definite conclusions were not reached. When silver cyanide was reduced with sodium solution, a compound was not formed, but only metallic silver precipitated. They also determined qualitatively that many of these compounds were reactive towards water and air.

PREPARATION OF SODIUM ZINC.

The freezing point study of the system sodium-zinc made by C. H. Mathewson[19] indicates the existence of a compound of composition $NaZn_{12}$. Most compositions of this system give two immiscible phases. The work of Kraus and Kurtz[2] showed that a reaction took place in which $NaZn_4$ was formed. This was prepared by adding zinc cyanide or zinc iodide to a solution of sodium in liquid ammonia until the blue color just disappeared. In this way the end point of the reaction was determined quite accurately. This work was the starting point of the present investigation.

The materials necessary for the work were (1) a supply of anhydrous ammonia, (2) metallic sodium, and (3) zinc cyanide. The liquid ammonia used was obtained in large stock cylinders. While this ammonia could be used directly in cooling baths, it was necessary to completely dry it before using it as a solvent. The drying was accomplished by the method of Franklin and Kraus[20]. By means of a steel pipe the liquid ammonia was transferred to a smaller cylinder containing metallic sodium. The ammonia reacts with this, and in time converts it into sodium amide, which is the active drying agent, as it removes water according to the following reaction:

$$NaNH_2 + HOH = NaOH + NH_3.$$

The drying cylinder was fitted with two valves, one of which was connected on the inside to a tube leading to the bottom of the cylinder, while the other valve opened directly into the top of the cylinder. The first valve was used in transferring liquid ammonia into the cylinder, while the second was used when a supply of completely anhydrous ammonia gas was desired. To obtain anhydrous liquid ammonia it was merely necessary to distill some of the liquid from the drying cylinder into the vessel in which the liquid was to be used. This was easily accomplished by cooling the latter (usually by means of a bath of ordinary liquid ammonia through which a stream of air was bubbled) and allowing the gas to pass over at a proper rate. During this operation, connection was always made by means of a side tube to a mercury gage so that the pressure inside the system was known.

The metallic sodium was cut under petroleum ether, transferred to a weighing bottle filled with dry gaseous ammonia which was immediately weighed and then the sodium was dropped into liquid ammonia as soon as possible. The zinc cyanide used was a Kahlbaum product. The analysis of this gave the following results, which were used in all calculations.

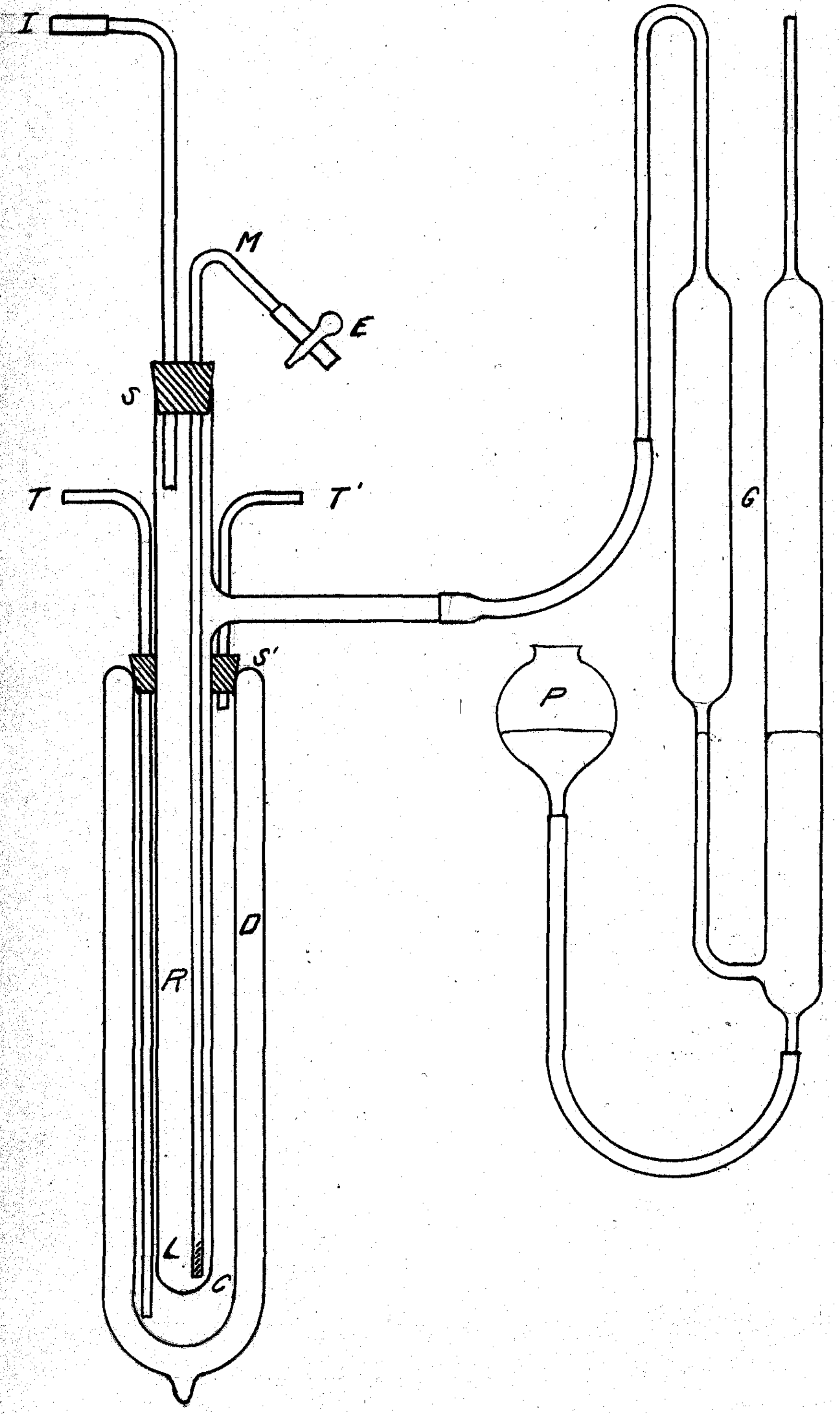

Fig. 1

Table I.

gms. sample	gms.Zn(calc.)	gms.Zn(found)	% Zn(Cn).
0.1996	0.1112	0.1093	98.31
0.2014	0.1121	0.1103	98.33

The nature of the apparatus used in the preparation of sodium zinc is shown in Fig.1. The essential parts are a reaction tube (R) fitted with connecting tubes for the introduction and removal of ammonia, a cooling bath (C) surrounding the reaction tube, and a gage (G) to regulate the pressure in the system. The method of preparation is best made clear by giving in detail the procedure which was finally adopted, including discussions of apparatus and methods wherever they seem desirable.

The reaction tube and connecting tubes, after being cleaned and dried by washing with alcohol and ether, and removing the latter by a stream of air dried by phosphorus pentoxide, were set up as shown in Fig.1. Anhydrous ammonia was then passed in through M for some time, this displacing the air from the reaction tube. When this was accomplished the tube I was closed by means of a pinch clamp. Ordinary liquid ammonia was then transferred from a Dewar tube into C. During this operation it was necessary to temporarily disconnect the stopper S' and raise the reaction tube slightly. Next the temperature of the bath was lowered by forcing a current of air through the tube T, so that it bubbled through the ammonia in C, and escaped through T′ into a water bottle which absorbed ammonia. The pressure in the system was then adjusted by means of the mercury pear P. Condensation began immediately in the reaction tube and was continued until sufficient ammonia was obtained. Since the air bubbling through the cooling bath causes the ammonia to evaporate rather rapidly, it was necessary to refill C from time to time. The dry ammonia gas may enter the reaction tube through either I or M. If the former were chosen M was closed by means of a pinch clamp. In this case the efficiency of the condensation decreases as the level of the liquid in the reaction tube rises. If the second of the above methods were chosen I was closed by means of a pinch clamp and condensation was more efficient since the entering ammonia had to bubble through the liquid already condensed. However there was the danger that the stopper S of the reaction tube might be loosened and release the pressure inside suddenly. Should this happen the entire contents of the reaction tube might be violently thrown out. Sometimes one method was used and sometimes the other. The rate of condensation depended upon the pressure inside the reaction tube, the amount of ammonia in the cooling bath, and its temperature. The pressure was controlled by means of the valve on the small ammonia cylinder, and the gage, G. The temperature of the bath was regulated by the rate at which air was bubbled through. If no air were bubbled through, the temperature would be near -33° C., the boiling point of the solvent. It might rise above this due to superheating or fall below if spontaneous evaporation were sufficiently rapid. By use of a stream of air the temperature could be lowered to -50° C.

After a sufficient supply of ammonia had condensed in the reaction tube, metallic sodium was added to obtain the sodium solution. The method of cutting and weighing the sodium has already been described. When it was desired to transfer the sodium to the reaction tube it was necessary to loosen, raise slightly, and push to one side the stopper S of the reaction tube. The pressure inside the tube had first to be adjusted to a value only slightly greater than atmospheric. If it were too great the liquid in the tube would be blown out, due to too violent boiling, and if it were too small air and moisture would be drawn into the tube. These difficulties were overcome by shutting off the air bubbling through the cooling bath and waiting until the mercury gage indicated a slight positive pressure inside the tube. When all was in readiness, the piece of sodium could be quickly removed from the weighing bottle with tongs and dropped into the reaction tube. It immediately dissolved to give a homogeneous blue solution.

The next step in the procedure was to add zinc cyanide to the solution of sodium in liquid ammonia. The necessary amount of salt was weighed out on a watch glass, before adding the sodium to the liquid ammonia, so that no delay was encountered at this point. The zinc cyanide, which is a white non-hygroscopic powder, was transferred by means of a powder funnel placed in the top of the reaction tube. This operation had to be carried out deliberately or the heat which was evolved would cause the liquid ammonia to boil violently, and much frothing would take place. Thorough cooling of the solution prevented this. The solution could be stirred during and after the addition of salt by allowing ammonia gas to enter through M. Stirring avoided a local excess of zinc cyanide and also prevented enclosure of any undissolved salt by the precipitate. When sufficient salt had been added, the blue color of the sodium disappeared and the black flocculent precipitate of sodium zinc settled out more or less rapidly, leaving the supernatant liquid clear.

As soon as settling had taken place the purification of the precipitate was begun. This was done by filtration and washing, thus removing sodium cyanide, the soluble product of the reaction. However the filtration of liquid ammonia solutions is not a simple matter. The only method recorded in the literature for the separation of a precipitate from a solution is that of Franklin.[21] Most of his work was done in sealed two-legged reaction tubes and the purification carried out by decanting the solution from the precipitate into the other leg of the tube. The solvent was then distilled back onto the precipitate and the process repeated as often as necessary. This method was not applicable here without radical changes in the entire procedure so the following method was devised. A small amount of glass wool (L) was inserted in the end of the filter tube (M) before beginning the experiment. When the precipitate had settled out well, the filter tube was adjusted so that its lower end was several centimeters above the top of the precipitate. The pinch clamp at M was closed and I was connected to the source of dry ammonia. A piece of glass tubing was then connected to the rubber tubing at M, and a Dewar flask placed under the end of this. The mercury gage was adjusted to give a pressure of about 15 cm. of mercury in the system. Ammonia was allowed to enter through I and leave through G. On opening the pinch clamp E the pressure on the surface of the liquid forced it through the glass wool (L), up through M and down into the Dewar. The pinch clamp (E) had to be opened all at once or the ammonia first coming over, upon reaching the warm part of the tube, generated a back pressure which tended to stir up the precipitate. While the pressure was kept on the surface of the liquid, the tube M was gradually lowered until its bottom just reached the precipitate. Care was necessary to prevent the precipitate from getting into the glass wool filter, as this would slow down the rate of filtration and

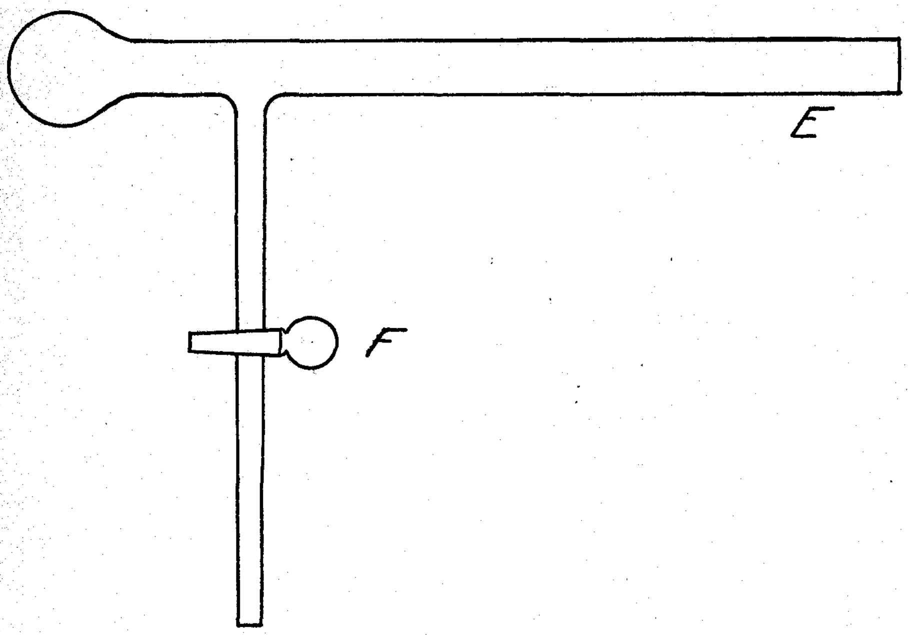

Fig. 2

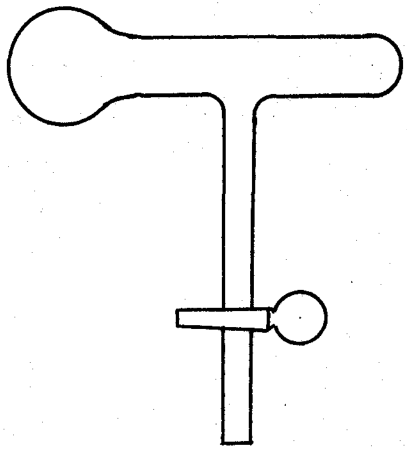

Fig. 2a

perhaps stop it altogether. As soon as filtration was completed the condensation of liquid ammonia was commenced again. When sufficient ammonia had condensed the solution was thoroughly stirred, the precipitate allowed to settle, and filtration again carried out. The washing was repeated from four to twelve times, the volume of the washings varying from one to ten times that of the precipitate and mother liquor remaining with it. These operations usually required the greater part of a day.

After numerous trials and modifications the following was adopted as the most satisfactory method for removing the precipitate from the reaction tube. A small sample tube like that shown in Fig.2 was then sealed (at E, Fig.2) to the side arm of the reaction tube. During the operation of sealing, a stream of ammonia gas was issuing from the side arm of the reaction tube, and also from the end of the sample tube (E), to prevent air or moisture from entering. Pressure for blowing was obtained by closing the end of the side arm of the sample tube with the finger. After the above seal was completed the stopper (S, Fig.1) of the reaction tube was removed and replaced by a tightly fitting rubber stopper. The end of the side arm of the sample tube was connected to the mercury gage until all of the residual solvent had evaporated, leaving a black powder in the reaction tube. The stopcock (F, Fig.2) was next closed and the reaction tube disconnected from the remainder of the apparatus. Then, by suitable manipulation of the reaction tube, the black powder was simply poured over into the sample tube, any lumps too large to pass through the side arm being broken by shaking. The side arm of the reaction tube was then scratched with a file, and the sample tube broken off at about the same place where it had been sealed on. Previously, suitable connections were made to the ammonia supply, so that dry ammonia gas was issuing from both openings. This prevented access of the atmosphere to the substance. The sample tube was sealed off just above the side arm (Fig.2a), the stopcock closed, and the substance was ready for further investigation. If desired, only a portion of the substance was transferred to the first sample tube, and the remainder placed in other sample tubes in the manner just described. Thus a number of samples could be obtained from the same preparation.

Modifications of the above procedure, and somewhat different forms of apparatus were used in some of the experiments, and the most important of these may be described here. In the first experiments a short Dewar tube (20 cm. in height) and a correspondingly short reaction tube with a stopcock in the side arm, were used. After the washing of the substance was complete, the reaction tube itself was sealed off just above the side arm, the residual solvent allowed to evaporate and the substance kept in the tube for further experiments. There were a number of disadvantages encountered with this type of apparatus. The condensation of ammonia was slow and inefficient since not more than 12 cm. of liquid could be kept in the cooling bath. A long period of time was required for a preparation. The washing of the precipitate was difficult due to the small volume of wash liquid and the limited number of washings possible in a given period. Only one sample of the substance was obtained from each preparation. The large weight and surface of the reaction tube made the numerous weighings less accurate. These disadvantages resulted in the use of a longer reaction tube and Dewar tube (35 cm.) and the transferring of the substance to small sample tubes.

COMPOSITION OF SODIUM ZINC.

Before presenting the results obtained in this study of the reaction between sodium and zinc cyanide in liquid ammonia, the data of Kraus and Kurtz[2] will be briefly presented. Their results were given in terms of the ratio of atoms of sodium to mols of zinc cyanide taking part in the reaction. From the equation:

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

it can be seen that this ratio should have the value 2.25 under ideal conditions. A value greater than this indicates that free sodium should be present at the endpoint, which would be shown by a blue color, or that the sodium zinc compound has a composition richer in sodium than that indicated by $NaZn_4$. A ratio smaller than 2.25 would indicate that excess zinc cyanide should remain in solution or that the composition of the sodium zinc compound is richer in zinc than that represented by $NaZn_4$. The lowest value of the ratio possible would be 2.0, and this would indicate that the precipitate was pure zinc. The results of Kraus and Kurtz on four determinations are given below.

Table II.

Ratio	Observation
2.29	solution light blue
2.24	colorless
2.23	colorless
2.29	nearly colorless

In view of these results, the ratio was accurately checked in only three experiments during this investigation, and these results are given in Table III.

Table III.

No.	Vol. of soln.	gms. Na	gms. $Zn(CN)_2$	Ratio	Observation
A30	97 cc.	0.3459	0.8109	2.18	colorless
A31	84 cc.	0.3288	0.7705	2.16	colorless
A32	108 cc.	0.2432	0.5535	2.26	slightly blue

In general the quantities of sodium and zinc cyanide were calculated from the equation, and these amounts added to liquid ammonia in the manner already described. In every case it was found that the solution remained blue, and this was discharged by adding a little more salt, never more than a trace being required. The low value of the ratio and the necessity of adding more than the calculated weight of zinc cyanide, was due to the loss of some of the salt during the process of addition, through sticking to the funnel and walls of the reaction tube. This source of error was avoided by Kraus and Kurtz by use of a slightly different apparatus.

In order to get a confirmation of the composition of the substance it was necessary to carry out an analysis. The first requisite here was to obtain accurately the weight of the sample. This was found to be quite difficult with the very reactive substance concerned. The procedure finally used was as follows. The tube containing the substance was connected to a vacuum pump and evacuated to a pressure below 0.05 mm. of mercury. The stopcock was then closed and the tube disconnected and weighed. The weight of the sample was obtained by subtracting from the above weight the weight of the empty evacuated tube, obtained after the completion of the experiment.

The next step in the analysis was to dissolve the sample, and remove it from the sample tube without loss. This was sometimes complicated by the fact that it was desirable first to oxidize, hydrolyze or otherwise treat the sample. These procedures are described in detail farther on, but in every case the final operation was treatment with a 6 N hydrochloric acid solution, which completely dissolved the sample. Such a treatment was carried out by placing the end of the side arm of the evacuated sample tube beneath the

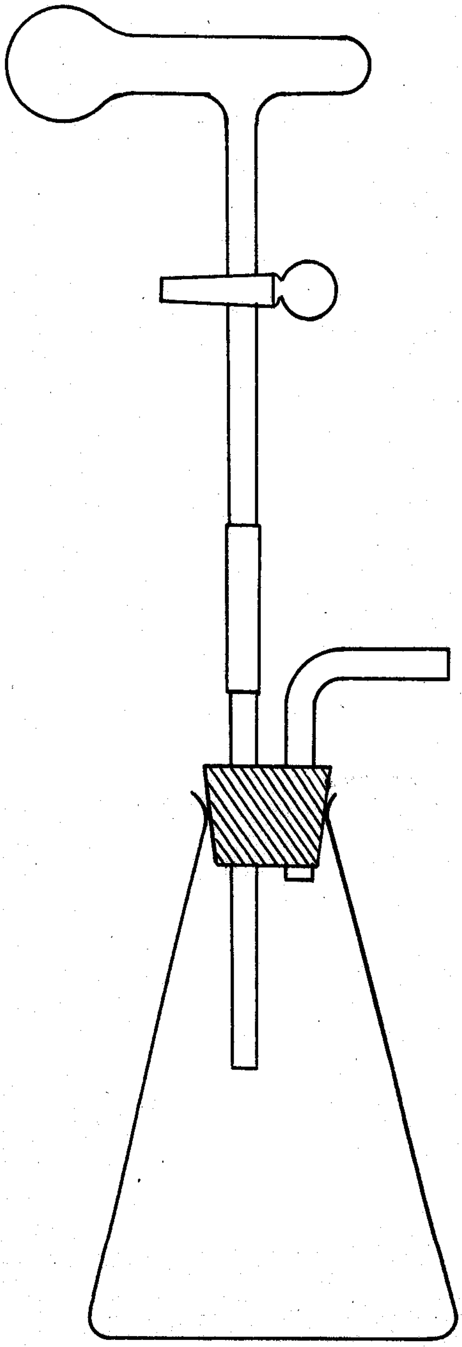

Fig. 3

surface of the hydrochloric acid, and opening the stopcock of the evacuated tube until about 3 cc. of acid had entered. It was necessary that the stopcock be closed before the hydrogen evolved created sufficient pressure to force the solution out of the side arm of the tube. In order to allow this hydrogen to escape without losing any of the solution the sample tube was connected to an apparatus as shown in Fig.3. The stopcock was then opened and any solution forced out went into the conical flask. When complete solution had occurred, suction was applied and the tube manipulated so that all the solution was forced into the conical flask. After closing the stopcock, the tube was disconnected and some water was allowed to enter. Air was then let in, the tube shaken, and the water withdrawn in the same way as the solution. By repeating this procedure as often as desired the tube was thoroughly washed out and the solution completely transferred to the conical flask. It was then necessary to rinse the tube through which the solution passed and lastly to transfer the solution to a beaker or a volumetric flask, depending upon whether the entire sample or aliquot portions were to be analyzed. Any insoluble residue such as glass wool from the filter was filtered off and weighed, and the necessary correction to the sample weight made.

Several methods of determing zinc were tried, including electrolytic deposition, the volumetric method of titration with potassium ferrocyanide and the gravimetric method involving precipitation of $ZnNH_4PO_4$. The latter was found to be most satisfactory, ordinarily giving values that checked to within 0.1%.

The values for the zinc determination in the product of the reaction of sodium and zinc cyanide as first carried out varied appreciably and did not agree with any definite formula. After the improved procedure for handling the substance was developed, the results were quite consistent. Table IV gives the results of all the determinations of zinc in samples which were prepared for analysis by the improved method.

Table IV.

No.	Substance	Aliquot	$ZnNH_4PO_4$ gms.	Zn found gms.	Zn calc. gms.	% Zn calc.	% Zn found
A20	1.0578	(0.1)	0.2636	0.0966	0.0971	91.9	
		(0.1)	0.2635	0.0965			91.4
A21	1.2703	(0.1)	0.3020	0.1114	0.1167		
		(0.1)	0.3014	0.1110			87.3
A23	1.0459	(0.1)	0.2635	0.0965	0.0960		
		(0.1)	0.2643	0.0970			92.5
A24	0.9017	(0.1)	0.2415	0.0885	0.0829		
		(0.1)	0.2411	0.0884			98.2
A30	0.2074	(1)	0.5155	0.1890	0.1908		91.2
A31	0.1295	(1)	0.3243	0.1188	0.1190		91.6
A32a	0.0778	(1)	0.1960	0.0718	0.0715		92.4
A32b	0.0851	(1)	0.2144	0.0787	0.0783		92.4
A32c	0.1479	(1)	0.3700	0.1358	0.1358		91.9

The values given in the several columns are, from left to right, the number of preparation and sample, the weight of substance taken for analysis, the portion of sample which was analyzed, the weight of $ZnNH_4PO_4$ obtained, the weight of zinc found, the weight of zinc calculated for pure $NaZn_4$, the % zinc calculated for pure $NaZn_4$, and the % zinc actually found. All the above analyses were made on samples prepared by adding to liquid ammonia the calculated quantities of sodium and zinc cyanide, with a very slight excess of the latter except in the case of A 32, where there was a slight excess of sodium at the end of the reaction. Samples A30, A31 and A32 were prepared solely for the purpose of an accurate analysis, and were not treated in any other way, while the other samples were either hydrolyzed, oxidized or heated previous to analysis. In the case of A21 and A24 inconsistencies in the weights of the sample tubes were discovered, due possibly to some mishap in the long period of time during which the hydrolysis experiments were made on these samples. For this reason these two results are to be discarded. The other values indicate quite definitely that the composition of the substance corresponds to $NaZn_4$.

Many of the first samples analyzed contained from 80% to 90% zinc, while the % zinc calculated for $NaZn_4$ is 91.9%. The low zinc content may have been caused by the presence of some substance containing a lower percentage of zinc. The possibilities are zinc cyanide enclosed by the precipitate, zinc amide or an ammonobasic zinc salt such as $ZnNH_2CN$. The fact that none of the samples tested showed the presence of either cyanide or ammonia rather discounts this hypothesis. The low zinc content may also have been caused by the action of air or moisture on the substance before the sample was weighed. This might happen at several places in the procedure and since no visible change in the appearance of the substance accompanies this action it could not be noted except by analysis. In many of these cases the total yield was greater than that calculated from the reacting amounts which also indicated that some oxidation took place.

At the beginning of this investigation it was assumed that an excess of zinc cyanide would have no effect on the reaction, but this was a mistaken assumption. This is shown by analysis of the product of the reactions when an appreciable excess of salt was present.

Table V.

No.	Sodium gms.	$Zn(CN)_2$ gms. calc.	$Zn(CN)_2$ gms. used	$Zn(CN)_2$ gms. excess	% Zn calc. for $NaZn_4$	% Zn found
A25	0.7890	1.7820	2.2776	0.4956	91.9	98.1
A26	0.9280	2.0960	2.5923	0.4956	91.9	95.3
A27	1.0144	2.2910	2.7066	0.4956	91.9	99.3

The first column gives the number of the preparation, the second gives the weight of sodium used, the third the weight of zinc cyanide equivalent to this, the fourth column the actual weight of zinc cyanide used, the fifth column the excess zinc cyanide, the sixth the calculated percent zinc for $NaZn_4$ and the last the percent zinc found. These values seem to indicate what when an excess of zinc cyanide is used some metallic zinc is formed. It is also worth noting that this precipitate settles out immediately and completely, and after drying is gray in color. Apparently either a simple displacement reaction takes place:

$$2\ Na + Zn(CN)_2 = 2\ NaCN + Zn,$$

or the compound is formed and then decomposed, altogether or in part, according to the following equation:

$$2\ NaZn_4 + Zn(CN)_2 = 2\ NaZn + Zn(Zn_4)_2.$$

The latter has been observed to be the case with those metallic compounds which are soluble in liquid ammonia. At any rate it is evident that the compound of sodium and zinc does not form in the presence of excess zinc cyanide.

It was also desired to check up on the sodium content of the substances but the work in this direction was not successful by methods of direct analysis. All the gravimetric methods for the determination of sodium involved the separation of sodium and zinc in a mixture where the weight of zinc was ten times that of the sodium. The first method tried was oxidation and then hydrolysis of the sample, since it was hoped that the sodium would enter the soluble portion while the zinc remained in an insoluble form. It was found however that some of the sodium remained in the insoluble portion. Attempt was next made to use the sulfide separation but this was quite unsatisfactory since the relatively large zinc sulfide precipitate apparently adsorbed a large portion of the sodium present. The precipitation of zinc by a known excess of sodium carbonate was discarded for reasons similar to those given for the sulfide separation. The electrolytic separation of zinc in ammoniacal solution was not successful due to incomplete precipitation of the zinc. Doubtless with a sufficient expenditure of time this method could be developed to give satisfactory results. Due to the failure of these direct methods of analysis, some indirect methods were tried.

It is evident that the total volume of hydrogen evolved when the sample reacted with 6 N hydrochloric acid should be a measure of both the sodium and zinc present. Considerable experimental difficulties were encountered due to the pressure exerted by the hydrogen generated in the small sample tube. The hydrochloric acid was let into the tube in the same manner as described under solution of the sample and the tube was then connected to a Toepler pump. Evacuation was begun immediately so as to relieve the pressure inside the sample tube. If this were not done the gas might generate enough pressure to loosen the stopcock from its socket. The gas was completely transferred to a burette over water, and its volume measured. It was analyzed by explosion with air. The results of such an experiment are given in Table VI.

Table VI.

	32a	32c
gms. substance	0.0778	0.1479
Total cc. gas (corrected)	28.4	54.7
% hydrogen in gas	96.7	97.1
Total cc. hydrogen	27.4	53.1
% zinc in substance	92.4	91.9
cc. hydrogen equivalent to zinc	24.5	47.2
cc. hydrogen equivalent to sodium (found)	2.9	5.9
cc. hydrogen equivalent to sodium (calc.)	3.1	5.8

The first line gives the grams of substance used in the experiment, the second the volume of gas (corrected to 0° and 760 mm.), the third the percent hydrogen in the gas, the fourth the total volume of hydrogen collected, the fifth the percent zinc in the sample, the sixth the volume of hydrogen equivalent to the zinc, the seventh the volume of hydrogen actually found equivalent to the sodium, and the last the calculated volume of hydrogen equivalent to the sodium. The agreement of the values in the last two lines establishes that the amount of sodium present agrees with the formual $NaZn_4$.

It appears then, from the results of determinations of the zinc content, and from the volume of hydrogen evolved on reaction with hydrochloric acid, that the compound $NaZn_4$ is formed by the reaction according to the following equation:

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

This confirms the results of Kraus and Kurtz, which were determined from the amount of sodium and zinc cyanide interacting.

PROPERTIES OF SODIUM ZINC.

OXIDATION.

A few qualitative experiments of Kraus and Kurtz indicated that the product of the reaction of sodium and zinc cyanide was very active toward air and water. With this as a starting point a number of experiments were carried out in this investigation, with the idea of establishing quantitatively the reactions taking place when sodium zinc reacted with dry oxygen, dry air, moist oxygen and moist air.

The oxidation reactions were carried out in two different ways. One of these involved the measurement of the volume of oxygen taken up, and the other method made it possible to obtain both the weight and volume of oxygen reacting with the substance. The apparatus employed is shown in Fig.4. The essential parts were a differential manometer (RR′), which served to indicate the pressure in the system, a burette (M) for measuring the gas entering the system, a sample tube sealed to the system at A, and connections to a vacuum pump.

In case only the volume of oxygen reacting with the sample was desired the procedure was as follows. The tube containing the sample to be oxidized was sealed to the

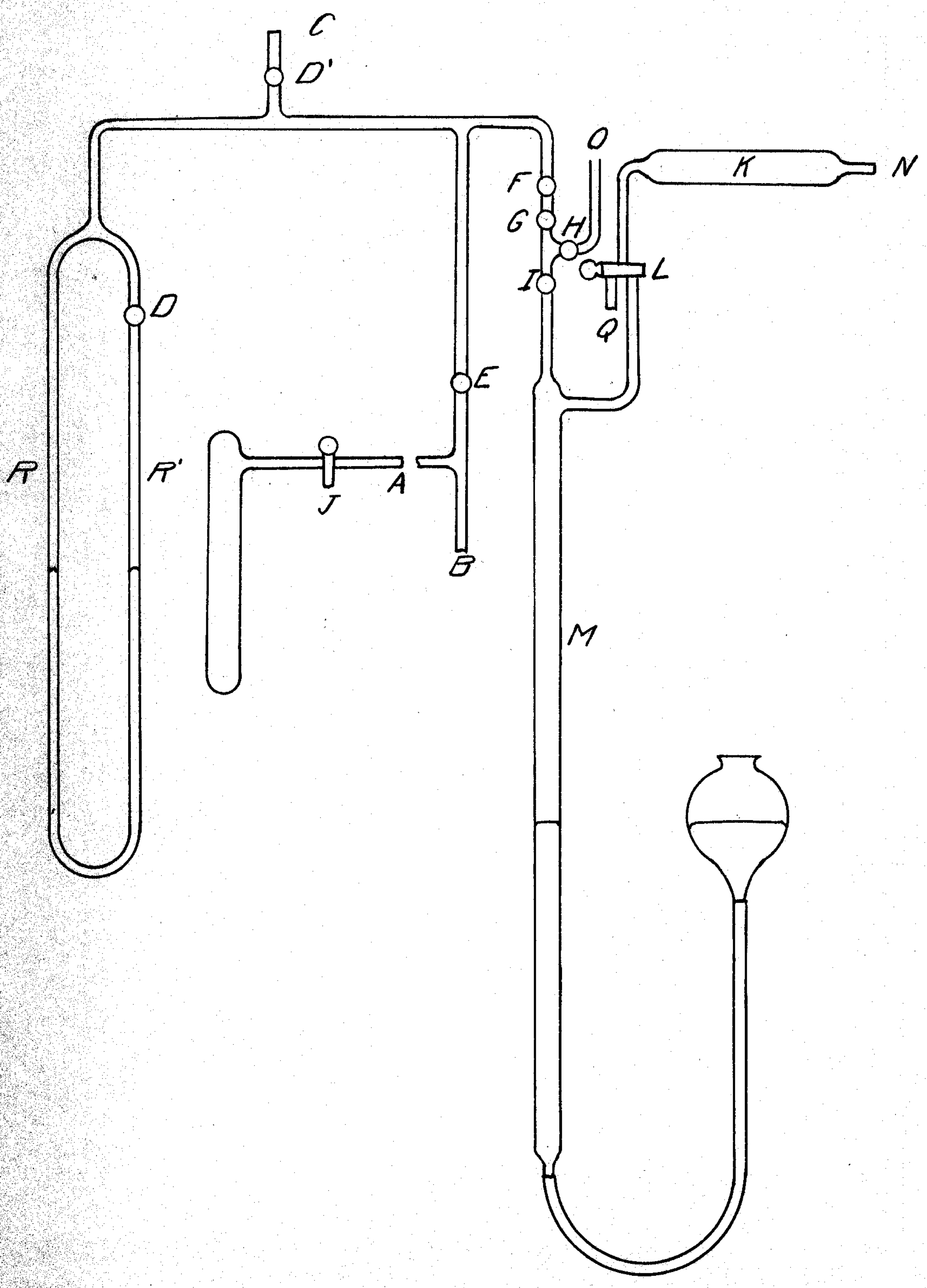

Fig. 4

system at A, pressure for blowing being obtained by connecting to B, which was later sealed off. The system was then evacuated through C while the stopcocks D, D', E were open, and F closed. When the pressure had reached 0.05 mm. the stopcock J was opened and the sample tube evacuated to the same pressure, after which D and D' were closed. While this was being done the burette M was filled with dry oxygen. This was accomplished by first filling the burette to stopcocks I and L with mercury, suction for this being obtained through O. On lowering the levelling pear sufficiently the level of the mercury dropped below P. Oxygen was then passed in through the drying tube K, and out through Q, until all the air in that part of the system was displaced. The stopcock L was then turned so that the dry oxygen entered the burette. When about forty cc. had entered, L was closed and the burette read.

With the entire system to stopcock I evacuated to below 0.05 mm. and the burette filled with dry oxygen, everything was ready for the actual oxidation of the sodium zinc. Stopcock I was opened to let a little oxygen into the rest of the system. If it was necessary to let oxygen in very slowly, stopcocks F and G were used; otherwise they were left open. After the desired volume of gas had entered the system, I was closed and the burette reading again taken. The pressure in the system was shown by the difference in level of the mercury columns in R and R'. The progress of oxidation was followed by noting the decrease in pressure as shown by the gage. When the reaction had stopped, the gage was accurately read, and then the system evacuated through C. The volume of the oxygen in the system at the end of the reaction could be obtained by measuring the volume of gas that must be added to the system to give the same pressure reading on the gage as that at the end of the reaction. Actually this residual volume was determined by plotting a number of gage readings obtained when different volumes of gas were added against the corresponding volumes of gas. This gave practically a straight line over the range considered. The volume of the system corresponding to the final gage pressure was then read from this graph. The difference between the volume of oxygen originally let in, and that remaining after oxidation was completed, gave the volume which reacted with the sample.

In case it was desired to obtain both the volume and the weight of oxygen interacting with the sample the following procedure was used. The previously weighed sample tube containing the substance to be oxidized was fastened to the oxidizing system in the same position as in the first method, but by means of firmly wired rubber tubing rather than a glass seal. The procedure was the same as given above. After oxidation the tube was evacuated and weighed, and the increase in weight taken as that of the oxygen reacting.

The oxidation reaction is divided into two distinct stages. At first oxygen is taken up rapidly, and considerable heat is evolved, but no noticeable change in the appearance of the sodium zinc takes place. This primary oxidation is complete in a half-hour's time, but is followed by a secondary reaction which proceeds at a very slow rate for a long period of time, accompanied by a change in the color of the substance from black through gray to white. Dry air acts in the same manner as dry oxygen. All of the above is born out by the quantitative data given in Tables VII, VIII, and IX. Tables VII and VIII give the data obtained in all the oxidations with dry oxygen and dry air respectively.

Table VII.

Dry Oxygen at Room Temperature.

No.	gms. $NaZn_4$	cc. oxygen	gms. oxygen	mgm. atoms oxygen	millimols $NaZn_4$	Ratio
S5	0.6460	12.16	0.0174	1.086 ✓	2.271	.48
A3	0.4452	10.60	0.0151	0.946 ✓	1.565	.60
A6	0.3506	7.02	0.0100	0.628 ✓	1.232	.51
A7	0.4101	8.37	0.0119	0.747 ✓	1.441	.52
A8	0.6084	10.66	0.0152	0.952 ✓	2.138	.45
A9	0.4298	8.58	0.0120	0.499 ✓	1.519	.51
A10	0.4701	14.12	0.0202	1.261 ✓	1.652	.76
A12	0.4155	9.72	0.0139	0.868 ✓	1.460	.59
A15	0.5220	10.14	0.0145	0.906 ✓	1.831	.49
A15	0.5220	----	0.0158	0.988	1.831	.54

Table VIII.

Dry Air at Room Temperature.

A30	0.1244	----	0.0031	0.194	0.438	.45
A31	0.1295	----	0.0036	0.225	0.454	.49

The first column of each table gives the number of the preparation, the second the weight of sodium zinc used, the third the volume of oxygen reacting with the sodium zinc, the fourth the weight of oxygen reacting, the fifth, milligram atoms of oxygen as calculated from column four, the sixth the milligram mols of sodium zinc as calculated from column two, and the last the ratio of atoms of oxygen to mols of sodium zinc. The checked values in column four were calculated from the volume of oxygen in column three. All the values given were determined shortly after the primary reaction was complete.

The majority of the values for the ratio lie somewhere near 0.5. This means that two mols of the sodium zinc compound react with an atom of oxygen. This is exactly what would be expected as the result of the oxidation of the electronegative zinc anion to free zinc. This might be expressed:

$$2\ Na^+ + 2(Zn_4^-) + O = 2\ Na^+ + O^= + 8\ Zn.$$

It might be said that oxygen acquires the electrons from the zinc, i.e. displaces the zinc from its compound with sodium. That sodium oxide seems to be formed, rather than sodium peroxide, is in itself evidence that the sodium and zinc are chemically combined, since free sodium does not give the monoxide in direct oxidation.

The considerable variation in the values of the ratio given in tables VII and VIII indicates that something besides the simple oxidation reaction is taking place. The low values are no doubt due to the fact that some of the substance was oxidized before the measurements were begun, since all these experiments were done before the apparatus and technique had been perfected. Some of the values of the ratio are somewhat high. These are due to the secondary oxidation which ordinarily takes place at a slow rate after the rapid primary oxidation is completed. The extent to which the secondary oxidation takes place is shown by experiments in which two samples (A7 and A8, Table VII) were exposed to dry oxygen at room temperature for a period of four weeks after the primary oxidation was complete. The results are given in Table IX.

Table IX.

Secondary Oxidation at Room Temperature.

No.	gms. $NaZn_4$	gms. oxygen (1/2 hr.)	Ratio (1/2 hr.)	gms. oxygen (4 wks.)	Ratio (4 wks.)
A7	0.4101	0.0119	.52	0.0174	.75
A8	0.6084	0.0152	.45	0.0263	.77

The first column of the table gives the number of the sample, the second column the weight of sodium zinc, the third column the weight of oxygen taken up in the primary oxidation, the fourth column the ratio (atoms of oxygen to mols of sodium zinc) for the primary oxidation, the fifth column the weight of oxygen taken up after four weeks, and the sixth column the ratio after four weeks. At the end of the four weeks the reation was still proceeding slowly but the experiments were discontinued. The difference between the ratio for the primary oxidation and the ratio after four weeks shows the slow rate of the secondary reaction.

An experiment in which a sample (S5, Table VII) was exposed to dry oxygen at a temperature of 150° C. for twelve hours showed that the secondary oxidation was much more rapid at such a temperature. Table X gives the data for this experiment.

Table X.

Secondary Oxidation at Higher Temperatures.

		After 1/2 hour Room temp.		After 12 hours 150°C.	
No.	gms. $NaZn_4$	gms. oxygen	Ratio	gms. oxygen	Ratio
S5	0.6460	0.0174	.48	0.1342	3.70

The final value of the ratio represents enough oxygen to oxidize the sodium to sodium monoxide and 80% of the zinc to zinc oxide. That all of the zinc was not oxidized may very well be explained by the formation of a protective layer of the oxide. Evidently the secondary reaction is due to the oxidation of the metallic zinc formed in the primary oxidation.

Values appreciably higher than those obtained with dry oxygen are obtained if the oxidation is carried out with moist oxygen or moist air at room temperature. This action is accompanied by a greater evolution of heat and the substance becomes gray or white in color. A much larger proportion of oxygen is taken up, as is shown in Table XI.

Table XI.

Moist Oxygen and Moist Air.

No.	gms. $NaZn_4$	cc. oxygen	gms. oxygen	mgm. atoms oxygen	millimols $NaZn_4$	Ratio
A4	0.4418	21.51	0.0307	1.921	1.552	1.2
A14	0.1806	7.13	0.0129	1.018	0.505	2.0
A16	0.5274	----	0.0912	5.700	1.855	3.1

The headings used in this table are the same as those in Table VII. Samples A4 and A14 were treated with moist oxygen, while sample A16 was treated with moist air. The moisture probably catalyzes the oxidation of the zinc formed by the primary reaction. Also the larger amount of heat liberated may increase the amount of secondary oxidation taking place. This view is supported by the behavior of the product obtained by the action of dry oxygen when it is exposed to moist air. If some is transferred to a dry beaker no apparent action takes place but if a drop of water is added, a violent reaction occurs, beginning where the substance was moistened and spreading rapidly. The latter becomes red hot during this change, and on cooling somewhat is yellow, and then finally white. This change from yellow to white as the temperature drops shows the presence of zinc oxide.

The results of a quantitative investigation of the reaction of oxygen with sodium zinc show that a rapid oxidation takes place with liberation of heat and the displacement of the zinc by oxygen. The zinc thus formed is slowly oxidized at room temperature, but much more rapidly at high temperatures or in the presence of moisture.

HYDROLYSIS.

The reaction of the sodium zinc compound with water was also investigated from a quantitative point of view. In experiments in which sodium zinc was hydrolyzed by liquid water the procedure was as follows. The end of the side arm of the sample tube, previously evacuated, was placed beneath the surface of water and the stopcock opened until a few cc. had run in on the sample. The tube was evacuated from time to time with a Toepler pump, the gas collected over water, and its volume measured. It was then analyzed by explosion with air. Table XII gives the results of these experiments as far as they have been carried at present.

Table XII.

Hydrolysis with liquid water.

No.	gms. $NaZn_4$	cc. hydrogen obtained	Total cc. hydrogen calc.	cc. hydrogen (equiv. to Na)	Equivalents hydrogen per mol $NaZn_4$
A18	1.1316	189.0	396.7	44.1	4.3
A19	1.9280	334.6	687.6	76.4	4.4

The first column gives the number of the sample, the second the weight of sodium zinc, the third the total volume of hydrogen collected from the sample, the fourth the total volume of hydrogen which should be evolved by the complete decomposition of the sample, the fifth the volume of hydrogen equivalent to the sodium in the sample, while the last column gives the number of equivalents of hydrogen obtained per mol of sodium zinc. The values in the third and last columns are low, since some gas was lost in each case due to accidents. Only a very slight liberation of heat occurred, when the water first came in contact with the substance. The rate of evolution of hydrogen was very rapid during the first week (20 cc. per day) and then gradually decreased, so that at the end of a month it was about 1 cc. per day, and after 10 weeks it was less than 0.1 cc. per day. During this time a white precipitate gradually appeared in the tube, and the sodium zinc sample became gray in color.

The volume of hydrogen liberated allows of only one conclusion, and that is that the zinc displaces hydrogen from water. The reason the rate of reaction slows down with time is probably the formation of a protective layer of zinc hydroxide. The first equivalent of hydrogen evolved is easily accounted for by the reaction:

$$NaZn_4 + H_2O = 1/2\ H_2 + NaOH + 4\ Zn.$$

Since zinc displaces hydrogen from a sodium hydroxide solution, a second equivalent can be accounted for by the reaction:

$$NaOH + 1/2\ Zn = 1/2\ Na_2ZnO_2 + 1/2\ H_2,$$

although this would probably not go to completion. However, this would account for less than half of the hydrogen actually evolved, so it is necessary to assume that a catalyst for the reaction,

$$Zn + 2\ HOH = Zn(OH)_2 + H_2,$$

is present, or that the zinc is in an "activated" form. The latter is the more probable, since the zinc is present in a finely divided form, and furthermore has been set free from a compound by oxidation in contrast to the ordinary liberation of metallic zinc from a compound by reduction.

A few experiments were carried out in which the sodium zinc compound was hydrolyzed by water vapor. In this case only a very little water in liquid form was let into the side arm, and the sample tube was so manipulated that the liquid water could not run down on the sample. The tube was evacuated and the hydrogen collected from time to time, and the water replaced in the side arm after each evacuation. Unfortunately all of these experiments met with some sort of an accident so that no quantitative data can be given. However, the results were of the same nature as those obtained with liquid water, except that the reaction took place much more slowly. In every case considerably more than one equivalent of hydrogen per mol of $NaZn_4$ was collected.

While the experiments on hydrolysis show conclusively that at least four equivalents of hydrogen are evolved per mol of sodium zinc, they are incomplete in many respects, and further work should be done along this line.

MISCELLANEOUS PROPERTIES OF SODIUM ZINC.

Experiments were carried out to determine the nature of the gas given off on heating the sodium zinc samples, to show the action of nitrogen on sodium zinc, and to determine the action of an ammono acid, ammonium nitrate, on a suspension of sodium zinc in liquid ammonia.

In order to determine the nature of the gas given off on heating, the tube containing the sample was evacuated to 0.05 mm. and weighed. It was then heated on a water or oil bath for a period of time, and finally the tube was evacuated with a Toepler pump and then weighed again. Since the volume and also the weight of the gas could be determined, it was possible to get a value for its density. The gas was analyzed for hydrogen by explosion with air. Tests made for carbon dioxide and oxygen gave negative results. Furthermore there was no gas present which was soluble in water. Table XIII gives the results of these experiments.

Table XIII.

No.	gms. $NaZn_4$	hours heated	Temp. °C.	cc. gas	gms. gas	Density H = 2.016	% hydrogen in gas
A23	1.0417	19	100°	1.1	0.0011	22.4	---
		25	160°	1.8	0.0022	27.4	12
A24	0.9023	19	100°	3.7	0.0005	3.9	90
		13	100°	0.6	----	---	10
		24	160°	1.8	----	---	75

Experiments on the same sample were carried out successively. Apparently both hydrogen and nitrogen are evolved on heating the substance but the amounts are insignificant.

A few experiments were made to determine the action of nitrogen on sodium zinc. At room temperature there was no indication of any action.

Ammonium nitrate was added to a suspension of sodium zinc in liquid ammonia. Bubbles of gas began to be evolved from the precipitate and caused it to float in the liquid. After a time the action slowed down but increased when a little more ammonium nitrate was added. On removing some of the particles of precipitate to the atmosphere they sparked vigorously, leaving a white powder. This sparking in air is a characteristic property of sodium zinc, and indicates that the ammonium nitrate decomposes sodium zinc at a relatively slow rate.

In one experiment some mercury was accidentally allowed to enter the reaction tube and thus came into contact with the sodium zinc. This sample of sodium zinc showed no action at all towards dry oxygen at room temperature. The mercury was afterwards poured from the sodium zinc and dropped into water where it gave off a gas, indicating the presence of sodium amalgam.

PREPARATION AND PROPERTIES OF OTHER METALLIC COMPOUNDS.

Among the numerous reactions studied by Kraus and Kurtz[2] were those between sodium and mercuric cyanide, and between calcium and zinc cyanide. An attempt was made to extend their results but the work remains incomplete at present so that only a brief preliminary report will be given. The apparatus and procedure were essentially the same as previously discussed, so that a description of these will be omitted.

When mercuric cyanide was added to a solution of sodium in liquid ammonia much heat was liberated and the liquid boiled vigorously. If the sodium and mercuric cyanide were added in the proportions given by the equation:

$$5\ Na + 2\ Hg(CN)_2 = NaHg_2 + 4\ NaCN$$

the solution became colorless and a black precipitate settled out. This was washed thoroughly but no attempts were made to analyze it. It was exposed to the action of dry oxygen but was entirely inactive at room temperature. At higher temperatures a slow oxidation took place but no quantitative results were obtained. The product of the oxidation evolved a gas when it was dropped into water. No conclusions can be drawn from these experiments until further work is done.

Calcium behaves somewhat differently from sodium when it is dissolved in liquid ammonia. Two liquid phases are formed unless the concentration of calcium is very low. One of these phases is blue in color, while the other is bronze colored. Kraus and Kurtz found that the ratio of atoms of calcium to mols of zinc cyanide necessary to decolerize the solution was 8.0, as given by the equation:

$$8\ Ca + Zn(CN)_2 = Ca(CN)_2 + Ca_7Zn.$$

Four experiments of this nature were carried out during this investigation, but in each case the solution remained blue after the zinc cyanide had been added. This blue was discharged by adding more zinc cyanide and in this way it was found that the solution usually became colorless when the ratio had a value of four atoms of calcium per mol of zinc cyanide, the actual results varying from three to five. The product of the reaction was a very finely divided black precipitate which had no tendency to settle, and so the end point was difficult to determine. Analysis of some of the substance indicated that the relative amounts of calcium and zinc present were somewhere near those required by the above ratio (4.0) of calcium to zinc cyanide. But only about 60% to 70% of the weight of the sample was accounted for. At least part of the remainder was ammonia, since a qualitative test indicated the presence of this in considerable amounts. The product obtained was not very active toward either air or water. On exposure to air a very little heat was liberated but no change in appearance took place even after a period of six weeks. Liquid water caused the evolution of a small amount of hydrogen at first, while water vapor converted the black powder into a white substance in the course of a month's time. A quantitative study of the product of the reaction of calcium and zinc cyanide should give worth while results.

SUMMARY.

1. An experimental method has been developed so as to make possible the purification and quantitative study of highly reactive metallic substances formed in liquid ammonia solution.

2. By means of the above method, it has been shown through analysis that the product of the reaction between sodium and zinc cyanide in liquid ammonia is a compound of sodium and zinc of the formula $NaZn_4$.

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

3. If zinc cyanide is present in considerable excess of the amount called for by the equation, the product of the reaction is metallic zinc.

4. A quantitative study of the action of gaseous oxygen on sodium zinc showed that the reaction takes place in two distinct stages.

5. At room temperature one atomic weight of dry oxygen is absorbed by two molecular weights of sodium zinc in a half an hour. This leads to the view that sodium monoxide and zinc are produced.

$$2\ NaZn_4 + O = Na_2O + 8\ Zn.$$

6. The rapid primary oxidation is followed by a secondary oxidation which proceeds at a very slow rate at room temperature, but much more rapidly at a temperature of 150°C. It is probable that this is due to the oxidation of the zinc liberated in the primary action.

7. The product of the primary oxidation and also sodium zinc itself, react with a much larger proportion of oxygen in the presence of moisture. It seems that the rate of the secondary oxidation is increased due both to the catalytic action of the moisture and to the heat which it liberates.

8. Water in liquid form reacts with sodium zinc to give at least four equivalents of hydrogen per mol of sodium zinc. The only conclusion possible is that the zinc reacts with the water, probably because it is activated by being freed by oxidation rather than reduction.

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