SOME REACTIONS OF SODIUM-BISMUTH

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INTRODUCTION

SOME REACTIONS OF SODIUM-BISMUTH
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INTRODUCTION

The formation of alloys of sodium and bismuth and of sodium and lead were first noted by Gay Lussac and Thenard (1) when a mixture of the two metals were melted together. Alloys of these metals have since been observed to be formed in a number of different reactions in liquid ammonia.

Indications of compound formation in these systems was found in the freezing point curves of the alloys. Mathewson (2) observed that in the sodium-bismuth system there was a maximum at 775°C. corresponding in composition to the compound Na_3Bi. He also reported an incongruent melting point at 445°C. for the compound $NaBi$.

In liquid ammonia Joannis (3) obtained a compound approximating Na_3Bi by the action of a solution of sodium on a stick of bismuth metal. This bismuthide was described as being bluish-violet in color and is rapidly oxidized in moist air. There can be but little doubt that Joannis' compound was identical with the compound having the same composition found in the phase diagram.

Mathewson (2) also studied the sodium-lead system and found that there were four maxima on the freezing point curve which he identified as belonging to the following compounds: Na_4Pb, Na_2Pb, $NaPb$, and Na_2Pb_5. Later work by Calingeart and Boesch (4) indicated that the compound Na_2Pb existed, but that the maximum

actually corresponded to the compound Na_5Pb_2. In addition, on the basis of their X-ray analyses, Zintl and Harder (5) were able to show that the compound, originally thought to be Na_4Pb and later analyzed as $Na_{31}Pb_{18}$ by Stillwell and Robinson (6), was more accurately represented by the formula $Na_{15}Pb_4$. The crystals used by these workers were made by melting lead with excess sodium and extracting the free sodium with liquid ammonia. The compounds of sodium and lead, like those of sodium and bismuth, also oxidize readily in air and decompose in water.

Zintl and his co-workers (7) have extensively investigated reactions of sodium in liquid ammonia with S, Se, Te, As, Sb, Pb, Sn, Bi, Zn, Cd, Hg, Cu, Ag, and Au. They concluded that the elements belonging to the first, second or third groups of the periodic table formed only insoluble metallic compounds with atomic lattices, whereas the elements of the later groups formed soluble intermetallic compounds as well. Zintl has named these ammonia-soluble substances "polyanionic" salts and has described them as being similar in constitution to the polyhalides and polysulphides.

In his experimental work Zintl found that upon the addition of the more electronegative or amphoteric elements such as Pb, Sn, Sb, Bi, As, and S (or their binary compounds) to liquid ammonia solutions of sodium there was first obtained simple compounds of the type K_2S, Li_3As, etc.; these, for the most part, were partly soluble in liquid ammonia and reacted further to form compounds of the type K_2S_2, Na_3As_7, Na_4Pb_9, etc. These compounds were easily soluble in liquid ammonia to give very intensely colored electrically conducting solutions. It should be noted,

however, that Kraus (8) in the course of his investigations into the nature of electrically conducting solutions of metals in ammonia had observed much earlier the solubility of the sodium-lead compounds in liquid ammonia, and Smyth (9) had demonstrated the migration of lead to the anode and sodium to the cathode during electrolysis.
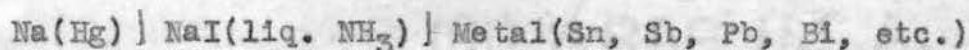
The elucidation of the composition of these substances in solution was accomplished, however, by the use of an exacting experimental technique developed by Zintl. The action of an excess of sodium on a solution of a salt of these metals in liquid ammonia was carried out in a specially designed titration apparatus. The course of the reactions was followed by conductometric and potentiometric titrations. The compounds formed with bismuth and lead were found to be Na_3Bi (black ppt.), Na_3Bi_3 (deep violet), Na_3Bi_5 (brown), Na_4Pb_7 (green), and Na_4Pb_9 (green).

Most of these compounds are different from the ones found in the study of the alloy phases by thermal analysis. In liquid ammonia solution these polyanionic salts are assumed to be in the form of ammines, such as $[Na(NH_3)_x]_4^+ - [Pb_9]^{-4}$. Upon the removal of the solvent ammonia, amorphous solids result which on deammonation are transformed into binary alloys, which in some cases are mixed with free metals. The resulting alloys are identical with those which separate from molten mixtures of the two components having the same atomic percentage (10, 11).

The colloidal nature of the ammonia solutions of the poly-anionic salts has received attention also. Zintl detected with the ultramicroscope negatively charged aggregates of the poly-anions. He suggests that perhaps the dissolution of lead by

liquid ammonia solutions of sodium may be a peptization in which the peptized materials are combined in stoichiometric proportions. The pronounced pleochroism of these solutions is in accord with Zintl's observations.

Further insight into the salt-like character of the metal-sodium compounds is found in the energy effects accompanying their formation. Kraus (12) has estimated the free energy of formation from cells of the type:

$$Na(Hg) \mid NaI(liq. NH_3) \mid Metal(Sn, Sb, Pb, Bi, etc.)$$

Although the exact composition of the compound formed at the electrode was not known, it was predicted to be the most insoluble one; e.g., Na_3Bi. Thus, he found for $NaPb_x$ and $NaBi_x$ respectively 39.1 and 44.2 kilo-calories per mole of sodium. This data, by comparison with the free energy of formation of substitutional type alloys, shows that the energy effects are high and indicates that the combinations are salt-like in nature.

The elements may be arranged in an electropotential series in the order of their electron affinity, and it is well known that an electropositive element will displace a less electropositive element from solutions of its salts. Also an electronegative element will displace a less electronegative element from solutions of its salts. Those elements that have the smallest electron affinity are found in an electropositive condition while those with the greatest electron affinity are in an electronegative condition. Between these two extremes are the amphoteric elements which may exist in an electropositive state when in combination with the strongly electronegative elements

or in an electronegative state in combination with the strongly electropositive elements. Salts containing such amphoteric elements in an electronegative state are in general very reactive with water which hinders their study in this solvent. Since many of these salts are soluble and stable in liquid ammonia the electron affinities of these elements can be determined in this solvent.

Bergstrom (13) has attempted to establish the order of the electron affinity of the amphoteric elements in their electronegative condition by means of a study of replacement reactions in liquid ammonia. A liquid ammonia solution of the potassium or sodium salt of Pb, Bi, Sn, Sb, As, P, Te, Se, S, I, and Hg was allowed to react with Zn, Fe, Cu, Pb, Bi, Sn, Sb, As, P, Te, Se, S, I, and Hg. From the results of his study of these displacement reactions he has formulated an electronegative displacement series which is substantially the reverse order of the electropositive series in water. His series was arranged as follows: Pb, Bi(?), Sn, Sb, As, P(?), Te, Se, S, I, with lead apparently being the least electronegative and iodine the most electronegative. The replacement of one element by another was found to be more definite and rapid the farther apart the position of the elements in the series. Some of the replacement reactions led to equilibrium conditions, and the reaction was dependent to some extent upon the concentration of the constituents.

The position of bismuth in the series was not definitely established by Bergstrom because some of the reactions involving bismuth and the polybismuthides were sluggish and inconclusive.

This, he suggested, may have been caused by the formation of a coating of one metal upon the other.

Although the chemistry of intermetallic salts described in the literature is not extensive, the published reactions of these substances with inorganic compounds can be divided into two classes, metathesis and reduction. The first of these is illustrated by the following reaction occurring in liquid ammonia (14):

$$2 \ Ca(NO_3)_2 + K_4Pb_x \longrightarrow Ca_2Pb_x + 4 \ KNO_3$$

This metathesis is analogous to the behavior of ordinary salts in water. An interesting reaction showing the reducing property of the intermetallic salts takes place between a liquid ammonia solution of a lead salt, such as $PbCl_2$, and an intermetallic compound containing lead as the anion. The following equation represents such a reduction (12):

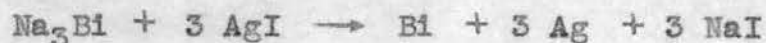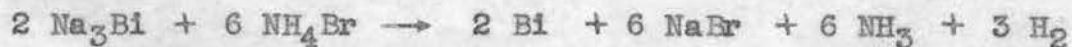$$2 \ PbCl_2 + K_4Pb_9 \longrightarrow Pb_2 \cdot Pb_9 + 4 \ KCl$$

Here the positive lead ion is reduced by the negative plumbide ion to give ordinary metallic lead as a precipitate.

Other reduction reactions have been studied. Johnson and Pechukas (15) have observed that the reduction of ammonium bromide by sodium polyarsenide proceeds almost to completion in accord with the equation:

$$Na_3As_x + 3 \ NH_4Br \longrightarrow 3 \ NaBr + 3 \ NH_3 + AsH_3 + (x-1) \ As$$
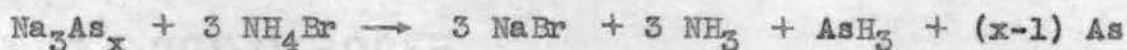
Watt and Moore (16) have also noted the complete reduction of the ammonium ion to hydrogen and silver ion to metallic silver by trisodium monobismuthide.

$$2 \ Na_3Bi + 6 \ NH_4Br \longrightarrow 2 \ Bi + 6 \ NaBr + 6 \ NH_3 + 3 \ H_2$$

$$Na_3Bi + 3 \ AgI \longrightarrow Bi + 3 \ Ag + 3 \ NaI$$

Molecular oxygen is easily reduced by these compounds as shown
by the work of McCleary and Fernelius (17) on the tellurides,
selenides and sulfides and Watt and Moore (16) on the bismuthides.
Some examples are as follows:

$$Na_2Te(Se, S) + O_2 \longrightarrow Na_2Te(Se, S)O_{3\&4}$$
$$4 Na_3Bi + 8 O_2 \longrightarrow 4 BiO + 6 Na_2O_2$$

Lowig (18) was the first to report the reaction of sodium-
lead alloys with organic halides. Since his early work much
interest has been attached to this type of reaction. An example
is shown by the equation:

$$Na_4Pb + 4 C_2H_5I \longrightarrow Pb(C_2H_5)_4 + 4 NaI$$

Many patents have been issued on the application of these alloys
in the formation of plumbanes which have assumed technical impor-
tance in the petroleum industry. A variation of the reaction is
illustrated by the investigations of Foster and co-workers (19)
who have shown that hexaphenyldilead may be prepared by the re-
duction of triphenyl lead chloride with tetrasodium nonaplumbide
in liquid ammonia:

$$4 (C_6H_5)_3PbCl + Na_4Pb_9 \longrightarrow 2 [(C_6H_5)_3Pb]_2 + 9 Pb + 4 NaCl$$
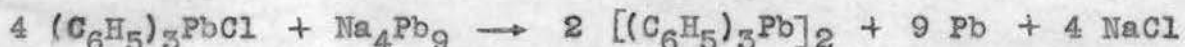
It was believed that a study of the reaction between inter-
metallic compounds and covalent inorganic halides would show the
formation of couplings similar to the ones illustrated above.

PART II

STATEMENT OF THE PROBLEM

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Although much work has been done on the reactions of sodium-lead alloys and their intermetallic compounds with organic halides, little or no information has been obtained on the reaction of substances of this type with the essentially covalent inorganic halides. Therefore, it seemed desirable to investigate such reactions. Phosphorus trichloride was chosen as a typical covalent inorganic halide for this work. It was decided to use the least ammonia-soluble intermetallic compounds of sodium and the Group V_B elements with the view of determining the effect of differences in electronegativity of the anions on the course of the reaction.

The relative electronegativity of the amphoteric elements in their polyanionic state has been studied, and the position of many of these elements has been definitely established. However, because of inconclusive data on reactions involving lead and bismuth, their relative position remains doubtful.

Because of the lack of information and inconclusive data the following problems were outlined for investigation:

FIRST: Prepare in liquid ammonia the compounds Na_3Bi, Na_3Sb, and Na_3As and study their reaction with phosphorus trichloride.

SECOND: Establish the relative electronegativity of bismuth and lead in their polyanionic state.

PART III

EXPERIMENTAL

EXPERIMENTAL

APPARATUS

Liquid Ammonia System: The experiments using liquid ammonia were carried out at approximately -33°C. and atmospheric pressure. These conditions were obtained by enclosing the reactor tubes in a Dewar flask filled with boiling liquid ammonia. The construction and details of operation of such equipment has been described by Johnson and Fernelius (20).

Reactor Tubes: The reactor tubes used in the experiments involving liquid ammonia were similar to those described by Watt and Moore (16). The reactors differed slightly from those of Watt and Moore in that all tubes used in the introduction and removal of materials were attached by means of ground glass joints; and further modification involved the enclosing of both reactors in the same Dewar flask, instead of in two separate ones. This was accomplished by bringing the filter tube through the side of the reactor head and connecting the two by means of a short section of tubing containing ball and socket joints and a stopcock.

Phosphorus Trichloride Purification Apparatus: This apparatus consisted of a micro distillation flask, condenser, and receiver which permitted small samples of phosphorus trichloride to be sealed in a thin glass bulb. The apparatus, shown in Figure I, was assembled and dried by passing dried nitrogen in through the phosphorus pentoxide drying tube and out the top of the distilling flask. Approximately a cubic centimeter of phosphorus pentoxide was introduced into the flask by forcing it

with a glass rod plunger from the end of a glass tube extending to the bottom of the flask. Next, about five milliliters of phosphorus trichloride were run into the flask with a pipette. The thermometer was inserted through the glass sleeve of the flask and connection made by a section of rubber tubing.

The flask was heated by means of an oil bath. The first milliliter or so of phosphorus trichloride that distilled over was caught in the discard tube; the receiver was then rotated so as to put into position the tube containing the stem of the glass bulb. The next two milliliters were caught in this tube.

The glass bulb, which was blown from small glass tubing, was dried carefully before use by passing dried nitrogen into it through a small capillary tube while the bulb was heated and then allowed to cool. Phosphorus trichloride was drawn into the bulb by repeated heating and cooling. When the bulb was nearly filled, it was sealed off with a small flame from an oxygen torch. The weight of phosphorus trichloride in the bulb was found from the difference in weight of the empty bulb and the combined weight of the filled bulb and the stem remaining.

Reaction Apparatus: The apparatus used in carrying out reactions of phosphorus trichloride with trisodium monobismuthide is shown in Figure II. This apparatus was equipped with a special means for introducing phosphorus trichloride. It consisted of a dropping funnel containing ligroin attached to a cup-like receiver by means of a rubber stopper. This receiver, which was used to hold the bulb filled with phosphorus trichloride, had attached at the bottom a tube which extended into the reactor. The receiver

also contained a glass rod used to break the bulb. The apparatus was swept continuously with dry nitrogen which was introduced through a glass tube and removed by means of a side connection attached to a water jacketed condenser.

After reaction the products were hydrolyzed in situ by substituting a different head, which is shown in Figure II. This head consisted of a ground glass joint having a glass tube extending through a ring-seal in the top. The gaseous products of the hydrolysis were swept out through the sidearm sealed onto the head.

FIGURE I

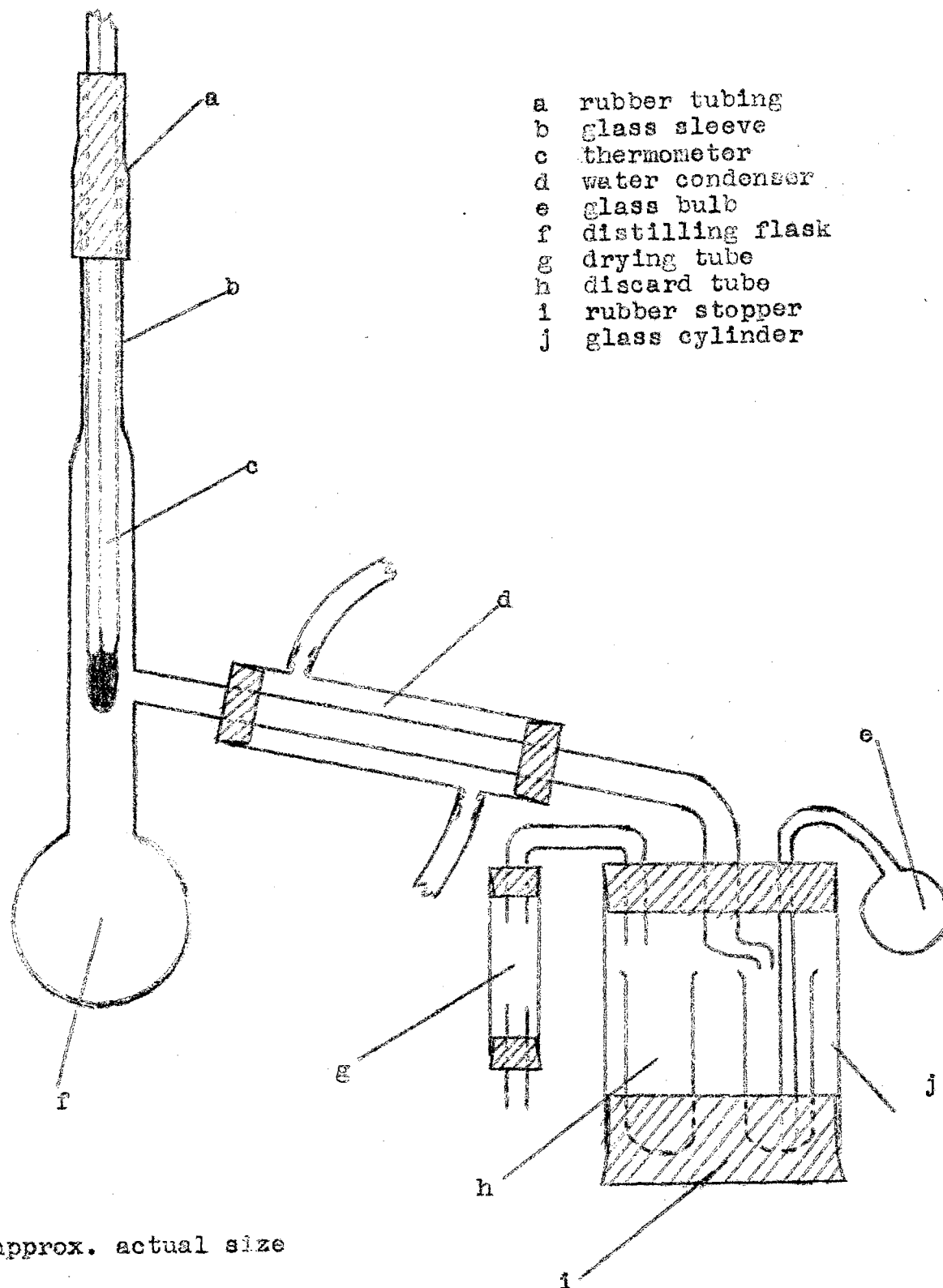Phosphorus Trichloride Purification Apparatus

a   rubber tubing
b   glass sleeve
c   thermometer
d   water condenser
e   glass bulb
f   distilling flask
g   drying tube
h   discard tube
i   rubber stopper
j   glass cylinder

approx. actual size

FIGURE II

Reaction Apparatus

a   dropping funnel
b   breaker rod
c   rubber stopper
d   receiver
e   glass bulb
f   glass wool
g   gas intake tube
h   introducer tube
i   outlet to condenser
j   reactor head
k   reactor
l   hydrolysis head
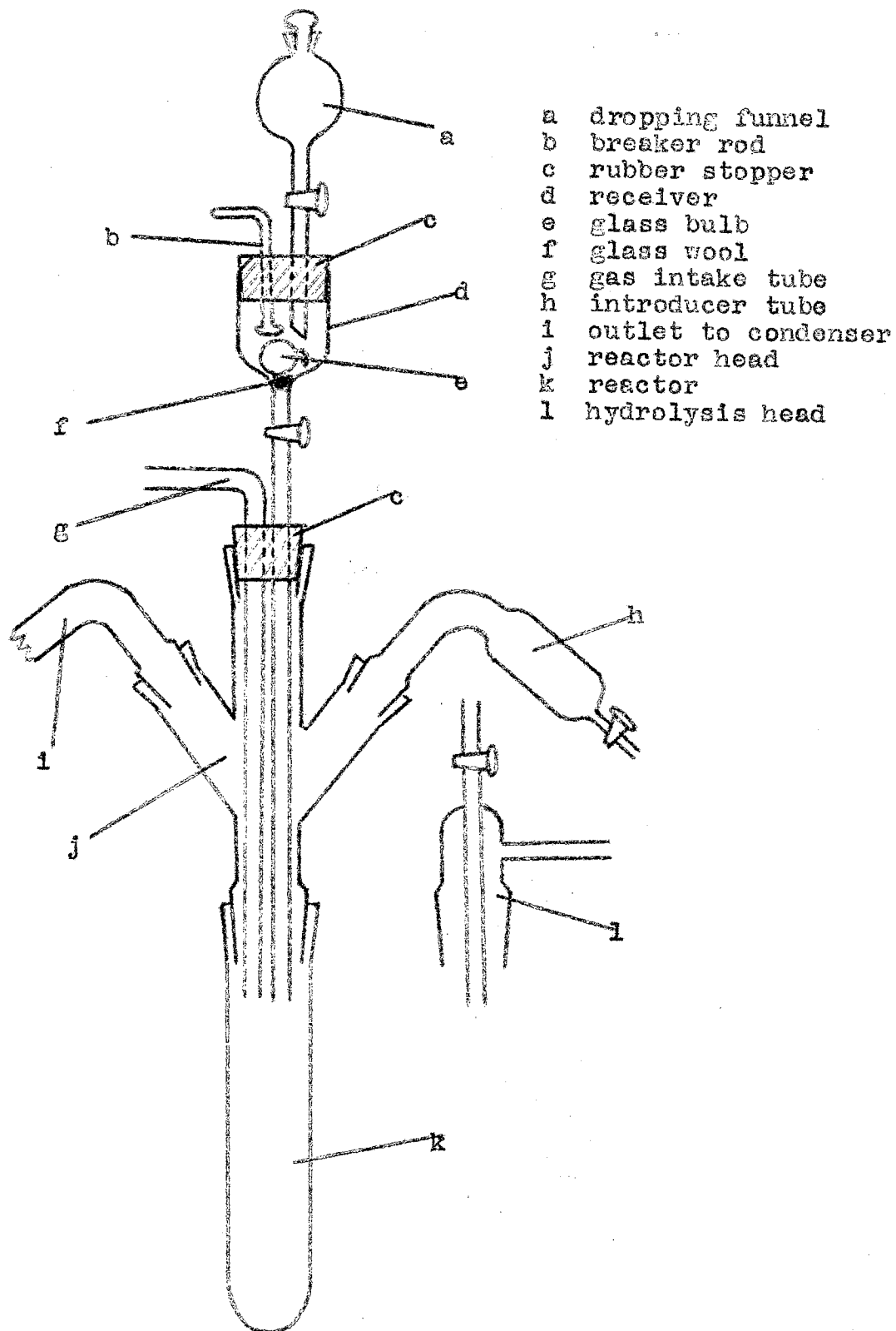
approx. 1/3 actual size

MATERIALS

Ammonia: Commercial anhydrous ammonia was distilled into small tanks containing sodium amide which served as a drying agent to remove any possible moisture in the ammonia. These tanks of ammonia were used to supply the solvent ammonia.

Petroleum Ether (Ligroin): The petroleum ether was a fraction boiling from 30°-$60^{\circ}C$. It had been dried over sodium shavings.

Nitrogen: Nitrogen gas was obtained from tanks of special "oxygen-free" nitrogen. This gas was further purified by first passing it through a gas washer containing potassium pyrogallate solution to remove traces of oxygen. Drying was accomplished by passing the gas first through a concentrated sulfuric acid washer and then through a phosphorus pentoxide drying tube.

Bismuth: The bismuth metal used in these experiments was "Baker's Analyzed" grade metal containing 99.8% Bi, manufactured by T. J. Baker Chemical Company. The metal which passed through a U. S. Standard #60 sieve was used.

Lead: The lead metal used was Merck and Company's "reagent grade" metal containing 99.95% Pb. The metal which passed through a U. S. Standard #60 sieve was used.

Sodium: The sodium employed was "reagent grade" metal manufactured by T. J. Baker Chemical Company. The sodium was stored under specially dried ligroin. Before using it was first cleaned by trimming off the oxide coating and melting under paraffin. The molten sodium was stirred so as to form small bright metal globules. The paraffin was then poured off and the globules

transferred quickly into dry ligroin. Both the ligroin and sodium were quickly poured into a filtering funnel with a sintered-glass bottom. A rubber stopper, through which the end of the introduction tube was inserted, was fitted to the top of this funnel. Most of the ligroin was drained off and the remainder vaporized by a stream of dried nitrogen. The sodium was then shaken into the introduction tube for use.

Bismuth Triiodide: This compound was prepared by the method of Birchenbach (21). The material was resublimed two times and analysis showed that it contained 35.2% Bi. The theoretical value is 35.4% Bi.

Lead(II) Iodide: This compound was made from potassium iodide and lead nitrate by metathesis. The product was recrystallized several times from hot water. Analysis showed that this material contained 44.6% Pb. The theoretical value is 44.8% Pb.

Phosphorus Trichloride: Baker and Adamson's "reagent grade" chemical was used. The phosphorus trichloride was distilled and the fraction which boiled in the range 44.5°–45.0° C. at 743 mm. pressure was caught. This material was further purified as needed.

ANALYTICAL METHODS

The analytical methods employed were, for the most part, similar to the standard procedures described in the well known treatises of Treadwell and Hall (22) and Furman (23).

Bismuth: Bismuth was determined gravimetrically by conversion to the insoluble basic nitrate followed by ignition to Bi_2O_3.

Lead: Lead was determined gravimetrically as lead molybdate.

Chloride: The chloride was determined volumetrically by the Mohr method. The silver nitrate was standardized by known samples of soluble chloride.

Sodium: Sodium was determined gravimetrically by conversion to sodium chloride after the removal of interfering heavy metals.

Hydroxide: Hydroxide ion was determined volumetrically by the use of standard hydrochloric acid. The acid was standardized with samples of sodium carbonate, using brom thymol blue as an indicator.

Phosphorus: Phosphorus, present as phosphine gas from the hydrolysis of phosphides, was determined by absorption in a solution of five per cent potassium permanganate containing enough nitric acid for the formation of the manganous ion. This reagent effected the conversion of the phosphorus to phosphate. Phosphate was then determined gravimetrically by first precipitation as ammonium phosphomolybdate and subsequent conversion to lead molybdate. The amount of phosphorus in the original sample was calculated from the weight of lead molybdate obtained.

PROCEDURES

Reduction of Bismuth Iodide to Trisodium Monobismuthide:

In the preparation of trisodium monobismuthide a known weight of
bismuth iodide, usually around ten grams, was introduced into
the bottom of the reactor which, in turn, was placed in the
Dewar flask and the head assembled. Specially dried gaseous
ammonia was admitted through the intake tube until the whole
apparatus was flushed completely free of air. Refrigerating
ammonia was run into the Dewar flask and kept stirred by means
of a stream of natural gas.

Dried gaseous ammonia was then condensed to the liquid by
increasing the pressure slightly in the reactor. The bismuth
iodide was completely ammoniated and suspended in about twenty
milliliters of solvent. This process was accompanied by a grad-
ual color change in the bismuth iodide from almost black through
orange to yellow. The final suspension was milky in appearance.
Previously prepared sodium, slightly in excess of the calculated
six equivalents necessary for the complete reduction of the
bismuth iodide to trisodium monobismuthide, was then gradually
added from the introducer tube. It was observed that the re-
action was strongly exothermic as evidenced by the violent boiling
of the ammonia, and a black metallic deposit of bismuth was rapid-
ly formed. Upon addition of more sodium, brown and violet colored
solutions characteristic of the ammonia-soluble polybismuthides
were observed. When an excess of sodium was present, the striking
blue color characteristic of liquid ammonia solutions of sodium
could be seen.

The reaction mixture was allowed to stand for about an hour to insure complete reaction. A finely divided black precipitate remained in the bottom of the reactor and the supernatant liquid was deep blue in color. In order to free the precipitate of sodium iodide and excess sodium it was thoroughly washed by repeated condensation and extraction of liquid ammonia through a fritted glass filter.

After removal of the reactor from the Dewar flask, the solvent ammonia was allowed to vaporize through a mercury trap leaving the precipitate of trisodium monobismuthide as a dry black powder. That part of the precipitate which could be shaken from the reactor was removed for further use by means of a take-off tube. The latter was quickly capped and evacuated by an oil pump for an hour to remove most of the adsorbed ammonia from the solid. After evacuation the tube was filled with dry nitrogen. Amorphous trisodium monobismuthide appeared black with a slight bluish-gray tint.

Reaction of Trisodium Monobismuthide with Phosphorus Trichloride: The reaction of trisodium monobismuthide with phosphorus trichloride was attempted six different times. During the course of these experiments many changes and improvements were made in technique. The fifth run will be discussed, as it is an example of the best procedure, and reference to other runs will be made where it seems advisable.

The apparatus, assembled as pictured in Figure II, was first dried and flushed free of all air by means of dry nitrogen. In the first run natural gas was used, but its use proved to be

unsatisfactory because it was found to contain some moisture. Beginning with the fourth run the nitrogen was further dried by passing it through a U-tube filled with phosphorus pentoxide.

An amount of trisodium monobismuthide equal to 1.2888 grams was put into the reactor from the introducer tube where it had been stored after preparation as previously described. The weight of trisodium monobismuthide was determined by weighing the introducer tube and cap before and after removal of the material. All weighings were made with the tube filled with nitrogen at atmospheric pressure. Approximately five milliliters of ligroin were run into the reactor from the dropping funnel. About ten milliliters, however, were retained in the receiver holding the glass bulb containing 1.287 grams of phosphorus tri-chloride. The bulb was broken and the phosphorus trichloride was mixed with the ligroin before being run into the reactor. Upon addition of this solution only slight bubbling was observed, and little or no change in the appearance of the solid could be detected.

The reaction mixture was then carefully heated until the ligroin boiled away. As the contents of the reactor approached dryness white fumes were noted. Finally the reactor was swept with nitrogen for an hour and the head was quickly replaced by the hydrolysis head. In order to remove any excess phosphorus trichloride the reactor was evacuated for one to two hours while warming slightly. When white fumes were observed the heating was stopped and the reactor was again filled with nitrogen.

Hydrolysis of the products formed was carried out by bubbling nitrogen through hot water and then into the reactor.

The gas outlet was connected to an absorber containing potassium permanganate solution. After hydrolysis was considered nearly complete, approximately twenty milliliters of water were condensed in the reactor tube by cooling it in an ice bath. Hot oxalic acid was added to the permanganate solution to destroy the excess reagent, and the solution was then diluted to 250 milliliters in a volumetric flask. Aliquots were analyzed for phosphorus.

The solid products remaining in the reactor were filtered through a weighed porous bottom filtering crucible, and the filtrate containing the soluble products was caught in a test tube placed in the filtering flask. This soluble portion was diluted to 200 milliliters in a volumetric flask for analysis. Aliquots of this solution were used to determine the amount of sodium, chloride, and hydroxide. The crucible containing the solid products was heated at 120°C. to constant weight, and the contents dissolved in concentrated nitric acid. After dissolution was complete the solution was filtered and the filtrate made up to volume in a 100 milliliter flask for analysis.

Data on amounts of reactants and analyses of products of the six runs performed on the reaction between trisodium monobismuthide and phosphorus trichloride are presented in Table I.

Reduction Reactions by Intermetallic Compounds: A series of four experiments was carried out to study the relative reducing properties of lead and bismuth as negative ions. Two of the experiments involved the reduction of an ammonia-soluble salt of one of these metals by the sparingly soluble intermetallic compound of the other. The remaining two experiments were anion displacements whereby elemental lead or bismuth was reduced to form a

soluble homoatomic anion. The use of twin reactor tubes greatly facilitated the execution of these reactions. As an example of the procedure employed in the first type of experiment, the reaction between trisodium monobismuthide and lead(II) iodide is described in detail.

Reduction of Lead(II) Iodide by Trisodium Monobismuthide: In this experiment 1.304 grams of lead(II) iodide were placed in the left hand reactor and 0.9703 gram of bismuth iodide in the right hand reactor. Bismuth iodide was then reduced with excess sodium so as to form trisodium monobismuthide in the manner previously described, and this precipitate was washed thoroughly to remove sodium iodide and unreacted sodium. Approximately 20 milliliters of ammonia were condensed in the tube containing the lead(II) iodide until a milky colloidal suspension was obtained. This suspension was then forced by ammonia pressure through the glass filter into the reactor containing trisodium monobismuthide covered with several milliliters of ammonia. There was little visible evidence of reaction except an apparent increase in the amount of dark insoluble material. After an hour of agitation with bubbling ammonia the solid products were filtered and washed to remove all soluble materials. The remaining solid was removed from the reactor by a take-off tube and evacuated to remove ammonia. A sample of the solid products consisting of 0.2414 gram was first dissolved in a small amount of nitric acid and then diluted to 50 milliliters in a volumetric flask. Aliquots of this solution were analyzed to determine the relative amounts of bismuth and lead formed by the reaction.

Reduction of Bismuth by Tetrasodium Nonaplumbide: Again, since much the same procedure was followed in each of the anion displacement experiments, only this one is described in detail. Finely divided bismuth required in this reaction was obtained by the reduction of 1.0165 grams of bismuth iodide by sodium in liquid ammonia. The metal was washed carefully to remove sodium iodide and other soluble impurities. Tetrasodium nonaplumbide was made by reaction of 0.7944 gram of metallic lead with 0.0395 gram of sodium.

When sodium was added to the liquid ammonia covering the metallic lead in the reactor, rapid formation of a dark green polyplumbide was noted. After allowing approximately an hour for completion of the reaction, this solution was forced through the filter into the other reactor containing the prepared metallic bismuth. The green color of the plumbide solution quickly changed to reddish-brown and a mirror-like deposit of metallic lead on the sides of the reactor tube could be seen. The solid products of the reaction were filtered and washed until free of soluble products. Ammonia was removed from the solid by vaporization and a 0.6431 gram sample was prepared for analysis.

Analytical data obtained on the four experiments carried out to study the reducing properties of intermetallic compounds are shown in Table II.

TABLE I

Reaction of Trisodium Monobismuthide

with Phosphorus Trichloride

Run No.	Na₃Bi (g.)	(equiv.)	PCl₃ (g.)	(equiv.)	Insol. (g.)	Bi (equiv.)	Na (equiv.)	Cl (equiv.)	OH (equiv.)	PH₃ (equiv.)
	Reactants				**Analysis of Products**					
1	0.9416	0.0034	1.60	0.016	——	0.0029	0.0105	0.0040	0.0050	——
2	3.9635	0.0143	7.90	0.057	——	——	0.0473	0.0258	——	——
3	1.6134	0.0058	4.70	0.034	1.2713	0.0057	0.0180	0.0128	0.0015	0.0011
4	1.2050	0.0043	1.329	0.0097	——	——	——	——	——	——
5	1.8888	0.0068	1.287	0.0094	1.3983	0.0065	0.0201	0.0013	0.0188	0.0002*
6	1.0462	0.0038	4.495	0.0327	0.5944	0.0027	0.0082	0.0025	0.0056	0.0001*

* estimated

TABLE II

Reduction Reactions by Intermetallic Compounds

Exp. No.	Reactants	Amounts Used (g.)	(equiv.)	Analysis of Insoluble Products — Sample Used (g.)	Bi (g.)	(equiv.)	Pb (g.)	(equiv.)
1	Na	0.431	0.0198					
	BiI_3	0.970	0.0016					
	Na_3Bi	(0.457)	(0.0016)					
	PbI_2	1.302	0.0028	0.2414	0.082	0.00039	0.144	0.00069
2	Na	0.350	0.0152					
	PbI_2	1.023	0.0022					
	Na_4Pb	(0.688)	(0.0022)					
	BiI_3	1.774	0.0030	0.7587	0.461	0.0022	0.236	0.0011
3	Na	0.117	0.0049					
	BiI_3	1.016	0.0017					
	Na	0.039	0.0017					
	Pb	0.794	0.0038					
	Bi	(0.356)	(0.0017)					
	Na_4Pb_9	(0.831)	(0.0004)	0.6431	0.280	0.0013	0.310	0.0015
4	Na	0.202	0.0088					
	PbI_2	2.001	0.0043					
	Na	0.044	0.0019					
	Bi	0.402	0.0019					
	Pb	(0.890)	(0.0043)					
	Na_3Bi_3	(0.440)	(0.0006)	0.8304	0.006	0.00003	0.795	0.0038

PART IV

DISCUSSION

DISCUSSION

Reaction of Trisodium Monobismuthide with Phosphorus
Trichloride: In this investigation of the reaction of inter-
metallic compounds with essentially covalent inorganic halides,
phosphorus trichloride was selected as a suitable representative
of such halides, while the least ammonia-soluble intermetallic
compounds of sodium and the group V_B elements were chosen because
of the possibility of their preparation and purification in
liquid ammonia. It was first planned to prepare the series of
compounds, Na_3Bi, Na_3Sb, and Na_3As, and to determine the effect
that differences in the electronegativity of the anions might
have on the course of the reaction of such compounds with phos-
phorus trichloride. Trisodium monobismuthide was the only inter-
metallic compound which was so studied, however.

The course of the reaction between these two compounds might
be expected to result in the formation of sodium chloride and a
bismuth phosphide as illustrated by the following equation:

$$Na_3Bi + PCl_3 \longrightarrow BiP + 3\ NaCl$$

This is the type of coupling reaction which takes place between
an intermetallic compound and an organic halide. On the other
hand, if the reaction is similar to that which has been shown to
occur with metallic halides, there would be a reduction of phos-
phorus by the bismuth anion and the equation would be:

$$2\ Na_3Bi + PCl_3 \longrightarrow Na_3P + 3\ NaCl + 2\ Bi$$

The problem became that of attempting to prove which, if
either, of these equations describes the reaction. The method

followed was to separate and quantitatively analyze the products of the reaction. A consideration of the first equation shows, if it correctly represents the reaction, that the number of equivalents of sodium and chloride in the product will be the same, and that this number is also three times the number of equivalents of bismuth and phosphorus. If the second equation is the correct one, however, there should be found in the products twice as many equivalents of chloride as sodium, while the number of equivalents of phosphorus and bismuth would be equal to one third and two thirds, respectively, that of the chloride.

On the assumption that the latter equation represents the reaction, a calculation of the number of equivalents of each product which would be formed from a known amount of trisodium monobismuthide is made and presented in Table III. Such a calculation assumes that all of the trisodium monobismuthide present enters into the reaction and that the quantity of sodium phosphide in the product may be found by determining the amount of hydroxide and phosphine resulting from its hydrolysis:

$$Na_3P + 3 H_2O \longrightarrow 3 NaOH + PH_3$$

TABLE III

Reaction of Na_3Bi with PCl_3

| Run No.	Na_3Bi (equiv.)	No. of equivalents theoretically formed				
		Bi	Na	Cl	OH	PH_3
1	0.0034	0.0034	0.0102	0.0051	0.0051	0.0017
2	0.0143	0.0143	0.0428	0.0214	0.0214	0.0071
3	0.0058	0.0058	0.0174	0.0087	0.0087	0.0029
4	0.0043	0.0043	0.0128	0.0064	0.0064	0.0021
5	0.0068	0.0068	0.0204	0.0102	0.0102	0.0034
6*	0.0038	0.0027	0.0081	0.0040	0.0040	0.0013

* Equiv. calculated from the amount of Bi found in product.

In discussing the several experiments which were performed in which the conditions of the reaction were varied, mention is made of the significant factors which apparently had the most effect on the outcome of the reaction. Each such complete experiment is referred to as a run.

Run # 1: In this exploratory run neither the protective atmosphere of natural gas nor the ligroin and phosphorus trichloride used had been previously treated in any way to remove moisture that might have been present. About 25 milliliters of ligroin was simply added to the trisodium monobismuthide in the reactor by means of a dropping funnel followed by approximately one milliliter of phosphorus trichloride added in the same manner. There was little immediate evidence of reaction, but upon evaporation to dryness an evolution of white fumes was noticeable. In this run the only operation performed to remove the excess phosphorus trichloride was the circulation of natural gas through the apparatus for about two hours. Hydrolysis of the products was accomplished by direct addition of water and the phosphine liberated was expelled by boiling the solution. Only a qualitative analysis was made for phosphine.

It can be seen, by comparing the number of equivalents of chloride found in the products (Table I) to the number which should theoretically be found (Table III), that the reaction was apparently 80 percent complete. If this were the case the total amount of hydroxide that would be produced by the hydrolysis of the sodium phosphide formed and the hydrolysis of the unreacted bismuthide would be equal to 0.0060 equivalents. However, the

amount of hydroxide actually found by analysis was only 0.0050 equivalent. A low value for the amount of hydroxide might be explained by the presence of hydrogen ions liberated in the hydrolysis of phosphorus trichloride according to the equation:

$$PCl_3 + 3 H_2O \longrightarrow 3 HCl + H_3PO_3$$
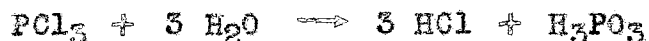
Such a hydrolysis would be expected to occur if moisture was not carefully excluded from the reaction.

If the reaction is considered to be 50 percent complete, corresponding to 0.0025 equivalent of chloride as sodium chloride, the excess chloride found (0.0015 equiv.) might be satisfactorily attributed to the hydrolysis of phosphorus trichloride. The ratio of the available hydrogen ions to the chloride ions would be 5/3 by the above equation, or 0.0025 equivalent of hydrogen ion. The amount of hydroxide formed would be 0.0025 equivalent resulting from a 50 percent reaction and 0.0050 equivalent due to the hydrolysis of remaining unreacted bismuthide. Therefore, the effective hydroxide, taking into account the hydrogen ions, would be equal to 0.0050 equivalent, which agrees with the amount found by analysis.

Run # 2: It was evident from the first run that precautions would have to be taken to exclude moisture from all the materials used in the reaction to prevent hydrolysis. Any hydrolysis of phosphorus trichloride or trisodium monobismuthide would lead to results which would be difficult to interpret.

Several improvements in procedure suggested by the results of the first run were adopted. These included the use of dried deoxygenated nitrogen, freshly distilled phosphorus trichloride, and sodium-dried ligroin. In an effort to minimize the error

resulting from phosphorus trichloride still remaining after completion of the reaction, the contents of the cell were evacuated with an oil pump.

An attempt was made to quantitatively estimate the phosphine liberated by absorbing it in a 5 percent potassium permanganate solution. It was thought that such a determination would serve as a valuable supplement to the other analytical data. In this run hydrolysis was attempted by the use of steam generated by a flask of boiling water. However, the arrangement actually used proved to be very inconvient since the rate of flow of steam could not be easily controlled and some of the permanganate solution was sucked back into the reactor. Analytical results obtained on this run were made inconclusive by the above incident.

Run # 3: Since there was little visible evidence of any reaction occurring until most of the diluent ligroin had been vaporized, a relatively larger initial concentration of phosphorus trichloride was used in the third run. The reaction appeared to proceed much as before, with only a moderate amount of heat being produced and almost no change in appearance of the solid materials in the reactor.

An improved technique of hydrolysis described in the section on procedure, permitted the amount of phosphine produced to be used as a measure of the extent of reaction. A calculation thus shows that the reaction proceeded to only 32 percent of completion. On the basis of the extent of reaction indicated above and using the method of interpretation of data as described under Run # 1, there should be present in the product 0.0017 equivalent of

effective hydrogen ion. Actually the product was slightly basic and it was found to contain 0.0015 equivalent of hydroxide ion. The fact that these results do not agree very closely could easily be the result of a small error in the phosphorus analysis.

Run # 4: Still further efforts were made in this run to remove the last traces of moisture that could possibly effect the results of the reaction. The techniques used were essentially those described in detail under the section on procedure. An exception to this was the method used in combining the reactants. A mixture of phosphorus trichloride and ligroin in the receiver was run directly onto the dry bismuthide in the reactor. As soon as the first drops of this mixture came into contact with the bismuthide a very violent exothermic reaction occured. A red flame accompanied by dense white fumes was visible in the bottom of the reactor. As more of the liquid mixture was added the white fumes were observed to dissolve. Under the circumstances it was believed best not to investigate the products of this reaction further since no control was possible over the conditions of such a reaction.

Run # 5: The fifth run differed little from the fourth except the sodium bismuthide was first moistened with ligroin prior to the addition of the phosphorus trichloride solution. In contrast, however, almost no visible signs of reaction were noted except a slight rise in temperature of the reaction mixture. The details of the procedure used in this run were completely described in the section on procedure. The amount of phosphine produced upon hydrolysis of the products of the reaction was so small that only

a rough estimate could be made on the phosphorus analysis. Since
the amount of phosphine formed was estimated to be 0.0002 equiv-
alent, the reaction was believed to be only about 6 percent com-
plete. On this basis there should have been 0.0186 equivalent of
effective hydroxide present in the products. The amount actually
found was 0.0188 equivalent, which is in reasonably good agreement.

Apparently the problem of moisture being present must have
been practically eliminated as shown by the very low amount of
chloride found. The contrasting reaction in the fourth and fifth
runs suggest that the rate of reaction must depend critically upon
the concentration of phosphorus trichloride and the temperature.

Run # 6: In this run, as in the previous one, just enough
ligroin was used to cover the bismuthide before the phosphorus
trichloride-ligroin mixture was introduced. Initially only a
slight rise in temperature occurred so it was decided to warm the
mixture slowly in an effort to bring the reaction to completion.
As the temperature neared the boiling point of the ligroin, a
violent reaction occurred producing a red flame and white fumes
similar to those observed in the fourth run. Although the vio-
lence of the reaction scattered the products throughout the entire
reaction apparatus, the run was completed in the hope that some
useful information could be obtained from it. Assuming the loss
of material was equal in each component, interpretation of the
analytical data obtained indicated the reaction to have been 8
percent complete.

Because of the unpredictable nature of the combination of
trisodium monobismuthide with phosphorus trichloride under the

experimental conditions set up, it was believed unprofitable to continue further along this line of investigation. The results of the investigation support the hypothesis that the reaction proceeds with the formation of sodium phosphide rather than a bismuth phosphide; however, the results are not conclusive on this point, and the possibility of the reaction taking some other course cannot be excluded.

Reduction Reactions by Intermetallic Compounds: It has been pointed out that the reducing properties of intermetallic salts have been studied by several investigators. The present investigation consisted of a series of four experiments designed to study the relative reducing properties of lead and bismuth as negative ions. Two of these experiments involved the reduction of an ammonia-soluble halide salt of each of these metals by the sparingly soluble intermetallic compounds of the other. The remaining two were performed in an attempt to determine which of the two metals is the more electronegative as a polyanion. The reactions used were anion displacements whereby elemental lead or bismuth was reduced to a soluble homoatomic anion by an ammonia-soluble intermetallic compound of the other metal. The experimental data for this series of reactions is given in Table II.

Experiment 1: This experiment was concerned with the reduction of lead(II) iodide by trisodium monobismuthide. Such a reduction might be expected to occur readily according to the following:

$$BiI_3 + 6\ Na \longrightarrow Na_3Bi + 3\ NaI$$

$$2\ Na_3Bi + 3\ PbI_2 \longrightarrow 3\ Pb + 2\ Bi + 6\ NaI$$
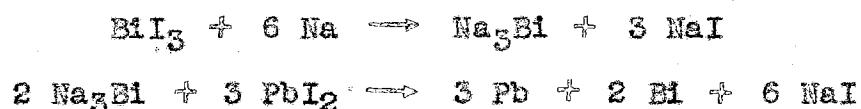
Since the weight of the insoluble products formed by the first reaction could not be determined conviently, the theoretical yield was calculated from the weight of bismuth iodide used. Yields calculated in this manner are shown in Table II and are enclosed in parentheses.

The amount of lead(II) iodide used was somewhat in excess of that required on the basis of the above equations, but the ready removal of this excess was believed possible when the products were washed with liquid ammonia, since lead iodide is soluble in ammonia.

A consideration of the equation written above shows that if the reaction between lead(II) iodide and trisodium monobismuthide is complete, the ammonia-insoluble product should contain lead and bismuth in the ratio of three equivalents to two. However, analysis of the product gave a ratio of lead to bismuth of 1.74. The sum of the percentages of lead and bismuth found accounted for only about 94 percent of the sample used for analysis. This fact, together with the observation that a distinct violet color was produced when the sample was dissolved in nitric acid, indicated the probable presence of iodide as an impurity in the sample. This could have been due to incomplete removal of the excess lead iodide. If the unaccounted for substance in the insoluble product is considered to be iodine, and half the corresponding number of equivalents of lead is deducted from that found by analysis, the corrected lead value would be 0.00063 equivalent. Using this value the ratio of lead to bismuth now becomes 1.61, which compares favorably with the theoretical value of 1.50. A lack of

homogeneity in the sample of the product used could easily account for the slight discrepancy in the two values.
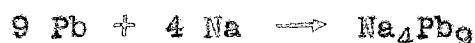
Experiment 2: The corresponding reduction of bismuth iodide by tetrasodium monoplumbide was demonstrated in this experiment. Equations representing the probable reactions are as follows:

$$PbI_2 + 6\ Na \longrightarrow Na_4Pb + 2\ NaI$$
$$3\ Na_4Pb + 4\ BiI_3 \longrightarrow 4\ Bi + 3\ Pb + 12\ NaI$$
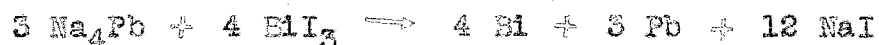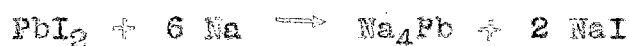
Reactions between tetrasodium monoplumbide and bismuth iodide were observed to be quite exothermic causing the liquid ammonia to boil violently. Analysis of the insoluble products showed the ratio of bismuth to lead as 2.00, whereas the theoretical ratio according to the above equation should be 1.33. The high ratio obtained might partially be explained by the presence of bismuth iodide in the product. It is more likely, however, the result of both unsatisfactory analyses for lead and the inability to obtain a sample having the ideal ratio of metals. The failure to account for more than 92 percent of the solid product as lead and bismuth provided additional support for this view. In spite of the unfavorable ratio of bismuth to lead, the results of the experiment do indicate definitely that tetrasodium monoplumbide does reduce the bismuth ion in ammonia solution to the element.

Experiment 3: An attempt was made in Experiments 3 and 4 to establish clearly the relative electronegativity of lead and bismuth in their polyanionic state. Bergstrom had studied displacement reactions involving both these elements but had been unable to satisfactorily establish their relative positions in his electronegativity series. He experienced difficulties in obtaining
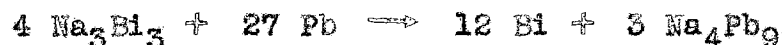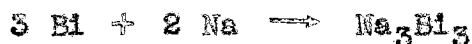
complete reaction because of the formation of a protective coating of one metal upon the other. It was believed that this difficulty could be overcome by use of finely divided metallic precipitates such as those prepared by the reduction of metal iodides with liquid ammonia solutions of sodium. The series of equations written below show step-wise the reactions involved:

$$BiI_3 + 3\ Na \longrightarrow Bi + 3\ NaI$$
$$9\ Pb + 4\ Na \longrightarrow Na_4Pb_9$$
$$3\ Na_4Pb_9 + 12\ Bi \longrightarrow 27\ Pb + 4\ Na_3Bi_3$$

The experimental results obtained in this experiment can be interpreted only in a qualitative manner. As a result of the failure to allow adequate time for the complete conversion of metallic lead to the soluble plumbide, there resulted a transfer of an insufficient amount of tetrasodium nonaplumbide to react with the weight of bismuth present. It was very difficult to determine experimentally the endpoints of these reactions because of the opaque dark colored solutions of the polyanionic salts in ammonia. This complication made the quantitative data almost useless except to indicate that partial reaction had occured. Observation of the rapid color change of the green plumbide solution to reddish-brown, indicative of polybismuthides, together with the formation of a mirror-like deposit of lead points to a displacement of lead by bismuth.

Experiment 4: Unfortunately the results of this experiment were no more conclusive than those of Experiment 3 as the same type of difficulties were also encountered in this experiment. A series of reactions analogous to those of the preceding experiment

were proposed for the formation of the reactants and the products
of their reaction:

$$PbI_2 + 2\ Na \longrightarrow Pb + 2\ NaI$$

$$3\ Bi + 2\ Na \longrightarrow Na_3Bi_3$$

$$4\ Na_3Bi_3 + 27\ Pb \longrightarrow 12\ Bi + 3\ Na_4Pb_9$$

This time the opaqueness of the strongly colored bismuthide
solution prevented the exact determination of the point of com-
plete reaction. Since only a very small percent of bismuth was
found in the final product, probably only a small quantity of
soluble bismuthide was actually formed. The presence of a consid-
erable amount of insoluble solid remaining after transfer of the
bismuthide solution further confirms this fact. A slow but com-
plete decolorization of the polybismuthide solution took place
after it was allowed to remain in contact for some time with the
metallic lead and this was interpreted as an indication that anion
displacement did occur. The absence of any formation of a green
color characteristic of nonaplumbide solutions is difficult to
explain on the basis of the proposed reactions.

The relative electronegativity of bismuth and lead in their
polyanionic states appears to be approximately the same from the
results of these experiments. The more rapid reaction, judging
from the rate of color change, occurring in the displacement of
lead from its polyanion by bismuth would seem to indicate that
bismuth is the more electronegative of the two metals. This is
of course the same as is found in the electronegative series in
aqueous solutions. It is believed that by improvement in exper-
imental techique and apparatus a more definite answer can be
realized for this problem.

PART V

SUMMARY

SUMMARY

A study of the reaction between trisodium monobismuthide and phosphorus trichloride dissolved in ligroin has been made. Due to the inability to control satisfactorily the experimental conditions, reproducible results were not obtained. The reaction was found to depend critically upon the temperature and the phosphorus trichloride concentration. Evidence was obtained supporting the hypothesis that the course of the reaction was probably the following:

$$2 \ Na_3Bi + PCl_3 \longrightarrow Na_3P + 3 \ NaCl + 2 \ Bi$$
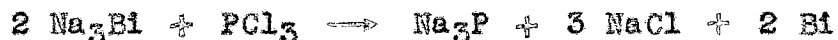
Metallic lead and bismuth were found to be precipitated from liquid ammonia solutions of their halide salts by trisodium monobismuthide and tetrasodium monoplumbide respectively.

The relative electronegativity of lead and bismuth in liquid ammonia solutions of their polyanions was not established definitely. Experimental results showed a more rapid displacement of lead from tetrasodium nonaplumbide by metallic bismuth than the corresponding displacement of bismuth from trisodium tribismuthide by metallic lead.

PART VI

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BIOGRAPHY

Charles Maitland Boyd, son of Theodore Maitland Boyd and Edna O'Bar Boyd, was born in Conway, Arkansas on October 16, 1926. He attended Conway Public Schools and received his diploma in 1943. He then entered Hendrix College at Conway and graduated with a Bachelor of Science degree from that school in 1947. He enrolled at Oklahoma Agricultural and Mechanical College at Stillwater, Oklahoma in September of 1947, where he served two years as graduate assistant in the Department of Chemistry while completing requirements for his Master of Science degree.

Mr. Boyd volunteered for Army Air Corps duty while enrolled at Hendrix and served one year as an Aviation Cadet.

He was married in 1947 to Martha Menard, of Conway, and is the father of one son, Charles Ray.

Typed by Charles M. Boyd