

# REACTIONS OF INORGANIC SUBSTANCES WITH SOLUTIONS OF METALS IN LIQUID AMMONIA

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This paper represents an effort to make available in concise form the existing information concerning the action of liquid ammonia solutions of metals upon inorganic substances, both elemental and compound. Where possible in the light of the available facts, the writer has attempted to interpret, to evaluate critically, and to call attention to unexplored areas of investigation. Largely for convenience for purposes of reference, much of the factual information is summarized in tabular form together with pertinent literature references. With but few exceptions, coverage of the published literature does not extend beyond January 1, 1949; at the same time a considerable amount of hitherto unpublished information is included in the pages that follow. In another paper, a similar treatment of the reactions of organic and organometallic compounds is provided.

## I. INTRODUCTION

The unique properties of liquid ammonia solutions of the alkali and alkaline earth metals present unusual opportunities for the study of reduction reactions (44). Although liquid ammonia is somewhat selective and limited in its solvent action toward inorganic substances, many electrolytes exhibit high solubility and many others participate in oxidation-reduction reactions even though they are substantially insoluble.

By comparison with water as a medium for the study of reactions of strong reducing agents, ammonia possesses certain distinct advantages. The utility of water is seriously limited by the fact that reducing agents stronger than hydro-

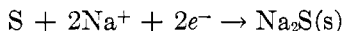
gen liberate hydrogen from water. Ammonia, on the other hand, permits of the study of the extremely strong reducing systems provided by solutions of the alkali and alkaline earth metals over a wide range of concentration and temperature. In the absence of catalysts, the rate of interaction of metals and ammonia is negligible in relation to the rates of most of the reactions in which these solutions participate. An additional advantage is a consequence of the relatively low degree of autoionization of ammonia. This property of the solvent permits the preparation and study of numerous substances that are unstable in aqueous systems because of hydrolysis.

The major disadvantage inherent in the use of liquid ammonia as a solvent and reaction medium lies in the fact that its use requires more elaborate equipment and somewhat more involved manipulative techniques than do solvents that are liquid under ordinary atmospheric conditions. It is worthwhile also to recall that ammonia is an extremely hygroscopic liquid and that its use under optimum conditions requires particular care in the exclusion of water from the atmosphere. These points, while worthy of emphasis, involve difficulties that are by no means as serious as they may appear to the uninitiated.

Despite the fact that liquid ammonia solutions of metals provide almost unlimited opportunities for the study of reduction processes, the field as a whole remains largely unexplored. This is particularly true with respect to inorganic substances. Noteworthy is the fact that there is essentially no information relative to reactions of solutions of metals at high concentrations or at high temperatures. The many cases considered in the pages that follow include not a single example of a reaction effected at a temperature in excess of that which is generally designated as "room temperature." As is evident from the examples cited below, the work that has been done has nevertheless brought to light a considerable number of unusual reactions and products.

The process of reduction by means of solutions of metals in ammonia consists in the addition of one or more electrons to an atom, a group of atoms, or an ion. The metal cation is present in the solution but does not usually influence the course of the primary reduction reaction.<sup>1</sup>

The reduction of elemental sulfur with a solution of sodium, for example, provides sulfide ion, which subsequently precipitates as white crystalline sodium sulfide.

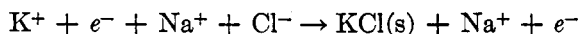


As will be shown later, negative polysulfide ions of the same charge type may be formed under appropriate conditions.

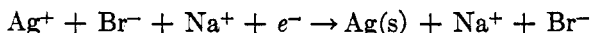
Reduction of a positive ion usually yields a neutral atom or group as the

<sup>1</sup> A notable exception is found in the work of Burgess and Holden (26), who have shown that, in the reduction of silver salts, solutions of calcium react more vigorously than solutions of sodium or potassium and produce more reactive elemental silver. They have also shown that calcium solutions reduce cyanate ion to cyanide, whereas cyanate ion is stable in the presence of solutions of sodium or potassium.

*primary* reduction product, e.g.,

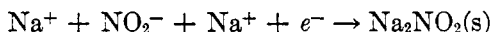


the course of reactions of this type being determined almost entirely by solubility relationships. Another example of the reduction of a positive ion is typical of the reduction of halides:

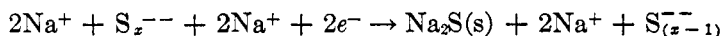


Depending upon the nature of the metal thus produced, it may (a) undergo reduction to lower oxidation states, (b) catalyze the reaction between the alkali or alkaline earth metal and the solvent, (c) react with the amide formed catalytically, or (d) participate in no further reactions. These possibilities will be illustrated and elaborated in connection with the discussion of reduction of different types of inorganic compounds.

The reduction of negative ions has been studied in only a few cases. On the basis of presently available information, it appears that the product consists of either an ion of lower oxidation number,



or of more than one negative ion,



The latter type of reaction is the one most commonly encountered.

## II. ELEMENTS

Only a relatively small number of the elements react with solutions of metals in ammonia. There is no conclusive evidence for reactions involving the inert gases and the transitional or rare earth elements, although some elements in these categories have not been studied adequately if at all. There is some evidence (159) that very finely divided transitional elements formed by the reduction of their compounds in liquid ammonia may react to a limited extent with solutions of metals. Predominantly, the elements that are reduced are those of atomic numbers two to four units less than the inert gases, i.e., the normal elements of Groups IV, V, and VI of the Periodic Table.

In numerous cases the composition of the reduction products has been established conclusively but the individual compounds have not been isolated. By means of potentiometric titrations, Zintl and his associates (159) have established the composition of many of these reduction products, and some of the best available information has been accumulated through the use of such methods. In general, each element that is reduced forms a white or slightly colored ammonia-insoluble salt having a composition that corresponds to the normally stable oxidation state of the element in question (e.g.,  $\text{Na}_2\text{Se}$ ,  $\text{Na}_3\text{Bi}$ , and  $\text{Na}_4\text{Sn}$ ). In addition, most of these elements form also one or more soluble salts containing homopolyatomic anions (e.g.,  $\text{Na}_2\text{S}_{2-5}$ ,  $\text{Na}_3\text{Bi}_3$ , and  $\text{Na}_4\text{Pb}_9$ ) which impart intense and characteristic colors to the solutions.

TABLE 1  
*Reactions of elements with solutions of metals in liquid ammonia*

ELEMENT	METAL	PRODUCTS	NOTES	REFERENCES
Group II				
Hg . . . .	Na	NaHg <sub>3</sub>		(67, 74)
	K	KHg <sub>13</sub>		(67, 74)
Group IV				
Ge . . . .	Na	Na <sub>4</sub> Ge <sub>2</sub>	See section on sulfides	(84)
Sn . . . . .	Na		Soluble compound	(130)
Pb . . . . .	Li	Li <sub>4</sub> Pb <sub>2</sub>	Green solution	(164)
	Na	NaPb <sub>4</sub> ·2NH <sub>3</sub>	Green solution <sup>(a)</sup>	(67)
		NaPb	Solid; sodium in excess	(68)
		NaPb <sub>2</sub>	Green solution	(74, 89)
		Na <sub>4</sub> Pb <sub>3</sub>		(99, 143, 159)
	K	KPb <sub>2</sub>		(68)
		K <sub>4</sub> Pb <sub>3</sub> ·xNH <sub>3</sub>	Soluble compound Green solution	(89) (164)
	Rb		Amethyst solution	(164)
Cs		Brown-violet solution	(164)	
Sr		Insoluble compound	(164)	
Group V				
N . . . . .	Na, K		No reaction	(71)
P . . . . .	Li		Incomplete reaction with red phosphorus	(19)
	Na	Na <sub>3</sub> P <sub>2</sub> H <sub>3</sub> , 3NaNH <sub>2</sub>	Sodium in excess	(60)
		NaP <sub>3</sub> ·3NH <sub>3</sub>	Phosphorus in excess	(59)
			Incomplete reaction with red phosphorus	(19)
K	KP <sub>5</sub> ·3NH <sub>3</sub>	Phosphorus in excess Incomplete reaction with red phosphorus	(59) (19)	
As . . . . .	Li	Li <sub>3</sub> As	Brown powder	(105) (19)

TABLE 1—Continued

ELEMENT	METAL	PRODUCTS	NOTES	REFERENCES
Group V—Continued				
Sb.....	Na	$\text{Na}_3\text{As}$ $\text{Na}_2\text{As}\cdot\text{NH}_3$	With either sodium or arsenic in excess	(64, 81) (61)
	K	$\text{K}_3\text{As}\cdot\text{NH}_3$ $\text{K}_2\text{As}_4\cdot\text{NH}_3$	Potassium in excess Arsenic in excess	(64) (64)
	Li	$\text{Li}_3\text{Sb}$ $\text{Li}_3\text{Sb}\cdot\text{NH}_3$	With either lithium or antimony in excess Blue-gray powder	(61, 109) (110, 111, 163) (60)
Bi.....	Na	$\text{Na}_3\text{Sb}$ $\text{Na}_2\text{Sb}_{5-7}$	Brown precipitate, yellow solution Red-brown solution	(68, 74) (130)
	Na	$\text{Na}_3\text{Bi}$ $\text{Na}_2\text{Bi}_3$ $\text{Na}_2\text{Bi}_{5-7}$	Black; insoluble Violet solution Brown solution	(68, 74, 154) (154) (154)
	Group VI			
O <sub>2</sub> .....	Li	$\text{Li}_2\text{O}$ , $\text{Li}_2\text{O}_2$		(131)
	Na	$\text{NaOH}$ , $\text{NaNH}_2$ , $\text{NaNO}_2$	Slow reaction	(69, 74, 103)
		$\text{Na}_2\text{O}_2$	Rapid reaction	(103)
		$\text{Na}_2\text{O}_3$	Not confirmed <sup>(a)</sup>	(69, 74, 103)
		$\text{NaO}_2$	At $-77^\circ\text{C}$ .	(139)
	K	$\text{KOH}$ , $\text{KNH}_2$ , $\text{KNO}_2$	Slow reaction	(103)
		$\text{K}_2\text{O}_2$ , $\text{K}_2\text{O}_4$ ( $\text{KO}_2$ )	Rapid reaction	(69, 74, 86, 100, 103)
		$\text{K}_2\text{O}_3$ $\text{KO}_2$	Not confirmed	(69, 74, 103) (53)
	Rb	$\text{Rb}_2\text{O}$ $\text{Rb}_2\text{O}_2$ , $\text{Rb}_2\text{O}_4$ ( $\text{RbO}_2$ ) $\text{RbO}_2$	$-60^\circ\text{C}$ . (?)	(54) (136) (53)
		Cs	$\text{Cs}_2\text{O}$	
$\text{Cs}_2\text{O}_2$ , $\text{CsNH}_2$ , $\text{CsOH}$ , $\text{CsNO}_2$ , $\text{CsNO}_3$			Slow reaction at $-60^\circ\text{C}$ .	(134, 135)
$\text{Cs}_2\text{O}_2$ , $\text{Cs}_2\text{O}_3$ , $\text{Cs}_2\text{O}_4$ ( $\text{CsO}_2$ )	Rapid reaction at $-60^\circ\text{C}$ .		(134, 135)	
$\text{CsO}_2$			(53)	
Ba	$\text{BaO}$ , $\text{BaO}_2$	Gelatinous precipitate	(52, 122)	

TABLE 1—Continued

ELEMENT	METAL	PRODUCTS	NOTES	REFERENCES
Group VI—Continued				
O <sub>3</sub> .....	Na	Ozonides assumed	Not isolated	(144)
	K	Ozonides assumed	Not isolated	(144)
	Rb	Ozonides assumed	Not isolated	(144)
	Cs	Ozonides assumed	Not isolated	(144)
	Ca	Ozonides assumed	Unstable brown compounds	(144)
	Ba	Ozonides assumed	Unstable brown compounds	(144)
S.....	Li	Li <sub>2</sub> S	White, very slightly soluble	(8)
		Li <sub>2</sub> S <sub>2</sub>	Yellow, slightly soluble	(8)
		Li <sub>2</sub> S <sub>4</sub>	Red solution	(8)
		Li <sub>2</sub> S <sub>z</sub>	Red solution	(8)
	Na	Na <sub>2</sub> S	White, very slightly soluble	(8, 63, 65, 87, 195)
		Na <sub>2</sub> S <sub>2</sub>	Yellow, slightly soluble	(8, 159)
		Na <sub>2</sub> S <sub>3</sub>	Red solution	(159)
		Na <sub>2</sub> S <sub>4</sub>	Red solution	(8, 159)
		Na <sub>2</sub> S <sub>5</sub>	Red solution	(63, 65, 159)
		Na <sub>2</sub> S <sub>6</sub>	Red solution	(159)
		Na <sub>2</sub> S <sub>7</sub>	Red solution	(159)
		Na <sub>2</sub> S <sub>z</sub>	Red solution	(8, 63)
	K	K <sub>2</sub> S	White, very slightly soluble 95% K <sub>2</sub> S at -60° to -30°C. <sup>(b)</sup>	(8, 63, 65, 86) (51)
		K <sub>2</sub> S <sub>2</sub>	Yellow, slightly soluble	(8)
		K <sub>2</sub> S <sub>4</sub>	Red solution	(8)
		K <sub>2</sub> S <sub>5</sub>	Red solution	(63, 65)
		K <sub>2</sub> S <sub>z</sub>	Red solution	(8)
	Rb	Rb <sub>2</sub> S		(87)
	Cs	Cs <sub>2</sub> S		(87)
	Ca	CaS	White, insoluble, calcium in excess	(124)
CaS <sub>z</sub>		Red crystals, sulfur in excess	(124)	
Se.....	Li	Li <sub>2</sub> Se	White, very slightly soluble	(8)
		Li <sub>2</sub> Se <sub>2</sub>	Red solution	(8)
		Li <sub>2</sub> Se <sub>3</sub>	Green solution	(8)
		Li <sub>2</sub> Se <sub>4</sub>	Red solution	(8)
		Li <sub>2</sub> Se <sub>5</sub>	Red-green solution	(8, 65, 87, 159)

TABLE 1—*Concluded*

ELEMENT	METAL	PRODUCTS	NOTES	REFERENCES
Group VI— <i>Concluded</i>				
Te . . . .	Na	Na <sub>2</sub> Se	White, very slightly soluble	(62)
		Na <sub>2</sub> Se <sub>2</sub>	Bright red solution	(8, 159)
		Na <sub>2</sub> Se <sub>3</sub>	Wine-red solution	(8, 159)
		Na <sub>2</sub> Se <sub>4</sub>	Green solution	(8, 62, 63, 65, 159)
		Na <sub>2</sub> Se <sub>5</sub>	Red-green solution	(8, 159)
		Na <sub>2</sub> Se <sub>6</sub>		(159)
	K	K <sub>2</sub> Se	White, very slightly soluble	(8, 62, 65, 87)
		K <sub>2</sub> Se <sub>2</sub>	Red solution	(8)
		K <sub>2</sub> Se <sub>3</sub>	Green solution	(8)
		K <sub>2</sub> Se <sub>4</sub>	Red solution	(8, 62, 63, 65)
		K <sub>2</sub> Se <sub>2</sub>	Red-green solution	(8)
	Rb	Rb <sub>2</sub> Se		(87)
	Cs	Cs <sub>2</sub> Se		(87)
	Na	Na <sub>2</sub> Te	White precipitate, yellow solution	(4, 63, 65, 87, 97, 98, 159)
			Violet solution	(32, 97, 98)
			Dark red solution	(63, 65, 98, 159)
			Na <sub>2</sub> Te <sub>4</sub> (?)	(97, 98, 159)
		K	K <sub>2</sub> Te	White, insoluble
K <sub>2</sub> Te <sub>2</sub>			Brown solution	(63, 65)
Rb		Rb <sub>2</sub> Te		(87)
Cs		Cs <sub>2</sub> Te		(87)

<sup>(a)</sup> Results modified by subsequent investigations.

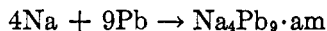
<sup>(b)</sup> Over the temperature range indicated, there were obtained 85–90 per cent yields of a product containing K<sub>2</sub>S (95.5 per cent), K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2.5 per cent), K<sub>2</sub>SO<sub>4</sub> (1.5 per cent), S (0.2 per cent), and traces of K<sub>2</sub>SO<sub>4</sub> and KNH<sub>2</sub>.

It is of interest to observe that such reactions in liquid ammonia commonly lead to the formation of intermetallic compounds of the alkali and alkaline earth metals that are not detected through the study of the phase diagrams for the corresponding binary systems. Attention is also called to the fact that Bergstrom (7) has developed an electronegative replacement series based upon the ability of one element to displace another from its combinations in the form of homopolyatomic anions in liquid ammonia solutions.

The literature relative to the reduction of elements is summarized in table 1. In addition, the inclusion here of supplementary information bearing upon certain elements seems warranted.

### A. Lead

Electrolysis of solutions of tetrasodium enneaplumbide has shown that 2.26 gram-atoms of lead per faraday are deposited at the anode and dissolved at the cathode (143). The energy of the reaction,



at  $-33^\circ\text{C}$ . has been found to be  $-88,000$  cal. (101).

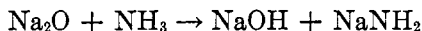
### B. Nitrogen, phosphorus, arsenic, antimony, and bismuth

As might be expected, nitrogen does not react with solutions of metals under any conditions of temperature thus far investigated. The four related elements, however, react (as indicated in table 1) to form a variety of phosphides, arsenides, antimonides, and bismuthides having compositions that are dependent upon the particular experimental conditions employed. The marked solubility of the alkali metals in ammonia has been utilized in the extraction of excess sodium from ammonia-insoluble compounds such as trisodium arsenide, antimonide, and bismuthide (107, 162).

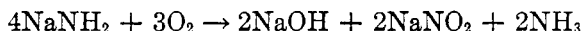
The oxidation of trisodium monobismuthide in ammonia at  $-33.5^\circ\text{C}$ . has been shown to yield bismuth(II) oxide and a mixture of oxides of sodium (153). The corresponding phosphide is similarly oxidized to phosphite and phosphate, and the antimonide yields antimonite and antimonate, while the arsenide provides only the arsenate (38). An arsenide of the formula  $\text{Na}_3\text{As}_x$  (where  $x > 1$ ) is oxidized to a mixture of elemental arsenic, arsenite, and arsenate; strictly analogous behavior is exhibited by the corresponding antimonide.

### C. Oxygen and ozone

The nature of the action of molecular oxygen upon solutions of metals is dependent upon the rate of addition of oxygen. If gaseous oxygen is slowly passed through solutions of sodium or potassium at  $-33^\circ\text{C}$ ., the alkali metal monoxide forms and is subsequently ammonolyzed (103):



Further oxidation converts the amide to nitrite:



Rapid addition of oxygen leads to the formation of  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{O}_2$ , and  $\text{K}_2\text{O}_4$  ( $\text{KO}_2$ ). Potassium tetroxide of 99 per cent purity may be formed at  $-50^\circ\text{C}$ .; at  $-33^\circ\text{C}$ . considerable quantities of potassium hydroxide and nitrite are formed. Attempts to prepare pure lithium peroxide have proved unsuccessful; the monoxide was formed to some extent regardless of the conditions employed (131). Potassium dioxide of 99 per cent purity is formed at  $-50^\circ$  to  $-60^\circ\text{C}$ . by passing oxygen through the solution until the blue color disappears. At lower temperatures, a colloidal sol and a viscous solution are formed, while at higher temperatures the dioxide is reduced to the monoxide, which is subsequently ammonolyzed. Studies on the absorption of oxygen by solutions of sodium at

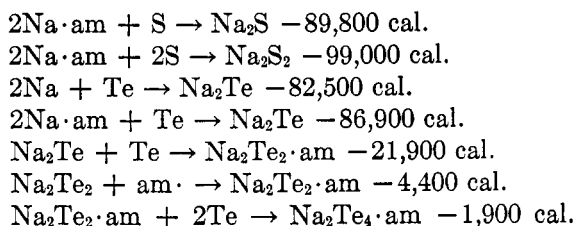


$-77^{\circ}\text{C}$ . indicate but do not prove conclusively the formation of sodium dioxide (139). The polyoxides are substantially insoluble in liquid ammonia.

The action of ozone on solutions of alkali and alkaline earth metals at temperatures of the order of  $-70^{\circ}\text{C}$ . probably results in ozonide formation, although these compounds are too unstable to permit isolation and study (144). With the alkali metals, one obtains first a precipitate of the alkali metal hydroxides but this product dissolves upon further addition of ozone to form an orange solution and a precipitate. Alkaline earth metals yield unstable brown solid products.

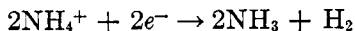
#### D. Sulfur, selenium, and tellurium

Measurement of the vapor pressures of solutions of the sodium-tellurium complexes in liquid ammonia have shown that two sodium ions are associated with each telluride ion (104),  $\text{Te}_x^{2-}$ . Products of the oxidation of the sodium mono- and poly-sulfides, selenides, and tellurides by means of molecular oxygen in liquid ammonia at  $-33^{\circ}\text{C}$ . have been determined (121). The heats of reaction of sodium solutions with sulfur and tellurium at  $-33^{\circ}\text{C}$ . are as follows (101):



### III. AMMONIUM SALTS

One of the simplest and most general reactions exhibited by solutions of metals is that with ammonium salts:



This was among the earliest of reactions studied in liquid ammonia, and it was of interest in connection with efforts to isolate the ammonium radical (125, 126). Because of their well-known role as acids in relation to ammonia as a parent solvent, ammonium salts find frequent application in the study of reactions of solutions of metals and it is consequently desirable to consider these salts before proceeding with the discussion of other types of compounds. Ammonium salts are commonly added to eliminate excess alkali metal from a reaction mixture. In other cases, ammonolytic reactions are sometimes brought to completion by neutralizing the ammonium salts with alkali metals (46, 47, 80), which have been used similarly in connection with certain reactions in amines (83, 95). A summary of reactions of ammonium salts is given in table 2.

It has been known for a long time that sodium and potassium dissolve readily in ammonia solutions of ammonium nitrate (Divers' solution) at room tem-

perature without evolution of hydrogen or other insoluble gas (34). More recently, Burgess and Holden (25) have shown that ammonium nitrate and potassium react in the ratio 1:3.1 without evolution of hydrogen. This ratio is that required for the reaction represented by the equation:



Ammonium sulfamate reacts rapidly with a solution of sodium in liquid ammonia to form sodium sulfamate,  $\text{NaSO}_2\text{NH}_2$ , and then more slowly to form disodium sulfamate,  $\text{NaSO}_2\text{NHNa}$  (ratio = 1:2.15). There is no degradation or

TABLE 2  
*Reactions of ammonium salts with solutions of metals in liquid ammonia*

AMMONIUM SALT	METAL	PRODUCTS	REFERENCES
$\text{NH}_4\text{Cl}$ .....	Li	$\text{LiCl}$	(125)
	Ca	$\text{CaCl}_2$	(125)
$\text{NH}_4\text{Br}$ .....	Na	$\text{NaBr}$	(46)
$\text{NH}_4\text{I}$ .....	Na	$\text{NaI}$	(47, 80)
$\text{NH}_4\text{NO}_3$ .....	K	$\text{K}_2\text{NO}_2$	(25)
$\text{NH}_4\text{N}_3$ .....	Li	$\text{LiN}_3$	(20)
	Na	$\text{NaN}_3$	(20)
	K	$\text{KN}_3$	(20)
	Ca	$\text{Ca}(\text{N}_3)_2$	(20)
	Mg	$\text{Mg}(\text{N}_3)_2$	(20)
$\text{NH}_4\text{CN}$ .....	Ca	$\text{Ca}(\text{CN})_2 \cdot 2\text{NH}_3$	(48)
$(\text{NH}_4)_2\text{S}$ .....	Li	$\text{Li}_2\text{S}$	(126)
	Ca	$\text{CaS}$	(126)
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ .....	Na	$\text{NaC}_2\text{H}_3\text{O}_2$	(102)
$\text{NH}_4\text{SO}_3\text{NH}_2$ .....	Na	$\text{NaSO}_3\text{NH}_2$	(31)
		$\text{NaSO}_3\text{NHNa}$	(31)
		$\text{NaSC}_6\text{H}_5$	(102)
$\text{NH}_4\text{ClO}_4$ .....	Na	$\text{NaClO}_4$	(42)
$(\text{NH}_4)_2\text{CrO}_4$ .....	K	Green precipitate	(42)
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .....	K	Green precipitate	(42)
$\text{NH}_4\text{CO}_2\text{C}_6\text{H}_5$ .....	Na	$\text{NaCO}_2\text{C}_6\text{H}_5$ + hydrogenation	(45)

disruption of the sulfamate group even in the presence of excess sodium over periods up to 3 hr. and upon treatment with ammonium chloride (31). Alkali metal sulfamates prepared in liquid ammonia are claimed in a patent (56). The use of these salts as primary standards in analytical work, as dehydration agents for organic liquids, and as intermediates in the synthesis of substituted sulfamic acids is mentioned in the specifications.

Ammonium chromate and dichromate in liquid ammonia are partially reduced by potassium to afford a green precipitate ( $\text{Cr}_2\text{O}_3$ ?). These reactions are complicated by the interaction of the dichromate ion with the solvent and by the catalytic conversion of potassium to the amide. In the case of ammonium chromate more reduction was observed when the compound was added to the alkali metal solution than when the reverse procedure was followed (42). Under

similar conditions, ammonium perchlorate forms sodium perchlorate and hydrogen, and ammonium iodate and periodate form the respective sodium salts together with sodium iodide and some hydrogen. Ammonium benzoate (45) reacts with sodium (*ca.* 2.5 gram-atoms per mole) to form the sodium salts of hydrogenated benzoic acids without the liberation of any hydrogen.

The hydrogen liberated upon addition of a metal to a liquid ammonia solution of an ammonium salt has been utilized in the *in situ* reduction of numerous organic substances. Reduction of inorganic materials in this manner has been attempted in only two instances. Addition of potassium to liquid ammonia (at  $-33.5^{\circ}\text{C}.$ ) containing an excess of ammonium bromide together with silver(I) iodide, bismuth(III) oxide, or germanium(IV) oxide failed to provide any evidence of reactions other than those that take place when the metal is added in the absence of the ammonium salt (152). Under similar conditions, and at room temperature as well, sodium chlorate and sodium perchlorate are not reduced by sodium and ammonium bromide (42). Further details concerning these and other related reactions are included in table 5.

#### IV. HYDRIDES

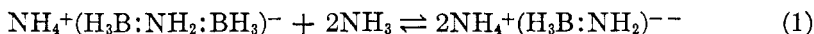
Despite the fact that reactions of hydrides with solutions of metals offer many interesting possibilities of potential importance in connection with problems in structure and synthesis, relatively few of these possibilities have been explored. Some of the reactions that have been investigated are of sufficient interest to warrant detailed consideration.

##### A. Diborane and related compounds

In solutions in liquid ammonia at  $-77^{\circ}\text{C}.$ , the "diammoniate" of diborane reacts with sodium (present in excess) to produce only 1 gram-atom of hydrogen for every 2 gram-atoms of boron present (140). The reaction may be written:



When the "diammoniate" is allowed to remain in contact with liquid ammonia for a short time at  $-40^{\circ}\text{C}.$  before sodium is added, more hydrogen than corresponds to 1 gram-atom per mole of compound is liberated by the subsequent action of sodium. This result indicates that additional ammonium ions are formed, as should occur when the following reaction,



proceeds toward the right and approaches equilibrium.

If dimethylether-borine,  $(\text{CH}_3)_2\text{O}:\text{BH}_3$ , is added to a solution of sodium in ammonia, 1 gram-atom of hydrogen is liberated per gram-atom of boron contained in the original etherate, and the salt  $\text{Na}(\text{H}_3\text{B}:\text{NH}_2)$  may be obtained from the reaction mixture.



If, on the other hand, the dimethylether-borine remains in contact with liquid ammonia for a short time before sodium is added, less than 2 gram-atoms (e.g., 1.8 or less) of hydrogen is evolved per 2 gram-atoms of boron in solution. This result indicates an approach to equilibrium 1 from the right (2, 140).

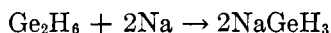
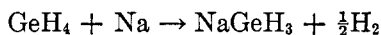
Trimethylamine-borine,  $(\text{CH}_3)_3\text{N}:\text{BH}_3$ , is inert toward sodium in liquid ammonia. When borine carbonyl 2-ammoniate,  $\text{H}_3\text{BCO}\cdot 2\text{NH}_3$ , is dissolved in liquid ammonia and treated with sodium, 1 gram-equivalent of hydrogen is rapidly liberated per mole of borine carbonyl; a second equivalent is produced more slowly (22). The substance  $\text{B}_2\text{H}_6\cdot\text{PH}_3\cdot\text{NH}_3$  reacts with sodium in liquid ammonia (50) to yield 1 gram-equivalent of hydrogen per mole of compound, as though the formula is  $\text{NH}_4^+(\text{H}_3\text{B}:\text{PH}_2:\text{BH}_3)^-$ .

The product obtained by the action of ammonia on tetramethyldiborane reacts with sodium in liquid ammonia in the same manner (including rate and point of cessation) as does the corresponding diborane compound. This fact argues strongly for a similarity of structure of the two compounds (141).

At  $-60^\circ\text{C}$ . the ammonia addition product of  $\text{B}_2\text{H}_7\text{N}$  liberates 1 gram-atom of hydrogen per mole of compound when treated with sodium in liquid ammonia for about 1 hr.; thereafter the reaction is very slow. At the end of the first stage of the reaction, a salt-like product of the composition  $\text{NaNH}_2\cdot\text{B}_2\text{H}_7\text{N}$  may be isolated (142).

### B. Germanes<sup>2</sup>

Both monogermane (96) and digermane (93) react with solutions of sodium in liquid ammonia to form sodium trihydrogermanide, thus:



Although sodium trihydrogermanide, which is the germanium analog of sodium methide, exhibits sufficient stability in liquid ammonia to permit its use in synthesis, this kind of application remains essentially unexplored.

### C. Ammonia, hydrazine, phosphine, and arsine

The result of the interaction of metals dissolved in liquid ammonia and the solvent molecules depends upon the nature of the metal involved. The alkaline earth metals dissolve in and combine with solvent molecules to form definite molecular species of the type  $\text{M}(\text{NH}_3)_6$  (15, 16); the known compounds are  $\text{Ca}(\text{NH}_3)_6$  (90),  $\text{Sr}(\text{NH}_3)_6$  (137), and  $\text{Ba}(\text{NH}_3)_6$  (123). Similarly, lithium forms the substance  $\text{Li}(\text{NH}_3)_4$  (66), and the compound  $\text{Mg}(\text{NH}_3)_6$  results from the action of liquid ammonia upon magnesium amalgam (119). All of these products

<sup>2</sup> Reactions of hydrides of carbon are discussed in another paper concerned with reactions of organic and organometallic compounds (Chem. Revs. 46, 317 (1950)).

<sup>3</sup> Although the entire question as to the physical nature of solutions of metals in liquid ammonia is one which has attracted much attention in the past and continues to be the subject of studies both experimental and theoretical, any further discussion of this particular problem is considered to be beyond the scope of the present paper.

may be isolated in definite crystalline form, but little is known concerning their physical properties or constitution.

Solutions of these compounds as well as solutions of the alkali metals other than lithium are remarkably stable in liquid ammonia at ordinary temperatures and in the absence of catalysts.<sup>3</sup> Conversion of the alkali and alkaline earth metals to the corresponding amides nevertheless occurs slowly. This type of reaction is catalyzed by short ultraviolet light (73, 128) and by a wide variety of metals and their compounds (5, 6, 9, 12, 13, 14, 27, 30, 85, 145). In those cases in which compound catalysts are added, it seems likely that the compounds are reduced by the action of the metal solutions and that the reduction products are the active catalysts (57, 127, 146). Thus, it is common practice to employ oxides of iron, or iron(III) nitrate 9-hydrate as catalysts in the preparation of ammonia solutions of the alkali amides. It is known, however, that these compounds are readily reduced to finely divided and extremely reactive elemental iron, which is one of the most effective catalysts for the reactions involved. The resulting alkali and alkaline earth metal amides are unquestionably among the most useful reagents for synthesis in liquid ammonia.

Free hydrazine is almost entirely unreactive toward solutions of sodium in liquid ammonia at its boiling point (40). Hydrazine dihydrochloride, however, reacts with sodium to liberate hydrogen which partially reduces the hydrazine. Use of 4.3 gram-atoms of sodium per mole of the dihydrochloride, followed by addition of ammonium chloride, results in the reduction of approximately 23 per cent of the hydrazine.

While the reaction between a solution of a metal and ammonia is slow in the absence of a catalyst, the corresponding reaction with phosphine is rapid. Thus, phosphine reacts readily with a solution of lithium (113) in liquid ammonia to form hydrogen and lithium dihydrogen phosphide,  $\text{LiPH}_2$ . At  $0^\circ\text{C}$ .  $\text{LiPH}_2$  forms the 4-ammoniate, and by thermal decomposition this solvate may be converted successively to the 2- and 1-ammoniates. The last molecule of ammonia cannot be removed without the simultaneous loss of 0.5 mole of phosphine per mole of phosphide. This decomposition takes place at  $50^\circ\text{C}$ ., leaving a residue of dilithium hydrogen phosphide,  $\text{Li}_2\text{PH}$ . If this latter substance is placed in liquid ammonia, it forms  $\text{Li}_2\text{PH}\cdot 5\text{NH}_3$ , which is soluble in excess ammonia and which forms 3- and 2-ammoniates upon thermal decomposition.

In a similar manner, sodium and potassium react with phosphine to form  $\text{NaPH}_2$  and  $\text{KPH}_2$  (72, 76). When heated,  $\text{NaPH}_2$  loses 0.5 mole of phosphine at  $70^\circ\text{C}$ ., leaving a residue of  $\text{Na}_2\text{PH}$  (115). At  $100^\circ\text{C}$ . hydrogen evolution begins and at  $380^\circ\text{C}$ . sodium is distilled out, leaving a residue of  $\text{Na}_2\text{P}_5$ . Similarly,  $\text{KPH}_2$  loses phosphine if heated to  $100^\circ\text{C}$ . At  $175^\circ\text{C}$ . it begins to darken and to lose pure hydrogen, the total loss of hydrogen being 1 mole per mole of phosphide. Further heating to above  $320^\circ\text{C}$ . results in the distillation of metallic potassium, leaving  $\text{K}_2\text{P}_5$ .

Calcium reacts with phosphine in liquid ammonia at  $-70^\circ\text{C}$ . to form a white precipitate of  $\text{Ca}(\text{PH}_2)_2\cdot 6\text{NH}_3$ . This substance has a dissociation pressure of 46 mm. of mercury at  $0^\circ\text{C}$ . and forms a 2-ammoniate (114). Upon elevation of the

temperature one obtains phosphine, ammonia, and a product corresponding to the formula  $\text{CaPH}$ , while still further heating leads to liberation of gaseous hydrogen and leaves presumably a phosphide of calcium (117). Under conditions similar to those employed in the studies involving calcium, strontium gave only ill-defined mixtures.

In view of the widespread use of alkali and alkaline earth metal amides in synthesis, it is somewhat surprising that these corresponding compounds of phosphorus have not been studied more extensively. They have been employed in this manner on only a relatively few occasions (88, 155).

In its behavior toward liquid ammonia solutions of lithium (116), sodium (82, 106, 112), and potassium (82), arsine is generally similar to phosphine. With lithium, arsine forms  $\text{LiAsH}_2 \cdot 4\text{NH}_3$ , which decomposes to the 2-ammoniate at  $0^\circ\text{C}$ . The latter in turn decomposes on further heating and leaves a residue of  $\text{Li}_2\text{AsH}$ , which loses all of its hydrogen at  $70^\circ\text{C}$ . but is not further changed on heating to  $450^\circ\text{C}$ . Potassium dihydrogen arsenide has been used in the synthesis of methylarsine, which was subsequently converted to the salt  $\text{CH}_3\text{AsHK}$  (82). The reaction between calcium and arsine in liquid ammonia results in a yellow compound which decomposes at  $150^\circ\text{C}$ . to form a brown solid product believed to be an arsenide of calcium (106, 112).

With reference to the preparation and use of compounds of the type described above, it is claimed (3) that  $\text{NaPH}_2$  and  $\text{NaAsH}_2$  of a high degree of purity are afforded by the reactions of phosphine and arsine with sodium triphenylmethide in ether.

#### *D. Water; hydrides of sulfur and the halogens*

As is to be expected, water reacts with solutions of metals in liquid ammonia in the same manner as it does under other conditions. A rapid method for the determination of moisture (and other impurities containing active hydrogen) in liquid ammonia is based upon the reaction between sodium and water (132). By this method, it is claimed that 0.01 per cent of water can be determined with an accuracy of 2–3 per cent in 10–15 min. If water is present in liquid ammonia used as a medium for the interaction of metals and reducible materials, the reaction between the metal and water may occur at a preferential rate and the resulting hydrogen may participate in reduction reactions. Although this kind of behavior has been observed in the study of the reduction of organic substances, it has not been reported as having any bearing upon the reduction of inorganic materials.

Hydrides of sulfur and the halogens combine with liquid ammonia to form ammonium salts; these have already been discussed.

#### V. OXIDES

The summary given in table 3 shows that studies of the reactions of oxides of nonmetals have not been extensive. Carbon monoxide is known to form carbonyls that have not been studied sufficiently to warrant statements concerning their structure. Carbon dioxide appears to react with ammonia to form carbamic

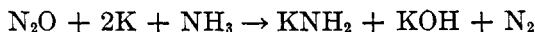
acid (or ammonium carbamate), which then forms a sodium salt; the hydrogen thus liberated reduces a portion of the carbamate to formate.

TABLE 3

*Reactions of nonmetal oxides with solutions of metals in liquid ammonia*

OXIDE	METAL	PRODUCTS	NOTES	REFERENCES
CO.....	Li	LiCO	-60°C.; white precipitate	(129)
	Na	Na(CO) <sub>2</sub>	-50°C.; very explosive	(70, 77)
	K	K(CO) <sub>2</sub>	-50°C.; rose-white, gelatinous precipitate	(70, 77)
	Rb	RbCO	-60°C.; white precipitate	(129)
	Ca	Ca(CO) <sub>2</sub>	-60°C.; white precipitate	(129)
	Ba	Ba(CO) <sub>2</sub>	-50°C.; gelatinous precipitate	(52, 122)
CO <sub>2</sub> .....	Na	H <sub>2</sub> NCOONa	-50° to -60°C.	(133)
		HCOONa	-25° to -35°C.	(133)
N <sub>2</sub> O.....	Na	N <sub>2</sub> , NaOH, NaNH <sub>2</sub> , NaN <sub>3</sub> , NaOH	Primary reaction Reaction of N <sub>2</sub> O with amide	(71, 75) (1, 71, 75)
	K		See under sodium	(71, 75)
NO.....	Na	NaNO (NaNO) <sub>n</sub>	Gelatinous precipitate	(71, 75) (161)
	K	KNO	Gelatinous precipitate	(71, 75)
	Ba	Ba(NO) <sub>2</sub>	Gelatinous precipitate	(122)
NO <sub>2</sub> .....	Ba	Ba(NO) <sub>2</sub> (?)	Gelatinous precipitate	(52)

The apparently complex mixture of products obtained by the action of nitrous oxide on metal solutions may be explained on the basis of two reactions. In the first, a molecule of the oxide is reduced to nitrogen,



and the other products (alkali amide and hydroxide) are those expected from ammonolysis of the alkali monoxide. The alkali amide then reacts with another molecule of the oxide:



The latter reaction is known to take place under somewhat different conditions (33, 58, 156) and is the basis for a patented process (1) for the production of sodium azide in liquid ammonia.

Nitric oxide reacts with solutions of sodium, potassium, and barium to form precipitates having the composition NaNO, KNO, and Ba(NO)<sub>2</sub>. Aqueous solutions of these products yield the characteristic silver salt of hyponitrous acid (71, 75, 139). It has been shown, however, that the diamagnetic (49) sodium nitrosyl gives an x-ray diffraction pattern different from that of sodium hyponitrite (161).

Nitrogen dioxide, while not thoroughly investigated, is apparently reduced by a solution of barium and forms the same product as nitric oxide (52).

Although the reduction of only a few oxides of the metals and metalloids has

been studied, the work that has been done seems sufficient to indicate in general the nature of the reduction products to be anticipated in relation to the nature of the metal. The primary product of the reduction of oxides of normal elements with solutions of potassium appears to be the free element, which then forms insoluble and/or soluble intermetallic compounds with any excess alkali metal present. Cases studied include bismuth(III) oxide, arsenic(III) oxide, antimony(III) oxide, tin(II) and tin(IV) oxides, lead(II) and lead(IV) oxides, zinc oxide, and cadmium oxide (151). An exceptional case is that of germanium(IV) oxide, which remains unchanged after long contact with a solution of potassium and exhibits only very limited catalytic activity toward the conversion of potassium to potassium amide.

Oxides of transitional elements generally yield either a lower oxide or the free element without the subsequent formation of intermetallic compounds. These reactions are frequently incomplete because of the high degree of catalytic activity of the reduction products. Thus, copper(II) oxide is quantitatively reduced to copper(I) oxide which, because of its marked catalytic effect upon the conversion of metal to amide, undergoes only slight reduction to metallic copper. Silver(I) oxide is reduced quantitatively to elemental silver (151).

Molybdenum(VI) oxide is reduced quantitatively to molybdenum(III) oxide (147) by the action of three equivalents of potassium in ammonia at  $-33.5^{\circ}\text{C}.$ ; this reaction provides the only direct method for the production of molybdenum(III) oxide. Use of a large excess of potassium results in the reduction of molybdenum(VI) oxide to a mixture of molybdenum(III) oxide and elemental molybdenum (149). This reduction requires 6 gram-atoms of potassium per mole of the original oxide, but as the quantity of potassium employed is progressively increased, the fraction that participates in the reduction of molybdenum approaches 5 gram-atoms as a limiting value. This result is attributable to the pronounced catalytic activity of the elemental molybdenum toward the formation of potassium amide. Under similar conditions, molybdenum(IV) oxide is not reduced by solutions of potassium (152).

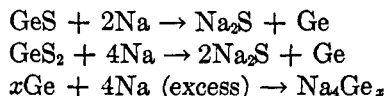
At  $0^{\circ}\text{C}.$  cobalt(III) oxide is reduced by solutions of potassium to cobalt(II) oxide and this in turn to metallic cobalt to an extent dependent upon the  $\text{Co}_2\text{O}_3/\text{K}$  ratio, while iron(II) oxide is reduced to iron only to a very limited extent. Iron(II) oxide (or its reduction products) is a much better catalyst for amide formation than cobalt(III) oxide (or its reduction products). The evolution of hydrogen is rather slow until some of the oxide is reduced (127). Similarly, nickel(II) oxide is reduced to elemental nickel to an extent dependent upon the concentration of potassium employed. With 2, 4, 8, and 12 equivalents of potassium, reduction occurs to the extent of 0.3, 0.5, 1.4, and 4.3 per cent, respectively. The weights of potassium amide formed concurrently (as shown by analysis) agree closely with corresponding values calculated on the basis of (a) the volumes of hydrogen liberated and (b) the quantities of elemental nickel produced. At  $25^{\circ}\text{C}.$  nickel(II, III) oxide was converted by a solution of potassium into an intractable mixture of insoluble products. The catalytic activity of nickel(II,



III) and iron(III) oxides<sup>4</sup> (or that of very small quantities of their reduction products) toward the conversion of potassium to its amide was so pronounced that appreciable reduction of these oxides by ammonia solutions of potassium could not be accomplished (57). The decreasing order of catalytic activity is  $\text{Fe}_2\text{O}_3 > \text{Ni}_3\text{O}_4 > \text{NiO}$ .

#### VI. SULFIDES

The sulfides of germanium are reduced by solutions of sodium in liquid ammonia at  $-33^\circ\text{C}$ . to sodium sulfide and sodium polygermanide (84):



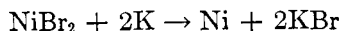
The potentiometric titration of arsenic(III) sulfide and antimony(III) sulfide by sodium in liquid ammonia provides evidence of the formation of the following compounds (159):  $\text{Na}_3\text{As}$  (brown precipitate),  $\text{Na}_3\text{As}_3$  (yellow),  $\text{Na}_3\text{As}_5$  (dark red-brown),  $\text{Na}_3\text{As}_7$ ;  $\text{Na}_3\text{Sb}$  (gray-brown precipitate),  $\text{Na}_3\text{Sb}_3$  (deep red),  $\text{Na}_3\text{Sb}_7$ .

#### VII. HALIDES AND SIMPLE CYANIDES

The products formed upon treatment of halides and simple cyanides with solutions of metals in liquid ammonia are in most cases similar to those obtained by direct reaction with the corresponding elements. In these reactions, the primary product is usually the free element in a highly reactive condition.

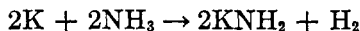
With respect to the nature of the electropositive constituent of the halides or cyanide, the same generalizations made in connection with the discussion of metal oxides appear to apply to halides and cyanides. One important difference, however, must be recognized. Because of the comparatively greater tendency for halides and cyanides to react at an appreciable rate with alkali and alkaline earth metal amides in liquid ammonia, competitive reactions often become a major factor. This is particularly true whenever a halide or cyanide of a transitional element is involved, because the corresponding free elements are usually excellent catalysts for amide formation. The halides of nickel serve as a good illustration of the complications that may arise. The reduction of these compounds has been studied extensively by Burgess and Eastes (24) and by Watt and Davies (148).

The primary result of the reaction between nickel(II) bromide, for example, and potassium in liquid ammonia at  $-33.5^\circ\text{C}$ . may be represented by the equation:

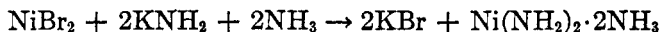


<sup>4</sup> Bergstrom (13) apparently observed no reduction of either iron(III) oxide or cobalt(II, III) oxide.

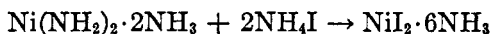
As quickly as any elemental nickel is thus produced, it catalyzes the formation of potassium amide,



which in turn reacts with the bromide to form nickel(II) amide 2-ammoniate:



The extent of formation of nickel(II) amide 2-ammoniate increases as the scale of operation (and hence the time of contact) is increased and although this competitive reaction cannot be eliminated completely, it may be minimized by short overall time of reaction, rapid addition of the alkali metal, and the use of alkali metal in only a slight excess over the stoichiometric quantity. The purity of the resulting nickel does not exceed 95-96 per cent unless an ammonium salt is added to convert the amide to a soluble nickel salt,



in which case the purity may be increased to 98-99 per cent.

In addition to attack of the original halogenide or cyanide by alkali amide, the latter may act upon the product of the primary reduction reaction. For example, manganese formed by the reduction of manganese(II) iodide with sodium participates in subsequent reactions leading to the formation of  $Mn(NH_2)_2$  and  $Mn(NHNa)_2 \cdot 2NH_3$  (30).

Particularly noteworthy are some of the properties of metals produced in these reactions. The products are nearly always very finely divided and are usually pyrophoric. Nickel, for example, exhibits pronounced catalytic activity toward amide formation (24) and in the hydrogenation of certain organic substances (148). The catalytic activity of nickel is known to vary as a function of both the salt reduced and the nature of the alkali or alkaline earth metal used as the reducing agent. This catalytic activity is attributable to the presence of adsorbed hydrogen that may be removed either by treatment with a liquid ammonia solution of an ammonium salt or by raising the temperature just above the Curie point (357°C.). Adsorption of hydrogen is either partially or completely inhibited by the presence of iodide ion during the reduction reactions. Thus, the nickel from the reduction of nickel(II) iodide is not appreciably pyrophoric and is a very poor hydrogenation catalyst (148). Similarly, the catalytic activity of nickel from nickel(II) bromide is markedly decreased when the reduction is effected in the presence of potassium iodide.

Information concerning the reduction of halides and simple cyanides is incorporated in table 4.

#### VIII. COMPLEX CYANIDES

The reduction of the complex cyanides of copper, silver, zinc, and cadmium [ $K_3Cu(CN)_4$ ,  $KAg(CN)_2$ ,  $K_2Zn(CN)_4$ , and  $K_2Cd(CN)_4$ ] by potassium in liquid

TABLE 4

*Reactions of halides and simple cyanides with solutions of metals in liquid ammonia*

SALT	METAL	PRODUCTS	NOTES	REFERENCES <sup>(a)</sup>
Group I				
CuI.....	Na	Cu		(159)
AgCl.....	Na	Ag		(29, 30)
	K	Ag		(25)
AgI.....	Na	Ag		(29, 30, 99, 159)
	K	Ag		(25)
			Heat of reaction = 51,185 cal.	(55)
AgCN.....	Ca	Ag		(25)
	Na	Ag		(25, 99)
	K	Ag		(25)
	Ca	CaAg	Not confirmed	(99)
		Ag		(25)
AuI.....	Na	NaAu		(159)
Group II				
ZnI <sub>2</sub> .....	Na	NaZn <sub>4</sub> NaZn <sub>12</sub> (?)		(99) (159)
Zn(CN) <sub>2</sub> .....	Na	NaZn <sub>4</sub> Zn	Zn(CN) <sub>2</sub> in excess	(28, 30, 99) (28)
	Ca	Ca <sub>7</sub> Zn		(99)
CdI <sub>2</sub> .....	Na	NaCd NaCd <sub>5-7</sub>		(99) (159)
Cd(CN) <sub>2</sub> .....	Na	NaCd		(99)
HgI <sub>2</sub> .....	Ca	Ca <sub>2</sub> Hg <sub>2</sub>		(99)
Hg(CN) <sub>2</sub> .....	Na	NaHg	2NaHg → Na + NaHg <sub>2</sub>	(99, 159)
	Ca	Ca <sub>2</sub> Hg <sub>2</sub>		(99)
Group III				
BF <sub>3</sub> ·NH <sub>3</sub> .....	Na	H <sub>2</sub>	Reaction in several steps	(94)
GaBr <sub>3</sub> .....	Na	Ga (?)		(78)
TlI.....	Na	Na <sub>3</sub> Tl <sub>2</sub> NaTl, NaTl <sub>2</sub>		(99) (159)
Group IV				
SnI <sub>2</sub> .....	Na	Na <sub>4</sub> Sn Na <sub>4</sub> Sn <sub>2</sub>	Unstable	(99; cf. 162) (99; cf. 162)
	Ca	Ca <sub>5</sub> Sn		(99)
PbBr <sub>2</sub> .....	Na		Heat of reaction measured <sup>(b)</sup>	(101)
PbI <sub>2</sub> .....	Na	Na <sub>4</sub> Pb Na <sub>4</sub> Pb <sub>7</sub> Na <sub>4</sub> Pb <sub>9</sub>	Unstable	(99, 162) (159) (159)
	K	K <sub>4</sub> Pb <sub>9</sub>	Dark green	(159)
	Ca	Ca <sub>2</sub> Pb <sub>3</sub>		(99)

TABLE 4—Concluded

SALT	METAL	PRODUCTS	NOTES	REFERENCES <sup>(*)</sup>
Group IV—Concluded				
ZrBr <sub>4</sub> .....	K	Black precipitate, red solution	Neither permanent	(157; cf. 18)
ThBr <sub>4</sub> .....	K	Zr(NK) <sub>2</sub> ·NH <sub>3</sub> , H <sub>2</sub> Th(NH)NK·NH <sub>3</sub> , H <sub>2</sub> Th(NK) <sub>2</sub> ·KNH <sub>3</sub>	Secondary reactions Bromide first ammonolyzes Slow secondary reaction Continued action	(157) (157) (157) (157)
Group V				
Ni <sub>2</sub> ·3NH <sub>3</sub> .....	Na	NaI, N <sub>2</sub>		(65)
SbBr <sub>3</sub> .....	Na	NaSb <sub>4</sub> ,s		(99)
BiCl <sub>3</sub> .....	Na	NaBi <sub>2</sub> ,s		(99)
BiI <sub>3</sub> .....	Na	Bi Na <sub>3</sub> Bi Na <sub>3</sub> Bi <sub>2</sub> Na <sub>3</sub> Bi <sub>5</sub>	Black precipitate Violet solution Brown solution	(153) (153, 159) (153, 159) (153, 159)
Group VII				
MnI <sub>2</sub> .....	Na	Mn Mn NaNH <sub>2</sub> , Mn(NH <sub>2</sub> ) <sub>2</sub> , Mn(NHNa) <sub>2</sub> · 2NH <sub>3</sub>	Probable initial product Highly reactive metal Secondary reactions	(30) (118) (30)
Group VIII				
NiX <sub>2</sub> <sup>(c)</sup> .....	Na K Ca	Ni Ni Ni	Reduction incomplete	(24) (24, 148) (24)
Ni(CN) <sub>2</sub> .....	Na K	Ni Ni		(24) (24)

(\*) Important references relating to the nature of homopolyanionic salts and intermetallic compounds (or phases) include the following: 10, 43, 79, 91, 92, 158, 160, 164.

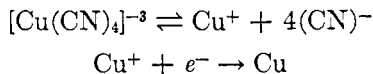
(b)  $\text{PbBr}_2 \cdot \text{am} + 6\text{Na} \rightarrow 2\text{NaBr} \cdot \text{am} + \text{Na}_4\text{Pb} - 104,400 \text{ cal.}$

$\text{PbBr}_2 \cdot \text{am} + 2\text{Na} \rightarrow 2\text{NaBr} \cdot \text{am} + \text{Pb} - 91,200 \text{ cal.}$

$\text{PbBr}_2 + 2\text{Na} \cdot \text{am} \rightarrow 2\text{NaBr} \cdot \text{am} + \text{Pb} - 123,700 \text{ cal.}$

(c) Where X = Cl, Br, or I.

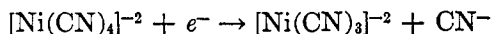
ammonia follows the course that would be expected if the complex ion is markedly dissociated in solution (36):



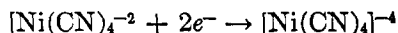
For these salts, the products have the following characteristics: copper, black, pyrophoric, no hydrogen; silver, black, pyrophoric, very little hydrogen; zinc, not reactive with water, no hydrogen.

The behavior of the cyanonickelate ion toward solutions of metals is entirely different from that of the cyanocuprate, cyanoargentate, and cyanozincate. With cyanonickelate, the following reactions take place (35, 36):

$[\text{Ni}(\text{CN})_4]^{-2}$  in excess:

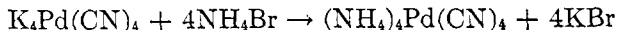


Na, K, or Ca in excess:



These reactions take place equally well at  $-33^\circ$  and at  $0^\circ\text{C}$ . Ordinarily, the addition of excess alkali metal to  $\text{M}_2\text{Ni}(\text{CN})_3$  (with MCN in the supernatant solution) converts it to  $\text{M}_4\text{Ni}(\text{CN})_4$ , but occasionally at  $-33^\circ\text{C}$ . the precipitated  $\text{M}_2\text{Ni}(\text{CN})_3$  is resistant toward further reduction. No hydrogen is evolved except when calcium is used as the reducing agent. The tricyanonickelates(I) are dense, bright red precipitates, while the tetracyanonickelates(0) are bulky yellow precipitates or amorphous copper-colored solids. The former may be prepared in low yield in aqueous solutions, while the latter are unknown except in liquid ammonia. Both of these compounds possess strong reducing properties. Potassium tricyanonickelate(I) may be heated to  $200^\circ\text{C}$ . without change; potassium tetracyanonickelate(0) is stable at room temperature but begins to turn green at  $160^\circ\text{C}$ . and rapidly becomes dark green with further increase in temperature (21). Neither compound showed any alteration when treated with ammonia bromide in liquid ammonia solution at  $-33^\circ\text{C}$ .

Potassium cyanopalladate(II) resembles the nickelate in that reduction by a solution of potassium at both  $-33^\circ$  and  $0^\circ\text{C}$ . produces a moderately soluble white precipitate having the composition  $\text{K}_4\text{Pd}(\text{CN})_4$  without liberation of hydrogen (21). There is no evidence for an intermediate of the type represented by  $\text{K}_2\text{Ni}(\text{CN})_3$ . Potassium tetracyanopalladate(0) is capable of reducing silver(I) and mercury(II) ions<sup>5</sup> and of reducing azobenzene to hydrazobenzene. While the cyanopalladate(0) is stable enough to permit isolation, it slowly decomposes in a vacuum or in contact with liquid ammonia, the more rapidly the higher the temperature. The decomposition is fairly rapid in liquid ammonia when a decided excess of potassium is used. Treatment of the cyanopalladate(0) with a solution of ammonium bromide results in the dissolution of the precipitate and the subsequent precipitation of potassium bromide. Presumably, the reaction represented by the equation,



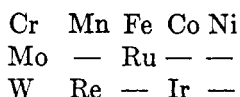
takes place. However, upon concentrating the solution in order to isolate the ammonium cyanopalladate(0), the solute decomposes and liberates elemental palladium.

It is interesting to note that in the compounds  $\text{K}_4\text{Ni}(\text{CN})_4$  and  $\text{K}_4\text{Pd}(\text{CN})_4$  the central atom of the complex ion exhibits an *effective atomic number* (E.A.N.)

<sup>5</sup> Unlike the behavior of the corresponding nickelate(0), the precipitated metals are mixed with palladium.

equal to the atomic number of the inert gas at the end of the period in which the element is placed in the periodic classification, i.e.,  $(E.A.M.)_{Ni} = 36 = Z_{Kr}$ ; similarly,  $(E.A.N.)_{Pd} = 54 = Z_{Xe}$ . Hence, these complex ions are comparable to the known carbonyl of nickel,  $Ni(CO)_4$ , and the anticipated carbonyl of palladium,  $Pd(CO)_4$ . The difference lies in the fact that the  $CN^-$  ion, although isoelectronic with the carbon monoxide molecule, carries with it a negative charge which must be balanced by a corresponding charge on a positive ion. Hence, the same pattern of combination leads to a neutral molecule in one case and to a complex ion in the other (17).

If this point of view is valid, one might then expect to find stable complex cyanide ions of oxidation number less than 2 for those elements that form stable carbonyls:



No systematic attempt to verify this suggestion has been made, but certain miscellaneous observations bear upon the subject. Potassium cyanoplatinate(II) reacts with a solution of potassium in liquid ammonia, but the complete characterization of the product is handicapped by the relative insolubility of  $K_2Pt(CN)_4$  and the marked evolution of hydrogen. The reaction ratios for  $K/K_2Pt(CN)_4$  at  $-33^\circ C$ . are greater than 2:1 even when correction is made for hydrogen evolved. However, on adding potassium to a solution of  $K_2Pt(CN)_4 + 5KNH_2$ , very little gas is evolved and the reaction ratio is 2.057:1. At  $0^\circ C$ . addition of a potassium solution to one of  $K_2Pt(CN)_4$  produces a white precipitate (intermediate brown coloration) which has an analytical composition close to that of  $K_4Pt(CN)_4$ .

Potassium cyanoferrate(III),  $K_3Fe(CN)_6$ , is reduced to potassium cyanoferrate(II),  $K_4Fe(CN)_6$ , but no further by a solution of potassium (23). Both potassium cyanochromate(III),  $K_3Cr(CN)_6$ , and potassium cyanocobaltate(III),  $K_3Co(CN)_6$ , react with potassium in liquid ammonia, but neither the reaction ratios at  $-33^\circ C$ . nor the analytical composition of the brown precipitates formed at room temperature are consistent. Large quantities of hydrogen are liberated (37). Potassium cyanomanganate(III),  $K_3Mn(CN)_6$ , reacts with potassium in liquid ammonia solution to form first a gray violet and then a light orange precipitate (41). This latter apparently is  $K_5Mn(CN)_6 \cdot NH_3$ .

#### IX. OTHER ORGANIC COMPOUNDS

Although the possibilities for study of reactions of inorganic substances other than those discussed above are essentially unlimited, only relatively few substances have been investigated. A brief summary of the available information is given in table 5.

As shown in table 5,  $KMnO_4$  is reduced to  $K_2MnO_4$  and oxides of manganese by the action of solutions of potassium in ammonia (42). This reduction occurs

TABLE 5

*Reactions of ternary and more complex compounds with solutions of metals in liquid ammonia*

COMPOUND	METAL	PRODUCTS	NOTES	REFER- ENCES
NaNO <sub>2</sub> .....	Li	LiNaNO <sub>2</sub>		(120)
	Na	Na <sub>2</sub> NO <sub>2</sub>		(120, 165)
KNO <sub>2</sub> .....	K	KNaNO <sub>2</sub>		(120)
	Na	KNaNO <sub>2</sub>		(120)
NaNO <sub>3</sub> .....	Na	Na <sub>2</sub> NO <sub>2</sub>	Explosive	(25)
KNO <sub>3</sub> .....	K	K <sub>2</sub> NO <sub>2</sub>	Not explosive	(25)
AgNO <sub>3</sub> .....	Na	Ag		(25)
	K	Ag		(25)
Cu(NO <sub>3</sub> ) <sub>2</sub> .....	Na	Cu		(118)
Fe(NO <sub>3</sub> ) <sub>3</sub> .....	Na	Fe		(118, 145)
Co(NO <sub>3</sub> ) <sub>2</sub> .....	Na	Co		(118)
Ni(NO <sub>3</sub> ) <sub>2</sub> .....	Na	Ni		(118)
	Ca	Ni		(24)
NaClO <sub>3</sub> .....	Na		No reaction at -33°C. or at room temperature; no reduction by Na + NH <sub>4</sub> Br	(42)
NaClO <sub>4</sub> .....	Na		Same as for NaClO <sub>3</sub>	(42)
NaBrO <sub>3</sub> .....	Na	NaBr, NaOH, NaNH <sub>2</sub>	Ratio Na:NaBrO <sub>3</sub> = 6:1	(42)
NaIO <sub>3</sub> .....	Na	NaI	Reaction with Na or Na + NH <sub>4</sub> Br slow and incomplete at -33°C. and at room temperature	(42)
Na <sub>2</sub> H <sub>2</sub> IO <sub>6</sub>	Na	Na <sub>2</sub> H <sub>2</sub> IO <sub>6</sub>	ca. 3 per cent of hydrogen liberated	(42)
Na <sub>3</sub> H <sub>2</sub> IO <sub>6</sub> .....	Na	NaI	Very slow and incomplete reaction with Na or Na + NH <sub>4</sub> Br at -33°C.	(42)
KMnO <sub>4</sub> .....	K	K <sub>2</sub> MnO <sub>4</sub> + manganese oxides	Initial rapid reaction	(42)
	Na	KNaMnO <sub>4</sub> + manganese oxides	Initial rapid reaction	(42)
	K	MnO, KNH <sub>2</sub> , KOH	Slow secondary reaction	(42)
	Na	MnO, NaNH <sub>2</sub> , NaOH	Slow secondary reaction	(42)
AgOCN.....	Na	Ag	OCN <sup>-</sup> not reduced	(25)
	K	Ag	OCN <sup>-</sup> not reduced	(25)
	Ca	Ag	OCN <sup>-</sup> partially reduced to CN <sup>-</sup>	(26)
AgSCN.....	Na	Ag	Slight reduction of SCN <sup>-</sup>	(25)
	K	Ag	Slight reduction of SCN <sup>-</sup>	(25)
	Ca	Ag	Complete reduction of SCN <sup>-</sup> to CN <sup>-</sup> and S <sup>-</sup>	(26)
Ni(SCN) <sub>2</sub>	Na	Ni	SCN <sup>-</sup> reduced	(24)
	K	Ni	SCN <sup>-</sup> reduced	(24)
	Ca	Ni, H <sub>2</sub>	SCN <sup>-</sup> reduced	(24)

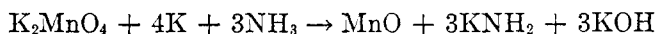
TABLE 5—*Concluded*

COMPOUND	METAL	PRODUCTS	NOTES	REFER- ENCES
Ni(NH <sub>2</sub> ) <sub>2</sub> .....	Na	Ni		(24)
	K	Ni		(24)
	Ca	Ni		(24)
[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NH	Na		Not reduced at -33°C.	(138)
GeNH.....	Na		Not reduced at -33°C.	(80)
SnNH.....	K	K <sub>4</sub> Sn <sub>2</sub>		(11)
Zr(NH) <sub>2</sub> ·7NH <sub>4</sub> Br· 5NH <sub>3</sub> <sup>(a)</sup> .....	K	Zr(NH) <sub>2</sub> <sup>(b)</sup>	Reaction at 0°C.	(18)
BiOI.....	Na	Bi	Three equivalents of sodium	(150)
		Bismuthides	Six equivalents of sodium	(150)
	K	Bi	Three equivalents of potassium	(150)
Ni(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .....		Bismuthides	Six equivalents of potassium	(150)
	K	Ni	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> not reduced	(24)

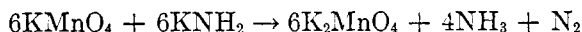
<sup>(a)</sup> Produced by the ammonolysis of zirconium tetrabromide.

<sup>(b)</sup> Contains ammonozirconate impurity.

rapidly, and is followed by a much slower reaction which reduces the manganese to MnO, perhaps as follows:



It is also of interest in this connection to note that potassium permanganate is reduced by liquid ammonia solutions of *potassium amide*:



Upon reaction with liquid ammonia, VBr<sub>3</sub> is ammonolyzed to a brownish-black mixture of ammonobasic salts, VBr<sub>2</sub>(NH<sub>2</sub>) and VBr(NH<sub>2</sub>)<sub>2</sub>. These react rapidly with ammonia solutions of potassium to form potassium amide and V(NH<sub>2</sub>)NK; in none of these changes is there any evidence of change in oxidation state of vanadium (39).

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