REACTIONS OF SOLUTIONS OF METALS IN LIQUID AMMONIA

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Part I. Foreword

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I. INTRODUCTION

The idea of a *solution* of a metal in a non-metallic solvent is one which the mind trained in chemistry and physics may ponder profitably. While these sister sciences have devoted much effort to the study of metals, have amassed a great fund of information concerning the characteristics and behavior of these interesting materials, and have developed elaborate theories to correlate the experimental data, the existence of simple solutions of metals in *non-metallic* solvents continues to impress many an otherwise well-informed person as a unique situation, the real importance of which only slowly dawns upon his consciousness. Yet systems of exactly this type with such solvents as liquid ammonia and the simple aliphatic amines are readily realized experimentally, have long been known, and have been the subject of numerous investigations. The study of the true nature of these solutions and of their chemical reactions has led

to important conclusions concerning the nature of the metallic state, intermetallic compounds, free radicals, organoalkali compounds, and certain reaction mechanisms, as well as the structural relationships of certain compounds. These solutions constitute one of the most effective reducing agents available and have become important synthetic reagents, especially for numerous organic compounds and for practically all substances in a highly reduced condition. The necessary techniques for handling such solutions have been developed and are comparatively easy to use. Surprisingly, only a beginning has been made in the study of metallic solutions, and the future holds much in store for those investigators who would proceed along paths already well marked and others only dimly suggested. One may state with certainty that these solutions will come to play an increasingly important rôle in organic syntheses and in the preparation of highly reduced inorganic compounds; and further, that they will prove useful in the study of intermediate stages of reduction.

The physical properties and nature of solutions of metals (84, 150, 160, 179, 188) have been discussed in detail in this journal and elsewhere, as well as some of the *general* aspects of the chemical reactions which these solutions exhibit (37, 151, 186). However, the many known reactions of these solutions have never been brought together in one place so that the wide usefulness and great possibilities of such systems may be clearly realized by one not thoroughly familiar with this field. The present writing is an attempt at a comprehensive review and somewhat critical discussion of the literature on reactions of metal solutions. This survey is prefaced by a short general review of the nature of solutions of metals to acquaint the reader with the character of the systems under discussion. Where references are given in this section they refer to recent work not covered in previous reviews. A few articles which have already appeared in this journal are closely related to certain portions of this review and may be consulted with profit in connection with it. The subjects of these articles are: (1) "The chemistry of the alkali amides" (18, 22); (2) "Metallic salts of alcohols and alcohol analogs" (73); and (3) "Organoalkali compounds" (388).

II. SYSTEMS CONSISTING OF SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; STABILITY OF THESE SOLUTIONS

The alkali metals, lithium (165), sodium, potassium, rubidium, and cesium, are freely soluble in liquid ammonia without any considerable heat effect (231, 235) and without chemical reaction to form dark blue solutions which are much less dense than pure ammonia (161), conduct the electric current with great facility (80), and are strongly paramagnetic (104, 356). The early literature on these solutions is confusing and erroneous, in that

the solutions are taken to contain "metal ammoniums," definite combinations between metal and solvent, such as $NaNH_3$, $Li \cdot 4NH_3$, and $Na_2N_2H_6$. Such combinations have been shown definitely not to exist but some workers, especially the French (117, 119, 257), have been loath to abandon the early view and references to "metal ammoniums" appear occasionally even in recent years.[2]

The alkaline-earth metals (calcium, strontium, and barium) are also markedly soluble in liquid ammonia to give the same blue solutions, but in these cases definite compounds, $M \cdot 6NH_3$ (23, 24), analogous to salt ammonates rather than "metal ammoniums," are formed: $Ca(NH_3)_6$ (174), $Sr(NH_3)_6$ (328), and $Ba(NH_3)_6$ (286). The physical properties of these solutions have not been extensively investigated. Magnesium likewise dissolves to a slight extent to give a pale blue solution.[3] While no other metals are definitely known to be soluble in liquid ammonia, it may be argued on the basis of certain chemical reactions that a few metals (beryllium (15), zinc (86), aluminum (6), gallium, lanthanum, cerium (10), and manganese (8)) also are soluble to a very slight extent. The tetra-substituted ammonium radicals, whose behavior closely resembles that of the alkali metals, impart a blue color to their liquid ammonia solutions (90, 173, 302, 332, 333).

Solutions of metals in liquid ammonia are remarkably stable, considering the extreme reactivity of the alkali and alkaline-earth metals with such solvents as water and the alcohols. Ammonia solutions of pure metals may be preserved for long periods (i.e., a couple of weeks in the case of sodium) even at room temperature. On long standing, especially at higher temperatures, amide formation becomes appreciable,

$$2M + 2NH_3 \rightarrow 2MNH_2 + H_2$$
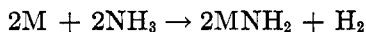
One may seek an explanation for this lack of reaction in the very small autoionization of liquid ammonia as compared to water, in the marked basicity (i.e., low proton availability) of liquid ammonia, and the relatively lower electrode potentials of these metals in liquid ammonia as compared to water (316). Such reaction, however, is markedly influenced by catalysts (5, 7, 14, 16, 17, 19, 38, 169, 360). Thus, an otherwise stable potassium solution is converted into the amide in from twenty minutes to an hour when a bit of iron oxide or finely divided platinum is present. Short ultra-violet light also catalyzes the reaction of the alkali metals with liquid ammonia (144, 300).

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[2] All reactions in this paper are formulated in terms of the simple metals only, even when this involves rewriting the equations given in the original reference.

[3] Under special conditions $Mg(NH_3)_6$ may be obtained (277a).

Metals are also soluble in some of the amines of low molecular weight: lithium (112, 292), sodium, potassium (111, 293), cesium (111, 319), and calcium (111, 293) are soluble in methylamine; lithium is less soluble in ethylamine than in methylamine (172); cesium (318) is soluble in ethylamine; sodium (172, 318), potassium (172), and calcium (318) are insoluble in ethylamine; lithium is insoluble in propylamine (172); cesium is soluble with reaction in isopropylamine (318); lithium, sodium, and potassium are insoluble in secondary and tertiary amines (172); lithium, sodium (81), potassium (172), and cesium (81) are soluble in ethylenediamine; in hydrazine lithium is slightly soluble, sodium is soluble but reactive, potassium is too reactive to note solubility, and calcium is insoluble (371, 372). These solutions of metals in amines have not been extensively studied. All are more or less unstable, owing to interaction between solvent and solute to produce hydrogen and substituted amides. Each of these solutions is blue in color, closely resembling ammonia solutions. In the case of methylamine, the light-absorption curves have been determined and are of somewhat different character than those of ammonia solutions (109). The molten alkali amides (82) and molten sodium hydroxide (83) also dissolve the alkali metals to give blue solutions. Calcium forms a similar blue solution in a molten mixture of sodium and potassium chlorides (108). Even water appears to form transitorily blue solutions of the alkali metals (383).

III. THE NATURE OF SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS

In many respects the properties of solutions of metals are intermediate in character between those of metals and those of electrolytic solutions, or perhaps one should say that these solutions constitute a connecting link between metallic and electrolytic conductors. Thus at high concentrations the atomic conductance of solutions of metals compares favorably with that of such metals as iron and strontium (220). In the more dilute region, on the other hand, solutions of metals exhibit the characteristics of electrolytes. The curve representing the variation of the temperature coefficient of conductance as a function of dilution also shows the same transition from that characteristic of a metal to that typical of electrolytes. Calculations (data from electromotive force of concentration cells) of the ratio of the transference numbers of negative to positive ions in liquid ammonia solutions of sodium show that, near saturation, the negative ion has a mean speed some two hundred eighty times that of the positive ion (178). This ratio diminishes with decreasing concentration until the relative carrying capacity becomes seven in the most dilute regions. Finally, the electrical conductance data show that the negative ion is the same for solutions of lithium, sodium, and potassium (the differ-

ence in the equivalent conductances of these solutions is due to the independently known different carrying capacities of the positive ions concerned) and that the conductances of dilute solutions of sodium and potassium and of sodium and lithium are practically additive (118). Also the light-absorption data show that, at equivalent concentrations, the absorption spectra of dilute solutions of lithium, sodium, potassium, cesium, magnesium, and possibly calcium are identical.

All of the facts known at present concerning solutions of metals in liquid ammonia may be harmonized by making two very simple assumptions: (1) In concentrated solution one may picture the metal atoms dissociating in accordance with the equation,

$$M \rightleftarrows M^+ + e^-$$

into the ordinary positive ions of salts of the metal and electrons. The electrons, however, have much the same mobility which they have in a solid, so that the solution possesses a very high conductance. (2) Upon dilution, the above dissociation is accompanied by a second reaction: i.e., the association of ammonia molecules with the electrons,

$$e^- + xNH_3 \rightleftarrows e^-(NH_3)_x$$
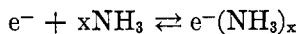
The mobility of the ammonated electron is much less than that of the free electron. Thus, as the solution becomes progressively more and more dilute, more of the electrons are associated with ammonia until the conduction process becomes truly electrolytic in character. Further, it is readily seen that the negative ion of all metals in liquid ammonia is the same.

Although there are very few data on the subject, it is entirely reasonable to assume that solutions of metals in solvents other than ammonia have the same general character as those in ammonia.[4] It has been shown for methylamine that the metals are less ionized in this solvent than in ammonia and that the minimum in the molecular conductivity occurs at a somewhat higher concentration (113). Further, the solvation of electrons in methylamine is not as complete as in liquid ammonia, and diminishes as the temperature is increased.

With the above picture of the nature of metal solutions in mind, one may logically expect that the chemical reactions exhibited by these solutions will be of two types: (1) ionic double decomposition reactions and (2)

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[4] There are some who regard these metal solutions as colloidal in character (301). Few, if any, of the properties of ammonia solutions of metals are in harmony with this point of view. More recently a modified form of the colloidal metal theory has been proposed (63), but neither the experimental work nor the theoretical interpretation is convincing.

reduction reactions. As will be seen in subsequent discussions, many examples of both types of reaction are known. In passing, mention should be made of the unusually favorable conditions presented by solutions of metals for carrying out reductions. It is universally recognized today that reduction consists in the addition of electrons to a given atomic system. Then a solution of electron-ions should be an extremely active reducing agent. Consider further that a *solution* of a metal eliminates one of the very serious limitations in the use of metals as reducing agents, i.e., surface area, by making it infinite. Add to this factor the marked solvent power of liquid ammonia for a great variety of substances (29, 41, 97, 103, 116, 156, 275) and the normally low reactivity of the solvent toward the dissolved metal, and it can easily be seen why so many reductions take place readily and rapidly in liquid ammonia. Indeed, the use of an excess of the reducing agent is the exception rather than the rule and, because of the high tinctorial power of dissolved metal, most reactions—even of a complicated character—can be *titrated* to a definite endpoint. Where the solvent power or reactivity of the ammonia (toward either the metal or the substance being reduced) are unsuited to a given reaction, then recourse to some of the simple amines may frequently be had.

IV. EXPERIMENTAL PROCEDURES INVOLVED IN THE STUDY OF REACTIONS OF SOLUTIONS OF METALS

No review of the reactions of metal solutions would be complete without some discussion of the techniques employed in handling these solutions. There are many reasons for making such a statement. It is certainly true that the development of methods for studying solutions in low-boiling solvents has been of extreme importance in leading to the present state of knowledge concerning reactions of metals. These techniques have become widely used and fairly well standardized. Despite the fact that on many occasions these techniques have been entirely inadequately described in the literature, there is really nothing about them which is so extremely difficult as to prevent the uninitiated from attempting to carry out reactions involving them. Further, these techniques are readily adaptable to a wide variety of differing experimental conditions and may be easy or more or less difficult depending upon the kind of results one desires. Finally some appreciation of the usefulness and limitations of the experimental methods is needed in order to evaluate properly the work of various investigators. In a careful reading of the literature on the reactions of metals in liquid ammonia, it is evident that much valuable information has been missed by the failure to realize the full possibilities of existing techniques.

Some of the considerations which govern the usage of the various tech-

niques so far developed are these. Ammonia is a low-boiling (normal boiling point, −33.35°), hygroscopic liquid. The metal solutions, some of the common reactants, and many of the products of reaction are sensitive to both air and water. Frequently gases (particularly hydrogen) are evolved during the reduction or subsequent reactions and arrangements should be made to collect these gases. On some occasions the reactants or reaction products, while much less volatile than ammonia, "steam-distill" with evaporating ammonia. The predominating practice has been to treat the final reaction products with ammonium salts, water, or alcohol. Such procedure frequently alters to a greater or lesser degree the primary products of the reaction, including by-products. In many cases, isolation, in relatively pure form, of one or more of the products of the reaction is desirable, since this may shed considerable light on the mechanism of the reaction, or show if simultaneous or consecutive side reactions are taking place.

The techniques for working with liquid ammonia solutions may be divided into two major groups: (1) reactions at low temperatures (atmospheric pressure or less) and (2) reactions under pressure (temperature from 0°C. to those in excess of 100°C.). In either event it is necessary to decide first whether the commercial anhydrous ammonia is suitable or whether further purification is necessary. Most of the liquid on the market is a synthetic product made directly from its constituent elements. It is a remarkably pure material which is very nearly anhydrous, contains only slight amounts of non-condensible gas, and is free from any appreciable amount of volatile and condensible impurities as well as organic contamination (282). For many purposes, this product may be used directly. In most other cases, it is necessary only to store the liquid in the presence of sodium (sodium amide) to remove the last traces of water (153). The complete purification of ammonia has been studied by McKelvy and Taylor (282; cf. 4).

A. Reactions at low temperatures

The recommended apparatus for carrying out reactions at low temperatures (normal boiling point or below) in liquefied gases consists of numerous modifications of a single general type.[5] A system is constructed (preferably on a permanently mounted rack consisting of rigid horizontal and vertical iron rods) which consists of a reaction cell immersed in a cooling bath usually containing liquid ammonia or solid carbon dioxide and some organic liquid. The cell is so arranged that its contents may be observed visually and is equipped with certain fittings which permit of (1) condensa-

[5] For typical apparatus see references 115, 152, 195, 199, 202, 226, 228, 239, 375, and 394.

tion of purified ammonia, (2) stirring the reaction mixture, (3) stepwise or continuous addition of known or measurable amounts of reacting material (gaseous, liquid, or solid), and (4) collection of volatile products (normally accomplished by scrubbing out the ammonia with water, separating the condensible material, and, after suitable drying, etc., analyzing the insoluble gases). In many cases it is also advisable to arrange the system so that the cell may be evacuated and removed for weighing. Simple modifications may also be made to wash an insoluble material (35). The kinds of information which may thus be obtained from a simple study include reacting ratios, amount of excess reactant added, products formed including isolation of intermediates and purification, color changes, phases present and their appearance and disappearance, and by-products. More or less extensive modifications of the apparatus mentioned permit the determination of the conductance of solutions (209, 214) (including temperature coefficients) (221), transference numbers of ions (96), potentials of cells (177, 314, 415), electrode potentials (315), products of electrolysis (26, 91, 105, 176), absorption spectra of solutions (106, 110), solubility of compounds (103, 157, 167, 329), potentiometric changes during titration (407), density of solutions (158, 162, 200), molecular weights (76, 98, 335, 337), vapor pressure of solutions (159, 212), viscosity of solutions (87, 336), and heats of reaction and of solution (230, 231, 235, 338a).

There are many cases where the use of open Dewar vessels or even unjacketed flasks and beakers is not objectionable. In such cases, however, it is well to remember that, while the use of such procedures may save time and may make some manipulations a little easier, it also seriously limits the investigator in many operations, in that the reaction is not under as delicate control, the ingress of air and moisture may be definitely harmful, serious loss of volatile material may occur, and the study of intermediates and by-products is seriously hampered if not entirely prevented.

B. Reactions under pressure

Under the leadership of Franklin, the use of sealed glass Faraday tubes for reactions at temperatures near that prevailing in the average laboratory has been perfected to a fine art (95, 154). This technique permits of a wide variety of operations such as visual observation, especially of intermediates, recrystallization and purification of moderately soluble products, purification of insoluble products by washing, freeing of soluble products from insoluble impurities, isolation of products for analysis or subsequent study *before* their destruction by water, etc., collection of gases evolved, freedom to alter the temperature at will over a wide range (slightly above room temperature to that of a mixture of carbon dioxide snow and ether), and ability to transfer the contents of one tube to another container.

Probably the greatest advantage of the Franklin technique is the marked solubility at room temperature of many substances which are only slightly soluble at the boiling point of ammonia.

While such a technique is ideally adapted for certain operations, it suffers a tremendous handicap in that the quantity of material which may be treated in this fashion is always rather small (not over a few grams) and also (assuming careful glass work and freedom from shock) in the constant danger of breakage of such tubes, especially if the internal pressure becomes much greater than that of liquid ammonia (viz., when a gas is liberated) or if the temperature rises. In many cases these limitations may be overcome by the use of autoclaves. Since liquid ammonia solutions of ammonium salts attack metals above hydrogen in the electrochemical series (11) and most metals act as catalysts for the conversion of the alkali metals to amides, autoclaves should be made of the less active metals (nickel, monel metal, etc.) or be glass-lined. They should also be equipped with a needle valve for filling with ammonia and for "blowing off" or collecting gases. By suitable modification, autoclaves may be fitted for conducting electrolyses, gradual addition of an ammonia solution of a reactant, extraction of a mixture of reaction products, etc.

Many investigators have been active in devising apparatus for carrying out the following operations with liquid ammonia solutions at or near room temperature: determination of potentials of cells (77), electroplating (26, 355), measurement of optical activity (340, 344), determination of the solubility of compounds (133, 275, 303, 341), molecular-weight determinations (342, 354), vapor-pressure measurements (134, 175, 255, 343), determination of viscosity (349), ultramicroscopic examination (410), and extraction of soluble products from solids (409).

For reactions above room temperature autoclaves may be used or a bomb which permits heating a sealed glass tube surrounded by liquid ammonia (25).

PART II. INORGANIC REACTIONS

I. INTRODUCTION

While water is well adapted as a medium in which to carry out reactions with strong oxidizing agents, it is not well adapted to carrying out reactions with strong reducing agents. The reducing power of reducing agents in water is limited by the fact that stronger reducing agents than hydrogen liberate hydrogen from water. Liquid ammonia suffers no such handicap, since the strongest reducing agents, the alkali metals, form stable solutions in this solvent. Thus, ammonia (and the simple amines) becomes the

ideal medium for the study of reduction reactions by means of strong reducing agents, a field which remains largely unexplored. Liquid ammonia is further of great usefulness because of its wide solvent power for electrolytes.

The process of reduction by means of metals in liquid ammonia consists essentially in the combination of an electron with an atom (or a group of atoms) or an ion. The positive ions of the metals are, of course, also present, but they take no part in the reduction process. The positive ions possess no metallic properties, and they are concerned in the process of reduction only to the extent of supplying the counterbalancing electrical charge for negative ions. When an atom undergoes reduction, a negative ion is formed,

$$S + 2e^- \rightarrow S^{--}; \qquad S^{--} + 2Na^+ \rightarrow \underline{Na_2S}$$
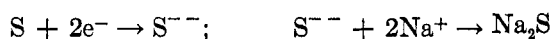
When a positive ion is reduced a neutral atom or group is commonly formed,
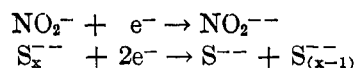
$$K^+ + e^- + Na^+ + Cl^- \rightarrow \underline{KCl} + Na^+ + e^-$$
$$Ag^+ + X^- + Na^+ + e^- \rightarrow Na^+ + X^- + \underline{Ag}$$
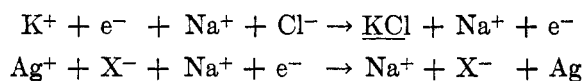
the course of the reaction being determined in most cases by the relative solubilities. A few cases are known where a negative ion undergoes reduction. In such cases an ion of higher charge or a number of ions are formed,

$$NO_2^- + e^- \rightarrow NO_2^{--}$$
$$S_x^{--} + 2e^- \rightarrow S^{--} + S_{(x-1)}^{--}$$

II. AMMONIUM SALTS

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

$$NH_4^+ + e^- \rightarrow NH_3 + 1/2 H_2$$
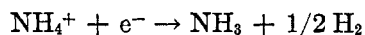
A summary of such reactions is given in table 1. The early observations on this reaction were prompted by a desire to isolate the ammonium radical (295, 296). Certain ammonolytic reactions have been brought to completion by neutralizing the ammonium salts with alkali metals. Among such reactions are:

$$GeI_2 + 3NH_3 \rightarrow GeNH + 2NH_4I \qquad (164)$$
$$(C_2H_5)_2GeBr_2 + 3NH_3 \rightarrow (C_2H_5)_2GeNH + 2NH_4Br \qquad (88)$$
$$C_2H_5GeI_3 + 4NH_3 \rightarrow C_2H_5GeN + 3NH_4I \qquad (89)$$
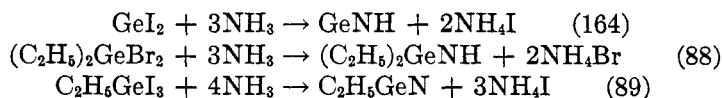
The alkali metals have also been utilized in a similar capacity for certain reactions taking place in amines:

$$BF_3 \cdot C_2H_5NH_2 + 5C_2H_5NH_2 \rightarrow B(NHC_2H_5)_3 + 3C_2H_5NH_3F,$$
$$3C_2H_5NH_3F + 3Li \rightarrow 3LiF + C_2H_5NH_2 + 3/2 \ H_2 \quad (194);$$
$$GeI_4 + 6C_2H_5NH_2 \rightarrow Ge(:NC_2H_5)_2 + 4C_2H_5NH_3I,$$
$$4C_2H_5NH_3I + 4Li \rightarrow 4LiI + 4C_2H_5NH_2 + 2H_2;$$
$$GeI_4 + 8(C_2H_5)_2NH \rightarrow Ge[N(C_2H_5)_2]_4 \ (?) + 4(C_2H_5)_2NH_2I,$$
$$4(C_2H_5)_2NH_2I + 4Li \rightarrow 4LiI + 4(C_2H_5)_2NH + 2H_2 \quad (166)$$
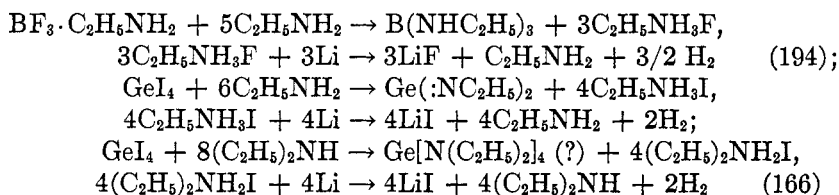
Sodium and potassium dissolve readily (room temperature) in an ammonia solution of ammonium nitrate (Divers' solution) without evolution of gas by reducing the nitrate to nitrite (75).

TABLE 1

Reactions of solutions of metals with ammonium salts

AMMONIUM SALT	METAL	PRODUCT	REFERENCES
NH_4Cl...........................	Li	LiCl	295
	Ca	$CaCl_2$	295
NH_4Br...........................	Na	NaBr	88
NH_4I...........................	Na	NaI	89, 163
	Li	LiN_3	30
	Na	NaN_3	30
NH_4N_3...........................	K	KN_3	30
	Ca	$Ca(N_3)_2$	30
	Mg	$Mg(N_3)_2$	30
NH_4CN...........................	Ca	$Ca(CN)_2 \cdot 2NH_3$	92
$(NH_4)_2S$...........................	Li	Li_2S	296
	Ca	CaS	296
$NH_4C_2H_3O_2$...........................	Na	$NaC_2H_3O_2$	243
$NH_4SC_6H_5$...........................	Na	$NaSC_6H_5$	243

III. ELEMENTS

Solutions of metals in liquid ammonia react with a number of the elements. Reactions with those elements which are two to four places in front of a rare gas (in the long-period or Bohr–Thomsen arrangement of the elements) form a particularly interesting group. Each of these elements forms with the metals an ammonia-insoluble, white or slightly colored salt of a composition to be expected on the basis of the customary valence of the element (Na_2S, K_3Sb, Na_4Sn) and one or more ammonia-soluble, strongly colored salts containing homoatomic anions (sometimes called polyanionic salts) (Na_2S_{2-5}, K_3Sb_7, K_4Pb_9). The application to liquid ammonia solutions of potentiometric titration methods by Zintl and coworkers (406) has been very fruitful in determining the composition of

TABLE 2

Reactions of solutions of metals in liquid ammonia with certain elements

ELEMENT	METAL	COMPOUNDS FORMED	NOTES	REFERENCES
Oxygen......	Na	$NaOH$, $NaNH_2$, $NaNO_2$	Slow reaction	140, 145, 252
		Na_2O_2	Rapid reaction	252
		Na_2O_3	Not confirmed	140*, 145*, 252
	K	KOH, KNH_2, KNO_2	Slow reaction	252
		K_2O_2, K_2O_4	Rapid reaction	140, 145, 229, 252
		K_2O_3	Not confirmed	140*, 145*, 252
	Rb	Rb_2O_2, Rb_2O_4	−60°C.(?)	322
	Cs	Cs_2O_2, $CsNH_2$, $CsOH$, $CsNO_2$, $CsNO_3$	Slow reaction at −60°C.	320, 321
		Cs_2O_2, Cs_2O_3, Cs_2O_4	Rapid reaction at −60°C.	320, 321
	Ba	BaO, BaO_2	Gelatinous precipitate	120, 285
Sulfur.......	Li	Li_2S	White; very slightly soluble	13
		Li_2S_2	Yellow solution; slightly soluble	13
		Li_2S_4	Red solution	13
		Li_2S_x	Red solution	13
	Na	Na_2S	White; very slightly soluble	13, 129, 131, 406
		Na_2S_2	Yellow solution; slightly soluble	13, 406
		Na_2S_3	Red solution	406
		Na_2S_4	Red solution	13, 406
		Na_2S_5	Red solution	129, 131, 406
		Na_2S_6	Red solution	406
		Na_2S_7	Red solution	406
		Na_2S_x	Red solution	13, 129
	K	K_2S	White; very slightly soluble	13, 129, 131
		K_2S_2	Yellow solution; slightly soluble	13
		K_2S_4	Red solution	13
		K_2S_5	Red solution	129, 131
		K_2S_x	Red solution	13
	Ca	CaS (white, insoluble)	Ca in excess	294
		CaS_x (red crystals)	S in excess	294

TABLE 2—*Continued*

ELEMENT	METAL	COMPOUNDS FORMED	NOTES	REFERENCES
Selenium....	Li	Li_2Se	White; very slightly soluble	13
		Li_2Se_2	Red solution	13
		Li_2Se_3	Green solution	13
		Li_2Se_4	Red solution	13
		Li_2Se_5	Red-green solution	13
	Na	Na_2Se	White; very slightly soluble	13, 128, 131, 406
		Na_2Se_2	Bright red solution	13, 406
		Na_2Se_3	Wine-red solution	13, 406
		Na_2Se_4	Green solution	13, 128, 129, 131, 406
		Na_2Se_5	Red-green solution	13, 406
		Na_2Se_6		406
	K	K_2Se	White; very slightly soluble	13, 128, 131
		K_2Se_2	Red solution	13
		K_2Se_3	Green solution	13
		K_2Se_4	Red solution	13, 128, 129, 131
		K_2Se_x	Red-green solution	13
Tellurium...	Na	Na_2Te	White precipitate; yellow solution	129, 131, 201, 208, 406 6
		Na_2Te_2	Violet solution	201, 208, 40
		Na_2Te_3	Dark red solution	129, 131, 208, 406
		$Na_2Te_4(?)$		201, 208, 406
	K	K_2Te	White; insoluble	129, 131
		K_2Te_3	Brown solution	129, 131
Nitrogen.....	Na, K		No reaction	142
Phosphorus..	Na	$Na_3P_2H_3 + 3NaNH_2$	Na in excess	126
		$NaP_3 \cdot 3NH_3$	P in excess	125
	K	$KP_5 \cdot 3NH_3$	P in excess	125
Arsenic......	Na	$Na_3As \cdot NH_3$	With either Na or As in excess	127
	K	$K_3As \cdot NH_3$	K in excess	130
		$K_2As_4 \cdot NH_3$	As in excess	130
Antimony...	Li	$Li_3Sb \cdot NH_3$	With either Li or Sb in excess	259–61
	Na	Na_3Sb	Brown precipitate; yellow solution	139, 145
		Na_3Sb_{5-7}	Red-brown solution	306

TABLE 2—*Concluded*

ELEMENT	METAL	COMPOUNDS FORMED	NOTES	REFERENCES
Bismuth......	Na	Na_3Bi	Black; insoluble	139, 145
Germanium...		See under GeS and GeS_2, section VII		
Tin..........	Na		Soluble compound	306
	Li	Li_4Pb_x	Green solution	413
		$NaPb_4 \cdot 2NH_3$	Green solution	138*
	Na	$NaPb$	Solid, Na in excess	139
		$NaPb_2$	Green solution	145, 171
		Na_4Pb_9		218, 347, 406
Lead				139
	K	KPb_2	Soluble compound	171
		$K_4Pb_9 \cdot xNH_3$	Green solution	413
	Rb		Amethyst solution	413
	Cs		Brown-violet solution	413
	Sr		Insoluble	413
Mercury.....	Na	$NaHg_8$		138, 145
	K	KHg_{18}		138, 145

* The results or conclusions of this work have been modified by later investigation.

the various compounds which a given element may form. Bergstrom (9) has developed an electronegative replacement series based upon the ability of an element to displace another from liquid ammonia solutions containing the latter element in a homoatomic anion. The literature on these compounds is summarized in table 2. In many cases the earlier work has not been confirmed by subsequent study and such instances have been noted in the table.

Elements more than four places in front of a rare gas are not prone to react with solutions of metals when in compact form, but often do so when present in finely divided form, as when produced by reduction of solutions of their compounds (see below) (406).

Oxygen. In the case of oxygen the products are different depending upon whether the reaction is performed rapidly or slowly. When oxygen gas is conducted slowly through a solution of sodium or potassium ($-33°C.$), the monoxide first formed is ammonolyzed to an equimolecular mixture of the hydroxide and amide (253),

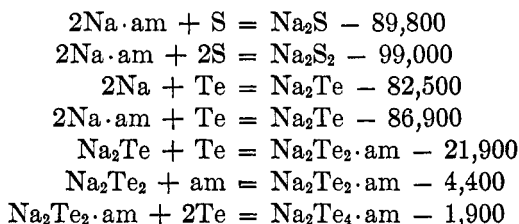$$M_2O + NH_3 \rightarrow MOH + MNH_2$$
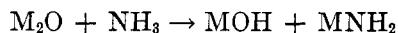
Subsequent oxidation converts the amide to nitrite,

$$2MNH_2 + 3/2\ O_2 \rightarrow MOH + MNO_2 + NH_3$$

The rapid oxidation of these metals produces the oxides Na_2O_2, K_2O_2, and K_2O_4 (no trioxides). Potassium tetroxide of 99 per cent purity may be formed at $-50°C.$; at $-33°C.$ considerable amounts of potassium hydroxide and potassium nitrite are formed. Potassium dioxide, also of 99 per cent purity, may be formed at $-50°$ to $-60°C.$ by passing oxygen through the solution until the blue color disappears. At lower temperatures a colloidal sol and viscous solution are formed, while at higher temperatures there is reduction of the dioxide to the monoxide and consequent ammonolysis. The polyoxides are unique in that they are not soluble in liquid ammonia.

Sulfur, selenium, and tellurium. Vapor-pressure measurements of the sodium–tellurium complexes in liquid ammonia have shown that two sodium ions are associated with each complex tellurium ion, Te_x^{--} (256). The oxidation products in liquid ammonia ($-33°C.$) of the sodium mono- and poly-sulfides, -selenides, and -tellurides have been determined (281). The heats of reaction ($-33°C.$) of sodium solutions with sulfur and tellurium have recently been measured (231):

$$2Na \cdot am + S = Na_2S - 89,800$$
$$2Na \cdot am + 2S = Na_2S_2 - 99,000$$
$$2Na + Te = Na_2Te - 82,500$$
$$2Na \cdot am + Te = Na_2Te - 86,900$$
$$Na_2Te + Te = Na_2Te_2 \cdot am - 21,900$$
$$Na_2Te_2 + am = Na_2Te_2 \cdot am - 4,400$$
$$Na_2Te_2 \cdot am + 2Te = Na_2Te_4 \cdot am - 1,900$$

Nitrogen, phosphorus, arsenic, antimony, and bismuth. As might be expected, nitrogen is unreactive toward solutions of metals.[6] Advantage has been taken of the solubility of the alkali metals in extracting the excess sodium from such ammonia-insoluble compounds as Na_3As, Na_3Sb, and Na_3Bi (258, 411a).

Germanium, tin, and lead. By electrolyzing solutions of sodium polyplumbide it has been shown that 2.26 gram-atoms of lead are deposited at the anode and dissolved at the cathode for each faraday of electricity passed (347). The energy of the reaction ($-33°C.$), $4Na + 9Pb \rightarrow Na_4Pb_9 \cdot am$, has been found to be $-88,000$ cal. (231).

IV. HYDRIDES

Since the hydrides of the halogens and of sulfur combine with ammonia to form ammonium salts, these have already been discussed in section II, page 205. Even though the reaction of hydrides with metal solutions offers a fertile field of research, only a few of them have ever been studied.
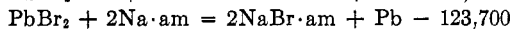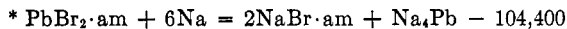
[6] For reactions in liquid ammonia of a polyphosphide of the formula Rb_2P_5, see reference 27.

TABLE 3

Reactions of halides of elements with solutions of metals in ammonia

HALIDE USED	METAL	SUBSTANCE FORMED	NOTES	REFERENCES†
		Group I		
CuI.............	Na	Cu		406
$AgCl$............	Na	Ag		33a, 36, 37
AgI.............	Na	Ag		33a, 36, 37, 217, 406
AgI.............	Ca	Ag		33a
$AgCN$...........	Na	Ag		33a, 217
$AgCN$...........	Ca	CaAg		217
$AgCN$...........	Ca	Ag		33a
AuI.............	Na	NaAu		406
		Group II		
ZnI_2.............	Na	$NaZn_4$		217
		$NaZn_{12}(?)$		406
$Zn(CN)_2$..........	Na	$NaZn_4$		34, 37, 217
		Zn	If $Zn(CN)_2$ is in excess	34
$Zn(CN)_2$.........	Ca	Ca_7Zn		217
CdI_2.............	Na	NaCd		217
		$NaCd_{5-7}$		406
$Cd(CN)_2$.........	Na	NaCd		217
HgI_2.............	Ca	Ca_3Hg_2		217
$Hg(CN)_2$.........	Na	NaHg	$2NaHg \rightarrow Na + NaHg_2$	217, 406
$Hg(CN)_2$.........	Ca	Ca_3Hg_2		217
		Group III		
$BF_3 \cdot NH_3$.........	Na	H_2	Reaction takes place in several steps	193
$BF_3 \cdot N(C_2H_5)_3$....	Li	No action in $(C_2H_5)_3N$ solution		193
	Na	No action in $(C_2H_5)_3N$ solution		193
$GaBr_3 \cdot 6NH_3$......	Na	Ga(?)		149
TlI.............	Na	Na_3Tl_2		217
		$NaTl, NaTl_2$		406
		Group IV		
SnI_2.............	Na	Na_4Sn	Unstable	217, cf. 411a
		Na_4Sn_x		217, cf. 406
	Ca	Ca_5Sn		217

TABLE 3—*Concluded*

HALIDE USED	METAL	SUBSTANCE FORMED	NOTES	REFERENCES†
		Group IV—*Concluded*		
$PbBr_2$...........	Na		Heat of reaction*	231
PbI_2.............	Na	Na_4Pb	Unstable	217, cf. 411a
		Na_4Pb_7		406
		Na_4Pb_9	Dark green	406
	K	K_4Pb_9		406
	Ca	Ca_2Pb_3		217
$ZrBr_4$.............	K	Black precipitate, red solution; neither permanent		403
		$Zr(NK)_2 \cdot NH_3, H_2$	Secondary reactions	403
$ThBr_4$............	K	$Th(NH)NK \cdot NH_3, \quad H_2$	Slow reaction	403
		$Th(NK)_2 \cdot KNH_2$	Continued action	403
		Group V		
$NI_3 \cdot 3NH_3$........	Na	NaI, N_2		132
$SbBr_3$............	Na	$NaSb_{4.8}$		217
$BiCl_3$.............	Na	$NaBi_{3.3}$		217
BiI_3..............	Na	Na_3Bi	Black precipitate	406
		Na_3Bi_3	Deep violet	406
		Na_3Bi_5	Brown	406
		Group VII		
MnI_2.............	Na	Mn	Probable initial reaction	37
		$NaNH_2, Mn(NH_2)_2$ $Mn(NHNa)_2 \cdot 2NH_3$	Subsequent reactions	37
		Mn	Highly reactive metal	276

* $PbBr_2 \cdot am + 6Na = 2NaBr \cdot am + Na_4Pb - 104,400$
  $PbBr_2 \cdot am + 2Na = 2NaBr \cdot am + Pb - 91,200$
  $PbBr_2 + 2Na \cdot am = 2NaBr \cdot am + Pb - 123,700$

† Important references, not otherwise mentioned, bearing upon the nature of salts of homoatomic anions (formed by elements two to four places in front of a rare gas) and of intermetallic compounds (or phases) (formed by elements more than four places in front of a rare gas) include the following: 12, 85, 155, 180, 182, 405, 408, 412.

Water reacts as it does with metals under other conditions. Phosphine reacts with both sodium and potassium in liquid ammonia to form substances of the formulas $NaPH_2$ and KPH_2, respectively (143, 147). Germane reacts similarly with a solution of sodium (198),

$$GeH_4 + Na \rightarrow NaGeH_3 + 1/2 H_2$$
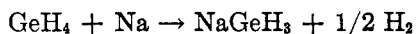
Digermane also forms sodium trihydrogermanide (189),

$$Ge_2H_6 + 2Na \rightarrow 2NaGeH_3$$
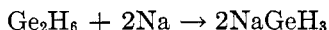
V. HALIDES (AND CYANIDES)

The products obtained by treating halides of elements with metal solutions (table 3) in most cases do not differ greatly from those obtained by direct reaction with the elements themselves, since the first step in the reduction of salts is undoubtedly the liberation of the free element. It appears, however, that the elements when so liberated are in a very reactive condition, since substances are produced under these circumstances which are not obtainable by direct reaction with the compact metal. The elements two to four places before a rare gas stand out in sharp contrast to the remainder of the elements. Among the former certain generalities have already been noted. For the latter group about all one can say is that when the element itself (silver, copper) is not precipitated, then some compound of an alkali or alkaline-earth metal with the element will be precipitated whose formula seemingly disobeys all valence rules and concerning which few generalities have as yet been discovered. This latter field is greatly in need of further investigation. Aside from the formation of the free element and of compounds of the element with the reducing metal, one other type of reaction is encountered. The element (metal) reduced may act as a catalyst for the conversion of the reducing metal to the amide which will react with the reduced element (manganese) or with the salt (zirconium, thorium).

VI. OXIDES

The compilation of data given in table 4 shows that investigations on the oxides of non-metals have not been extensive. Carbon monoxide forms carbonyls, which await further work to establish their structure definitely. Carbon dioxide seems to react with the 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.

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 gas:

$$N_2O + 2K + NH_3 \rightarrow KNH_2 + KOH + N_2$$
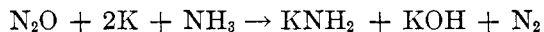
the other products, alkali amide and hydroxide, are those which would be expected from ammonolysis of the alkali oxide (see page 209). The resulting amide then reacts with another molecule of the oxide in this fashion,

$$N_2O + 2KNH_2 \rightarrow KN_3 + KOH + NH_3$$

The latter reaction is known to take place under somewhat different conditions (72, 124, 382).

Nitric oxide reacts with solutions of metals to form precipitates having the composition NaNO, KNO, and BaN_2O_2 which, after dissolving in water, will give the characteristic silver salt of hyponitrous acid (142, 146, 284). Zintl and Harder (411), however, have shown, by means of Debye–Scherer photographs, that nitrosyl sodium, $(NaNO)_n$, obtained from the interaction of nitric oxide and a solution of sodium, is not identical with sodium hyponitrite.

TABLE 4

Reactions of non-metallic oxides with solutions of metals in ammonia

OXIDE	METAL	PRODUCTS	NOTES	REFERENCES
CO..........	Li	LiCO	$-60°C.$, white precipitate	305
	Na	$Na(CO)_2$	$-50°C.$, very explosive	141, 148
	K	$K(CO)_2$	$-50°C.$, rose-white gelatinous precipitate	141, 148
	Rb	RbCO	$-60°C.$, white precipitate	305
	Ca	$Ca(CO)_2$	$-60°C.$, white precipitate	305
	Ba	$Ba(CO)_2$	$-50°C.$, gelatinous precipitate	120, 284
CO_2..........	Na	H_2NCO_2Na	$-50°$ to $-60°C.$	317
		HCO_2Na (due to H from above)	$-25°$ to $-35°C.$	317
N_2O..........	Na	N_2, NaOH $NaNH_2$	Primary reaction	142, 146
		NaN_3, NaOH	Reaction of N_2O with amide	142, 146
	K	see Na		142, 146
NO..........	Na	NaNO	Gelatinous precipitate	142, 146
		$(NaNO)_n$		411
	K	KNO	Gelatinous precipitate	142, 146
	Ba	BaN_2O_2	Gelatinous precipitate	284
NO_2..........	Ba	BaN_2O_2	Gelatinous precipitate	120

Nitrogen dioxide, while not fully investigated, is seemingly reduced by a solution of barium and forms the same material as nitric oxide (120).

The reduction of only a few oxides of the metals has been studied. Bergstrom (17) apparently observed no reduction of ferric and cobaltous-cobaltic oxides (Fe_2O_3 and Co_3O_4) by a liquid ammonia solution of potassium. A general study of the behavior of oxides of metals toward a solution of potassium (370) at room temperature has shown that the oxides of

bismuth (Bi_2O_3), tin (SnO and SnO_2), lead (PbO and PbO_2), zinc (ZnO), and cadmium (CdO) give intermetallic compounds, while silver oxide (Ag_2O) furnishes the free metal. Cupric oxide is quantitatively reduced to cuprous oxide which, because of its marked catalytic effect upon the conversion of metal to amide, undergoes only slight reduction to metallic copper. Germanic oxide (GeO_2) remains unchanged after long contact with a solution of potassium.

VII. SULFIDES

The sulfides of germanium are reduced by a solution of sodium in liquid ammonia ($-33°C.$) to sodium sulfide and sodium polygermanide (166a),

$$GeS + 2Na \rightarrow Na_2S + Ge$$
$$GeS_2 + 4Na \rightarrow 2Na_2S + Ge$$
$$xGe + 4Na \text{ (excess)} \rightarrow Na_4Ge_x$$
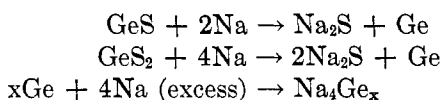
The potentiometric titration of arsenious sulfide (As_2S_3) and antimonous sulfide (Sb_2S_3) by sodium in liquid ammonia shows the following compounds: Na_3As (brown precipitate), Na_3As_3 (yellow), Na_3As_5 (dark red-brown), and Na_3As_7; Na_3Sb (gray-brown precipitate), Na_3Sb_3 (deep red), and Na_3Sb_7 (406).

VIII. NITRIDES AND IMIDES

Germanous imide, GeNH, does not react with an ammonia solution of sodium at $-33°C.$ (164).

The reaction of nitrogen iodide has already been discussed under the heading of halides (page 213).

IX. TERNARY COMPOUNDS

Despite the manifest opportunities for investigation presented by the field of ternary compounds, few such substances have been investigated. The outstanding case is that of sodium nitrite which forms a substance of the formula Na_2NO_2, variously known as disodium nitrite (279) and sodium hydronitrite (414). Similar reduction of sodium nitrite occurs using lithium and potassium and also of potassium nitrite using sodium.

Cobalt, nickel, cupric, and ferric nitrates are reduced by sodium in liquid ammonia ($-33°C.$) to the very finely divided and highly reactive metals (277). The particular technique used in these cases did not permit the isolation of any other products of these reactions.

No reduction of the cyanate ion takes place even in the presence of excess sodium and potassium, but appreciable reduction results when an excess of calcium is used. The thiocyanate ion, however, is partially re-

duced to sulfide and cyanide by sodium and potassium and completely reduced by calcium (33a).

Bismuth oxyiodide, BiOI, is reduced by solutions of sodium and potassium at room temperature according to the equation (370):

$$BiOI + 3K + NH_3 \rightarrow Bi + KI + KOH + KNH_2$$
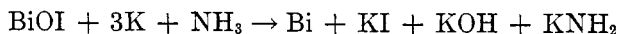
If excess alkali metal is present insoluble (K_3Bi) and soluble (K_3Bi_x) bismuthides are formed.

PART III. ORGANIC REACTIONS

I. INTRODUCTION

While it is certainly true that the reactions of metal solutions with organic substances have been more extensively studied than those with inorganic substances, it is also true that in many cases less is known concerning the mechanism of the organic reactions, by-product formation, etc. This situation is in large measure due to the greater complexity of the organic reactions, but in part is due also to failure of the synthetic chemist, in his desire to obtain a final product, to concern himself greatly either with the steps involved in the synthesis or with the influence of experimental conditions upon the yield or stability of the various intermediates. What has already been said about the failure of many investigators to take full advantage of existing techniques applies with particular force to those who have studied reactions of metals with organic substances. One may point to several cases where, with only slight modification of the apparatus or even with more complete use of the apparatus at hand, much additional valuable information might readily have been obtained.

Liquid ammonia is an ideal medium for carrying out reduction reactions, not alone because certain metals dissolve to form stable solutions but likewise because of the wide solubility of organic compounds in this solvent. In this latter respect liquid ammonia resembles most closely the lower alcohols (41, 97). The use of diluents, such as petroleum ether, benzene, ether, and amines, in reductions has been suggested on several occasions (70, 359, 376, 400). Not only are such diluents of value in altering solubility relationships and rates of reaction, but in some cases they seem to have a directive influence upon the course of the reaction. The behavior of such mixed solvents has not been fully investigated nor are the factors involved definitely understood.

It is well to recall that the active principle of a metal solution is the free electron, and that the reactions exhibited by these solutions are essentially those of the electron. In the case of organic compounds, the reactions of metals may, for convenience, be classified roughly into a number of types.

1. Displacement of an equilibrium involving an organic compound, the solvent, and an ammonium salt. Such reactions have already been discussed in section II of part II. Whenever a substance is ammonolyzed to form even a small amount of an ammonium salt,

$$RX + 2NH_3 \rightleftharpoons RNH_2 + NH_4^+ + X^-$$

the resulting equilibrium may be displaced completely to the right by removing the ammonium ion through reaction with a metal solution,

$$NH_4^+ + e^- \rightarrow NH_3 + 1/2\, H_2$$
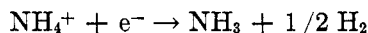
What has been said here concerning liquid ammonia applies equally well to the amines when used as solvents.

2. Displacement of hydrogen. Many of the reactions of organic compounds with solutions of metals are simply those of the displacement by a metal of active hydrogen from such compounds as $HC \equiv CH$, $(C_6H_5)_3CH$, ROH, RNH_2, acids and their derivatives, with the resulting formation of salts,

$$RH + e^- \rightarrow R^- + 1/2\, H_2$$
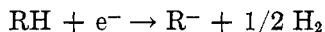
The hydrogen is not always liberated in the molecular form, however, and may serve to reduce a portion of the original compound. When this occurs there are then two competing reducing tendencies, i.e., (1) that of the electron and (2) that of the hydrogen. Careful study of a few such cases should serve to distinguish between the two reductants and to determine if and when hydrogen may be expected to reduce a compound that is not reduced by the metal. Salts formed by metals under one set of conditions may not be stable under another set, such as an increase in temperature. Under such circumstances ammonolysis may result,

$$R^- + NH_3 \rightarrow RH + NH_2^-$$
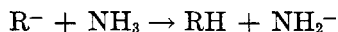
3. Metal addition. There are a number of occasions where the electron apparently adds directly to a molecule or ion. Such a reaction is encountered in the electrolysis of tetrasubstituted ammonium salts,

$$R_4N^+ + e^- \rightarrow R_4N$$
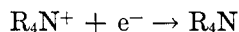
For solutions of metals, such reactions are usually of two types.

(a) Addition to double bonds. Addition of electrons to a double bond would be expected to result in the formation of a doubly charged ion,

$$R_{n-1}A : AR_{n-1} + 2e^- \rightarrow R_{n-1}A \cdot AR_{n-1}^{--} \quad (n = \text{valence of element A})$$

which may be stable under the experimental conditions or may be partially or completely ammonolyzed. Such reactions are known for $C:C$ (phenyl-

substituted ethylenes, higher benzenoid hydrocarbons, etc.), C:O, C:N, C≡N, N:O, and N:N.   Here again the information available is meager, since all possibilities have not been fully studied.   In a few cases only one electron adds at a double bond.   In such cases either one of two things may result: (1) a dimerization of the reduction product,

$$2CH_3CH:NC_2H_5 \rightarrow 2CH_3CH—NHC_2H_5 \rightarrow$$
$$| \qquad\qquad CH_3CH(NHC_2H_5)CH(NHC_2H_5)CH_3$$
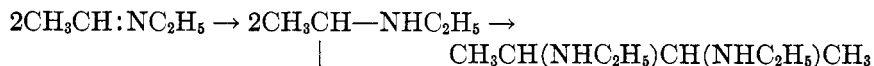
or (2) formation of a compound containing an element in an unusual state of valence,

$$(C_6H_5)_2CO \rightarrow (C_6H_5)_2CO^- \text{ (metal ketyl)}$$
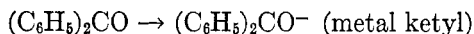
(b) *Addition to free groups*.   Most of the free radicals so far studied react with electrons to form ions.   Thus, R_3C, R_3Si, R_3Ge, and R_3Sn form singly charged anions and R_2Ge and R_2Sn form doubly charged anions. In the latter cases, a single equivalent of an alkali metal produces anions of the types $R_2Ge \cdot GeR_2^{- \, -}$ and $R_2Sn \cdot SnR_2^{- \, -}$.

4. Bond rupture.   In many instances the reducing action of a metal solution is of such a nature as actually to rupture a linkage between two atoms and for the electron to combine with each of the resulting fragments (cf. 74):

$$R_{n-1}A \cdot A'R'_{n'-1} + 2e^- \rightarrow R_{n-1}A^- + R'_{n'-1}A'^- \text{ (n = valence of element A)}$$
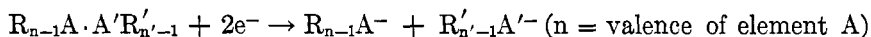
Some ions, such as methide and ethide, formed in this manner are not stable under the experimental conditions and are ammonolyzed,

$$CH_3^- + NH_3 \rightarrow CH_4 + NH_2^-$$
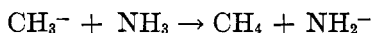
Instances of such bond rupture are known for the following cases: carbon–carbon, germanium–germanium, tin–tin, carbon–germanium, carbon–tin, silicon–germanium, silicon–tin, carbon–oxygen, germanium–oxygen, tin–oxygen, carbon–nitrogen, tin–nitrogen, sulfur–sulfur, carbon–sulfur, mercury–carbon, and carbon–halogen (see following paragraph).   Undoubtedly a thorough investigation would disclose more types.   (Some of these have been mentioned previously under the topic "addition to free groups.")

5. Removal of halogen.   The reactions of solutions of metals with halogen compounds are essentially bond ruptures, but for convenience may better be considered separately.   According to the general equation given above one would expect the following reaction to take place with organic halides,

$$RX + 2e^- \rightarrow R^- + X^-$$
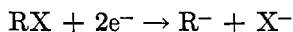
In cases where the organic radical R is capable of existence as a free group, the following reaction takes place,

$$RX + e^- \rightarrow R + X^-$$
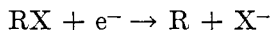
Further action may convert the free group into an ion,

$$R + e^- \rightarrow R^-$$
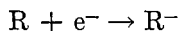
Probably it is well to look upon all reactions of halogens as proceeding in accordance with the two steps given. Thus there are likely to be present during the reduction of a halogen compound, in addition to the reactants and halide ions, both negative organic ions and free groups. In many cases the ions are unstable and ammonolyze, thus introducing amide ion, NH_2^-, into the system. Organic halogen compounds are reactive toward the amide ion to form either unsaturated hydrocarbons or amines. The latter and certain of the former form salts with metals, and these salts react with the halogen compound. The more reactive of the free groups may react either with the solvent or with themselves (Wurtz–Fittig synthesis). Thus it is easy to see that reductions of this type may become exceedingly complex (fortunately this does not happen often), and that it is very essential to examine all possibilities in order to learn just what is taking place in the reaction. Two cases are known of a hydrocarbon radical isomerizing in the formation of an ion.

6. *Removal of other elements.* In a few cases so far investigated, metals in solution are able to remove an oxygen atom from organic combination ($C_6H_5NO_2$ and $C_6H_5N(:O):NC_6H_5$). When this occurs the sodium oxide resulting is ammonolyzed to an equimolecular mixture of sodium hydroxide and sodium amide,

$$Na_2O + NH_3 \rightarrow NaOH + NaNH_2$$
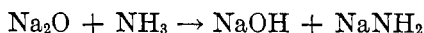
7. *Catalysis by solutions of metals.* Occasionally solutions of metals exert a catalytic effect upon a reaction (polymerization of styrene and interaction between triethylsilane and ethylamine).

II. HYDROCARBONS

A. Saturated hydrocarbons

There is no recorded instance of any reaction between a saturated hydrocarbon and a solution of a metal, nor is there any reason on the basis of known reactions in liquid ammonia to expect any such reaction.

B. Phenyl-substituted saturated hydrocarbons

Metallic sodium and potassium dissolved in liquid ammonia ($-33°C.$) directly displace hydrogen from triphenylmethane (184, 216, 232, 241),

$$(C_6H_5)_3CH + Na \rightarrow (C_6H_5)_3CNa + 1/2\ H_2$$
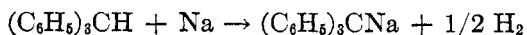
although the reactions take place slowly and the pure alkali salts may be more readily obtained by using the alkali amides (20, 390).

Diphenylmethane reacts slowly and incompletely with a liquid ammonia solution of sodium (room temperature) to give some of the sodium salt (271).

Wooster and Mitchell (393) have studied the action of potassium in liquid ammonia ($-33°C.$) upon phenyl-substituted methanes and ethanes. They observed no reaction with $C_6H_5CH_3$, $(C_6H_5)_4C$, $C_6H_5CH_2CH_3$, and $C_6H_5CH_2CH_2C_6H_5$; slight reaction with $(C_6H_5)_3CCH_3$ and $(C_6H_5)_3CCH_2$-C_6H_5; and formation of intense red or orange-yellow alkali salts with $(C_6H_5)_2CH_2$, $(C_6H_5)_3CH$, $(C_6H_5)_2CHCH_2C_6H_5$, and $(C_6H_5)_2CHCH(C_6H_5)_2$. Under similar conditions potassium ruptures a carbon–carbon bond in $(C_6H_5)_3CC(C_6H_5)_3$ (see section D below). The alkali metal salts of hydrocarbons readily react with alkyl and aryl halides, and are thus useful synthetic reagents.

C. Ethylenic hydrocarbons

The simple ethylenic hydrocarbons are not reactive toward solutions of metals in liquid ammonia: e.g., amylene (269) and cyclohexene (404). When isoprene reacts with a solution of sodium in ammonia ($-33°C.$) there is formed 2-methyl-2-butene in 60 per cent yield,

$$C_5H_8 + 2Na + 2NH_3 \rightarrow C_5H_{10} + 2NaNH_2$$
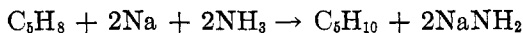
as well as hydrocarbons of high molecular weight. The 2-methyl-2-butene is not further reduced by an excess of sodium–ammonia reagent (287) (see section D, following).

## D. Phenyl-substituted ethylenic hydrocarbons

The reduction of a number of phenyl-substituted olefins with alkali metals in liquid ammonia solution has been studied. The results are summarized in table 5 (reactions at $-33°C.$ unless otherwise noted).

These data, together with those given in sections B and C above, have been carefully examined by Wooster and Ryan (399), who have pointed out the various types of reactions involved: (1) displacement of hydrogen; (2) addition to a double bond; (3) polymerization; (4) dimerization; (5) cleavage of carbon–carbon bonds; and (6) addition to but one of two double bonds in a molecule. In the case of derivatives of saturated hydrocarbons, reaction takes place to any considerable extent when, and only when, the compound contains the benzohydryl group, $(C_6H_5)_2CH$—. Many of the organoalkali compounds which might logically be considered as inter-

TABLE 5

Reduction of phenyl-substituted olefins with alkali metals in liquid ammonia

| OLEFIN	METAL	PRODUCTS REPORTED	NOTES	REFERENCES
$C_6H_5CH=CH_2$	Na	$C_6H_5C_2H_5$(50 per cent) + styrene polymers, $NaNH_2$	1.34, 1.38 equivalents of sodium react, slow reaction	266, 273, 398
$C_6H_5CH=CHC_6H_5$	Na, K	$C_6H_5CH_2CH_2C_6H_5$, $MNH_2(M = Na$ or K)	Intermediate red color; persists for a long time	398, 404
	Na (−78°C.)			331
	Na (room temperature)		Ammonolysis immediate	270
$(C_6H_5)_2C=CH_2$	Na	$(C_6H_5)_2CNaCH_3$, $NaNH_2$ $(C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2$ (10 to 30 per cent)		398
	Na (low temperature)	$(C_6H_5)_2CNaCH_3$ + small amount 1,1,4,4-tetraphenylbutane	Toluene diluent	404
$(C_6H_5)_2C=CHC_6H_5$	Na, K	$(C_6H_5)_2CMCH_2C_6H_6$, MNH_2		393, 397, 398
$(C_6H_5)_2C=C((C_6H_5)_2$	Na	$(C_6H_5)_2CNaCNa(C_6H_5)_2$ and $(C_6H_5)_2CHNa$ or $(C_6H_5)_2CNa_2(?)$	When in excess, 3.65 equivalents of sodium react	393, 398
$(C_6H_5)_2C=CHCH_3$	Na, K	$(C_6H_5)_2CMCH_2CH_3$, MNH_2	Reacts readily	397, 398
$(C_6H_5)_2C=CH—CH_2C_6H_5$	Na (low temperature)	$(C_6H_5)_2CNaCH_2CH_2C_6H_5$		404
$(C_6H_5)_2C=CHCH(C_6H_5)_2$	Na	$(C_6H_5)_2CNaCH_2CH(C_6H_5)_2$, $NaNH_2$	Reacts readily; 3.76, 4.3 equivalents of sodium react	398
$(C_6H_5)_2C=C'(C_6H_5)_2$	Na, K	$(C_6H_5)_2CMCH_2CM(C_6H_5)_2$, MNH_2		398

mediates in the reactions given in table 5 are not found because such substances are ammonolyzed,

$$RNa + NH_3 \rightarrow RH + NaNH_2$$
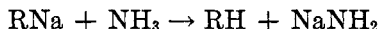
In general, the alkali metal atoms are replaced by hydrogen except when they are present in the grouping $(C_6H_5)_2CM-$ (M = alkali metal). When the organoalkali compounds are stable in liquid ammonia they are useful synthetic reagents.

E. Acetylenic hydrocarbons

When acetylene is passed into liquid ammonia solutions ($-40°$ to $-60°C.$) of lithium, sodium, potassium, calcium (291), rubidium, and cesium (297), the corresponding monoalkali acetylides, MHC_2, are formed. At the same time a limited amount of the acetylene is reduced to ethylene,

$$3C_2H_2 + 2Na \rightarrow 2NaHC_2 + C_2H_4$$
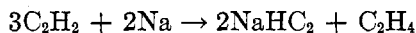
Magnesium is attacked by an ammonia solution of acetylene to form magnesium acetylide, $Mg(HC_2)_2 \cdot 7NH_3$ (from $2°$ to $-60°C.$) and $Mg(HC_2)_2 \cdot 5NH_3$ (above $2°C.$) (66). Monosodium acetylide and calcium acetylide have been used by a number of investigators for the preparation of substituted acetylenes (28, 123, 135, 170, 257, 264, 265, 280a, 283, 307–9, 358, 389). Because of the reduction of acetylene accompanying its reaction with sodium, Picon (310) prefers to use sodium amide to generate sodium acetylide.

The monosubstituted acetylenes also react with ammonia solutions of metals to form the corresponding salts and ethylenic hydrocarbons in the ratio 2:1,

$$3C_3H_4 + 2Na \rightarrow 2C_3H_3Na + C_3H_6$$
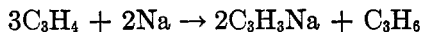
Such reactions are reported for allylene, n-hexyne, heptyne, and octyne (265). Phenylacetylene gives the salt and ethylbenzene with sodium in ammonia (266, 273),

$$3C_6H_5C\equiv CH + 4Na + 2NH_3 \rightarrow$$
$$2C_6H_5C\equiv CNa + C_6H_5C_2H_5 + 2NaNH_2$$

F. Aromatic hydrocarbons

The benzene nucleus is not attacked by ammonia solutions of metals (269, 331, 393). Benzene, toluene[7], xylene, etc., may be used advantageously as diluents for the reactions between metal solutions and many organic compounds (404) or for introducing a solution of a solid into

[7] For precautions see reference 391a.

ammonia (402). Naphthalene, however, is reduced by sodium and potassium solutions to tetrahydronaphthalene, with the concomitant formation of sodium amide (267, 331, 401). When this reaction is carried out at low temperatures ($-33°C$. or lower) a bright red solution results. This color may be regarded as due to a relatively unstable intermediate organoalkali compound. Wooster and Smith (401) have examined the reaction in detail and have shown that the intermediate is the 1,2,3,4-tetrasodium addition product, but that even at $-33°C$. this compound is three-fourths ammonolyzed. Other hydrocarbons similarly reduced are the following: anthracene (9,10-dihydroanthracene) (269, 290), phenanthrene (tetrahydrophenanthrene), acenaphthene (tetrahydroacenaphthene), biphenyl (tetrahydrobiphenyl) (269), and dimethylfluorene (tetrahydrodimethylfluorene) (271). When sodium or potassium is added to a liquid ammonia solution of 9,10-diphenylanthracene the 9,10-dialkali salts are formed (bright cherry-red solution, brick-red amorphous precipitate) (135a). Both fluorene and indene react with ammonia solutions of sodium to form sodium salts by substitution accompanied by some hydrogenation (268). An ammonia solution of fluorene reacts with magnesium (66).

The following compounds do not react with metal solutions: terpinene, terpinolene, carvene, α-pinene, and menthene (269).

G. Free radicals. Substituted stanno- and germano-methanes and -ethanes

1. Free radicals. Sodium solutions react with the free radical triphenylmethyl (hexaphenylethane) to produce sodium triphenylmethide (215). Similar reactions take place with other free groups: triphenylgermanyl (hexaphenylgermanoethane) (192, 205, 213, 227, 237), triphenylstannyl (hexaphenylstannoethane) (213), and trimethylstannyl (hexamethylstannoethane) (181, 183, 210, 236). That the electron in the trimethylstannomethide ion is not firmly held is shown by the following energy equation (235),

$$(CH_3)_3Sn + Na + am = (CH_3)_3SnNa \cdot am - 3,830$$
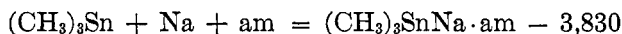
Triphenylsilicyl forms an addition compound with ethylamine, $(C_6H_5)_3Si \cdot C_2H_5NH_2$, which does not react with sodium in liquid ammonia to an appreciable extent. In liquid ethylamine the following reaction occurs (203):

$$(C_6H_5)_3Si \cdot C_2H_5NH_2 + Li \rightarrow (C_6H_5)_3SiLi + C_2H_5NH_2$$
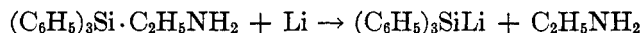
Triethylsilicyl shows no reaction with sodium in liquid ammonia or with lithium in ethylamine (225). Triethylgermanyl (hexaethylgermanoethane) reacts with lithium in ethylamine to form lithium triethylger-

manide. The latter compound is partially aminolyzed in ethylamine and completely ammonolyzed in liquid ammonia,

$$(C_2H_5)_3GeLi + NH_3 \rightarrow (C_2H_5)_3GeH + LiNH_2$$
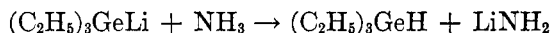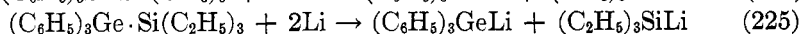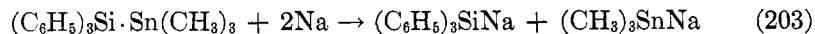
Potassium triethylgermanide prepared similarly in ethylamine is stable in liquid ammonia (204).

Tin and germanium form a type of free group which carbon does not form, i.e., dimethylstannyl, $[(CH_3)_2Sn]_x$ (207), diphenylstannyl,$[(C_6H_5)_2Sn]_x$ (62), and diphenylgermanyl, $[(C_6H_5)_2Ge]_4$ (192). Each of these substances reacts with a solution of sodium to form the corresponding disodium salt: $(CH_3)_2SnNa_2$, $(C_6H_5)_2SnNa_2$, and $(C_6H_5)_2GeNa_2$. In two of these cases intermediate substances, $NaSn(CH_3)_2 \cdot Sn(CH_3)_2Na$ and $NaGe(C_6H_5)_2 \cdot Ge(C_6H_5)_2Na$, respectively, are known to form first. All of the salts mentioned above may be employed for synthetic purposes. By using them it has been found possible to prepare hydrides, alkyl and aryl derivatives, and chains of tin and germanium atoms: e.g., octaphenylgermanopropane, $(C_6H_5)_3Ge \cdot Ge(C_6H_5)_2 \cdot Ge(C_6H_5)_3$, and dodecamethylstannopentane, $(CH_3)_3Sn[Sn(CH_3)_2]_3Sn(CH_3)_3$.

For reactions of the dimethylgallium group see section H.

2. Substituted ethanes. Closely allied to the reactions given above are those between sodium and trimethylstannyltriphenylsilane in liquid ammonia and that between triphenylgermanyltriethylsilane and lithium in ethylamine (greater solubility of the silane):

$$(C_6H_5)_3Si \cdot Sn(CH_3)_3 + 2Na \rightarrow (C_6H_5)_3SiNa + (CH_3)_3SnNa \quad (203)$$
$$(C_6H_5)_3Ge \cdot Si(C_2H_5)_3 + 2Li \rightarrow (C_6H_5)_3GeLi + (C_2H_5)_3SiLi \quad (225)$$

3. Trisubstituted methanes. Sodium in liquid ammonia reacts with trimethylstannane (183, 206) and triphenylstannane (61) to produce the sodium salt and hydrogen,

$$(CH_3)_3SnH + Na \rightarrow (CH_3)_3SnNa + 1/2 H_2$$
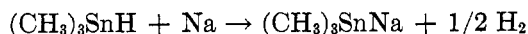
The sodium salt of triphenylstannane is in small part converted to the disodium salt, $(C_6H_5)_2SnNa_2$. Triethylgermane appears not to react with sodium in liquid ammonia (204). Triphenylgermane on the other hand gives the sodium salt and hydrogen but not quantitatively, since some of the disodium salt is formed (205). While lithium in ethylamine solution has no direct action on triethylsilane, the metal does serve as a catalyst for the homogeneous reaction (225),

$$(C_2H_5)_3SiH + C_2H_5NH_2 \rightarrow (C_2H_5)_3SiNHC_2H_5 + H_2$$
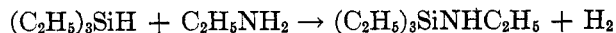
The chief products of the reaction between triphenylsilane and sodium in liquid ammonia are sodium bis(triphenylsilicyl)imide, $[(C_6H_5)_3Si]_2NNa$, and hydrogen (323),

$$2(C_6H_5)_3SiH + Na + NH_3 \rightarrow [(C_6H_5)_3Si]_2NNa + H_2$$
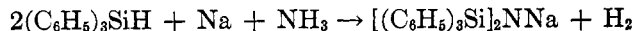
4. Tetrasubstituted methanes. Methyl- and *n*-propyl-triphenylgermane are not attacked by sodium in liquid ammonia (237). Tetraethylgermane, which is practically insoluble in liquid ammonia, shows no appreciable reaction with sodium in that solvent (204). Tetraphenylgermane, on the other hand, slowly reacts as follows:
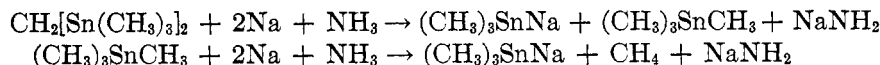
$$(C_6H_5)_4Ge + 2Na + NH_3 \rightarrow (C_6H_5)_3GeNa + NaNH_2 + C_6H_6$$
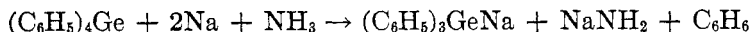
With a concentrated sodium solution, a second phenyl group is substituted by sodium to form $(C_6H_5)_2GeNa_2$ (205).

Tetramethylstannane undergoes the following reaction with an ammonia solution of sodium (223, 236),

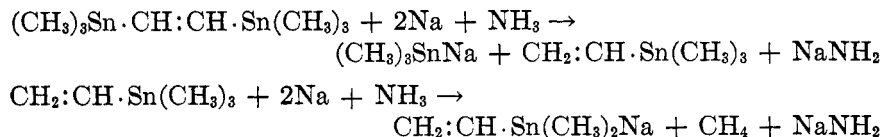$$(CH_3)_4Sn + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + NaNH_2 + CH_4$$
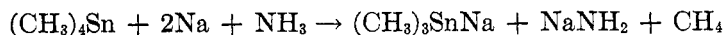
Tetraphenylstannane reacts similarly, with the exception that some of the sodium triphenylstannide is further substituted, forming the disodium compound (61).

Reactions with somewhat different types of compounds are those with bis(trimethylstannyl)methane and bis(trimethylstannyl)ethylene. The former reacts according to the equations (223):

$$CH_2[Sn(CH_3)_3]_2 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + (CH_3)_3SnCH_3 + NaNH_2$$
$$(CH_3)_3SnCH_3 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + CH_4 + NaNH_2$$

and the latter according to the following equations (224):

$$(CH_3)_3Sn \cdot CH:CH \cdot Sn(CH_3)_3 + 2Na + NH_3 \rightarrow$$
$$(CH_3)_3SnNa + CH_2:CH \cdot Sn(CH_3)_3 + NaNH_2$$

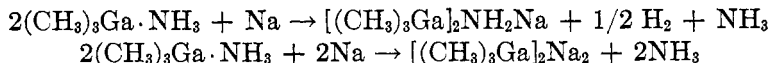$$CH_2:CH \cdot Sn(CH_3)_3 + 2Na + NH_3 \rightarrow$$
$$CH_2:CH \cdot Sn(CH_3)_2Na + CH_4 + NaNH_2$$

H. Trisubstituted derivatives of boron and gallium

Triphenylboron ammine reacts with sodium in liquid ammonia thus (185):

$$(C_6H_5)_3B \cdot NH_3 + Na \rightarrow (C_6H_5)_3B \cdot NH_3Na$$
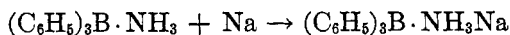
The reaction of trimethylgallium ammine with sodium in liquid ammonia is in accord with the equations:

$$2(CH_3)_3Ga \cdot NH_3 + Na \rightarrow [(CH_3)_3Ga]_2NH_2Na + 1/2 H_2 + NH_3$$
$$2(CH_3)_3Ga \cdot NH_3 + 2Na \rightarrow [(CH_3)_3Ga]_2Na_2 + 2NH_3$$

Depending on conditions, reaction takes place according to the first equation to the extent of from 60 to 100 per cent of the total gallium and according to the second from 30 to 0 per cent. A similar reaction takes place when trimethylgallium is treated with lithium in ethylamine, except that the first reaction is replaced by the following (238):

$$(CH_3)_3Ga \cdot C_2H_5NH_2 + Li \rightarrow (CH_3)_3Ga \cdot C_2H_5NHLi + 1/2 H_2$$
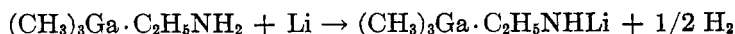
III. HALOGEN COMPOUNDS

A. The liquid ammonia–sodium method for determining halogens in organic compounds

Elements of the halogen family are removed quantitatively from all types of organic combination by solutions of metals in liquid ammonia. This fact constitutes the basis for one of the most convenient and rapid methods for determining organic halogen (including fluorine) (57, 65, 67, 68, 359). Those interested in the analytical determination of halogen have

TABLE 6

*Reactions of alkyl halides with sodium in liquid ammonia*

ALKYL HALIDE	PRODUCTS		REFERENCES
CH_3Cl	CH_4		256
	CH_4, CH_3NH_2, NaCl	(1)	42, 54, 263
CH_3I	CH_4, CH_3NH_2, NaI		54
C_2H_5Br	C_2H_6, NaBr, $NaNH_2$	(2)	387
C_2H_5I	C_2H_6		262
	C_2H_6, $C_2H_5NH_2$, NaI	(1)	263
	C_2H_6 (75 per cent), C_2H_4 (4 per cent), $C_2H_5NH_2$ (21 per cent), $NaNH_2$		54
n-C_3H_7Cl	C_3H_8, C_3H_6 (trace), $NaNH_2$		54
n-C_3H_7I	C_3H_8, $C_3H_7NH_2$, NaI	(1)	246, 263
	C_3H_8		262
	C_3H_8 (71 per cent), C_3H_6 (7 per cent), $C_3H_7NH_2$ (21 per cent), $NaNH_2$		54
n-C_4H_9Cl	C_4H_{10}, $NaNH_2$, NaCl		40
iso-C_4H_9Cl	C_4H_{10}, C_4H_8 (trace), $NaNH_2$		54
iso-C_4H_9I	C_4H_{10} (70 per cent), C_4H_8 (15 per cent), $C_4H_9NH_2$ (15 per cent), $NaNH_2$		54
iso-$C_5H_{11}Cl$	C_5H_{12}, C_5H_{10} (trace), $NaNH_2$		54
iso-$C_5H_{11}I$	C_5H_{12}, C_5H_{10} (trace), $NaNH_2$		54
$tert$-$C_5H_{11}I$	sec-pentane (and explosion)		246
$C_2H_5CHI(CH_2)_2CH_3$	C_6H_{14}, C_6H_{12} (trace), $NaNH_2$		54
$CH_3(CH_2)_5CHICH_3$	C_8H_{18}, $NaNH_2$		54

not concerned themselves with the fate of the hydrocarbon part of the molecule. It is sufficient to say that tars are sometimes encountered, and that polyhalogen compounds are very likely to form some cyanide. Compounds forming cyanide are the following: chloroform, bromoform (not iodoform), carbon tetrachloride, chloral and bromal hydrates, ethylidene chloride, tetrachloroethylene, and acetylene tetrachloride. Although the amount of cyanide thus formed is variable, it can be removed readily prior to determining the halogen. The liquid ammonia–sodium method is not quantitative for cyanide in nitriles.
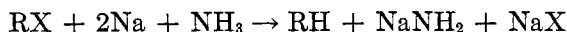
B. Alkyl halides

The monohalogen substitution products of the paraffin hydrocarbons react with a solution of sodium in liquid ammonia to form hydrocarbons, both saturated and unsaturated, sodium halides, and sodium amide, as table 6 shows.
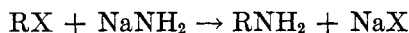
The reactions marked (1) in table 6 proceed in the following manner,

$$2RX + 2Na + NH_3 \rightarrow RH + RNH_2 + 2NaX$$
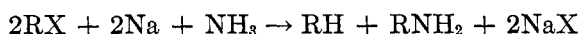
and those marked (2) proceed thus,

$$RX + 2Na + NH_3 \rightarrow RH + NaNH_2 + NaX$$

It seems that sodium amide is a constant product of most of these reactions, perhaps after the fashion of (2) above and that it reacts either to ammonolyze the alkyl halide,

$$RX + NaNH_2 \rightarrow RNH_2 + NaX$$

or to remove hydrogen halide,

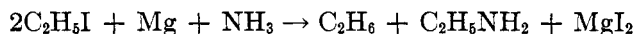$$C_3H_7Cl + NaNH_2 \rightarrow C_3H_6 + NaX + NH_3$$
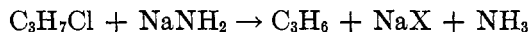
Sodium amide has been shown to enter into both types of reaction (21). The reaction of methyl iodide is complicated by the fact that this substance reacts readily with liquid ammonia to form tetramethylammonium iodide,

$$4CH_3I + 4NH_3 \rightarrow 3NH_4I + (CH_3)_4NI$$
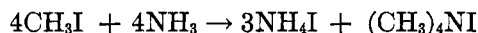
Sodium reacts readily with the ammonium iodide so formed (55),

$$2NH_4I + 2Na \rightarrow 2NH_3 + 2NaI + H_2$$

Magnesium reacts with ethyl iodide in the following manner (251):

$$2C_2H_5I + Mg + NH_3 \rightarrow C_2H_6 + C_2H_5NH_2 + MgI_2$$

For reactions of halogen-substituted ketones see section VIII.

C. Phenyl-substituted alkyl halides

The data relative to the reactions of phenyl-substituted paraffin halides are assembled in table 7. The reaction of β,β,β-triphenylethyl chloride (marked *) is interesting in that it involves a rearrangement of the hydrocarbon nucleus. The similar rearrangement of γ,γ,γ-triphenylpropyl iodide (marked **) is accompanied by a spontaneous cleavage of a carbon–carbon bond.

D. Unsaturated halides

On reaction with a solution of sodium in liquid ammonia acetylene dibromide yields a variable amount of acetylene gas and sodium acetylide.
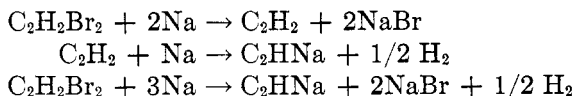
TABLE 7

Reactions of phenyl-substituted alkyl halides with metals in liquid ammonia

HALIDE	METAL	PRODUCTS	REFERENCES
$C_6H_5CH_2Cl$...............	Na	$C_6H_5CH_3$, $C_6H_5CH_2CH_2C_6H_5$, and a solid hydrocarbon	69, cf. 247
$C_6H_5CH_2Br$...............	Na	Bibenzyl	393
	K	Bibenzyl	393
$(C_6H_5)_2CHCl$..............	Na	$(C_6H_5)_2CHCH(C_6H_5)_2$ (65.6 per cent), $(C_6H_5)_2CH_2$ (27.6 per cent)	69, 71
$(C_6H_5)_3CCl$...............	Na	$(C_6H_5)_3CNa$	215
	K	$(C_6H_5)_3CK$	215
	Ca	Unstable reddish-brown compound	215
$C_6H_5CHCl_2$................	Na	Bibenzyl (7.3 per cent), benzylamine (37.6 per cent)	69
$(C_6H_5)_2CCl_2$..............	Na	Tetraphenylethylene (90 per cent)	69, 71
$C_6H_5CCl_3$.................	Na	Bibenzyl (5 per cent), nitrogenous substance	69
$C_6H_5CH_2CH_2Br$...........	Na	$C_6H_5C_2H_5$ (38.3 per cent), styrene (1.3 per cent)	69
$(C_6H_5)_3CCH_2Cl$............	Na	$(C_6H_5)_2CNaCH_2C_6H_5$*	395, 397
$(C_6H_5)_3CCH_2CH_2I$.........	Na	$(C_6H_5)_3CNa$, C_2H_4**	396
$C_6H_5(CH_2)_3Br$.............	Na	$C_6H_5C_3H_7$ (28.2 per cent), $C_6H_5(CH_2)_3NH_2$ (17.9 per cent)	69
$C_6H_5(CH_2)_4Br$.............	Na	$C_6H_5C_4H_9$ (43.1 per cent), $C_6H_5(CH_2)_4NH_2$ (16.5 per cent), unsaturated and other saturated hydrocarbons, other amines	69

TABLE 8

Reactions of bromoölefins with sodium in liquid ammonia

SUBSTANCE	MOLES USED		MOLES OBTAINED		ACETYLENE OLEFIN
	Olefin	Sodium	Acetylene	Olefin	
1-Bromo-1-propene..............	0.167	0.202	0.006	0.818	0.012
1-Bromo-1-octene...............	0.167	0.221	0.034	0.075	0.45
1,1-Dibromo-1-propene..........	0.167	0.389	0.050	0.070	0.71
1,1-Dibromo-1-octene..........	0.167	0.374	0.052	0.029	1.80

The products may be accounted for qualitatively if the following reactions are thought of as taking place in varying proportions (247):

$$C_2H_2Br_2 + 2Na \rightarrow C_2H_2 + 2NaBr$$
$$C_2H_2 + Na \rightarrow C_2HNa + 1/2\ H_2$$
$$C_2H_2Br_2 + 3Na \rightarrow C_2HNa + 2NaBr + 1/2\ H_2$$

Bachman (2) gives a table (table 8) summarizing his findings on the reactions of bromoölefins with sodium in liquid ammonia.

TABLE 9

Reactions of halogenated olefins with sodium in liquid ammonia

ORGANIC HALIDE	MOLES OF SODIUM USED	PRINCIPAL PRODUCT IDENTIFIED	YIELD IN PER CENT
β-Bromostyrene	2	Phenylacetylene	96
α-Chlorostyrene	2	Phenylethane	15
p-Methyl-α-chlorostyrene	2	Tolylacetylene	63
Stilbene dibromide	15	Bibenzyl	73
Styrene dibromide	3	Phenylacetylene	66
2-Bromo-1-decene	2	1-Decene	56

TABLE 10

Reactions of paraffin polyhalides with solutions of sodium in liquid ammonia

| HALIDE	PRODUCTS		REFERENCES
CH_2Cl_2	CH_4 (55 per cent), $NaNH_2$, NaCl		46, 56
$CHCl_3$	CH_4, $NaNH_2$, NaCl, small amounts of C_2H_4, C_2H_2, and NaCN		43
CHI_3	CH_4, NaI, some C_2H_4, C_2H_2, NaCN, H_2, and N_2		43
CCl_4	CH_4, NaCl, NaCN, small amount of N_2		43, 65
CH_2ClCH_2Cl	C_2H_4, NaCl	(*)	46, 56, 247
CH_3CHCl_2	C_2H_6 (51 per cent), C_2H_4 (5 per cent), $NaNH_2$		46, 56
C_2Cl_6	NaCN (not confirmed)		65, cf. 67
$CH_3CH_2CHCl_2$	C_3H_8, some C_3H_6		46
$CH_3CCl_2CH_3$	C_3H_8 (64 per cent), C_3H_6 (14 per cent), $NaNH_2$, NaCl		46, 56
Propylene dibromide	C_3H_6, NaBr	(*)	46, 56
Isobutylene dibromide	C_4H_8, NaBr	(*)	56, 65
$C(CH_2Br)_4$	$C(CH_2NH_2)_4$ (small amounts)		117

The monobromoölefins give principally the corresponding acetylenes and olefins, in a ratio, A/O, which increases with increasing length of the hydrocarbon chain. Under similar conditions the dibromoölefins also yield acetylenes and olefins, but high molecular weight polymers are formed at the same time and make up a considerable portion of the products. The ratio A/O is larger for the dibromoölefins than for the corresponding monobromoölefins, and also increases with increasing length

of the hydrocarbon chain. Small amounts of saturated hydrocarbons arise in all cases, owing to reduction of the olefins and acetylenes by the hydrogen formed in the reaction.

Vaughn (357) has examined the reaction of a number of halogenated olefins with sodium in liquid ammonia. His results are given in table 9. The acetylenes formed in no case were entirely free from hydrogenation products. Hence these reactions are not suitable for the preparation of *pure* acetylenes.
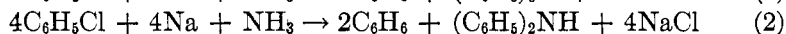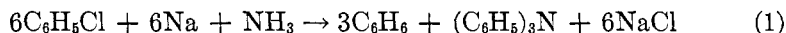
E. Paraffin polyhalides

The products of the reactions of various paraffin polyhalides with liquid ammonia solutions of sodium are given in table 10. It is to be noted that some of the reactions are somewhat complex. Those marked (*) follow essentially the course,

$$C_nH_{2n}X_2 + 2Na \rightarrow C_nH_{2n} + 2NaX$$
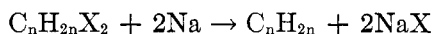
F. Aryl halides

The action of aromatic halides with solutions of metals has been studied but very little. The principal products of the reaction between sodium and chlorobenzene or iodobenzene in liquid ammonia are benzene, diphenylamine, triphenylamine, and sodium halide (374). The following equations suggest the course of the principal reactions:

$$6C_6H_5Cl + 6Na + NH_3 \rightarrow 3C_6H_6 + (C_6H_5)_3N + 6NaCl \qquad (1)$$
$$4C_6H_5Cl + 4Na + NH_3 \rightarrow 2C_6H_6 + (C_6H_5)_2NH + 4NaCl \qquad (2)$$

A small quantity of aniline is formed in accordance with the equation:

$$2C_6H_5Cl + 2Na + NH_3 \rightarrow C_6H_6 + C_6H_5NH_2 + 2NaCl \qquad (3)$$

Using petroleum ether as a diluent, the predominating tendency becomes the formation of tertiary amine. Ortho- and para-chlorotoluene seem to react according to equation 3 above and the action of magnesium on iodobenzene follows the same course (248). *o*-Bromoxylene reacts slowly with sodium solution to form *o*-xylene and a nitrogen-containing residue (69). *o*-Dichlorobenzene and sodium react thus (249):

$$2C_6H_4Cl_2 + 4Na + 2NH_3 \rightarrow C_6H_6 + C_6H_4(NH_2)_2 + 4NaCl$$
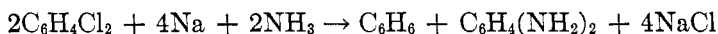
G. Organohalides of silicon, germanium, tin, gallium, and mercury

As much as from five to six atomic equivalents of sodium are consumed when triphenylsilicyl chloride is treated with an excess of sodium in liquid ammonia. It is evident that the phenyl–silicon linkage is broken in this treatment (234). Triphenylsilicyl bromide and metallic lithium react in ethylamine solution according to the equation (203),

$$(C_6H_5)_3SiBr + Li + C_2H_5NH_2 \rightarrow LiBr + (C_6H_5)_3Si \cdot C_2H_5NH_2$$
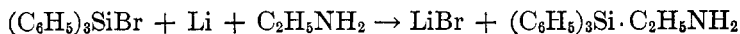
While lithium does not act upon triethylsilicyl bromide in ethylamine solution, it does serve to neutralize the products of the aminolysis of the bromide and thus to bring the following reaction to completion (225):

$$(C_2H_5)_3SiBr + C_2H_5NH_2 + Li \rightarrow (C_2H_5)_3SnNHC_2H_5 + LiBr + 1/2\ H_2$$
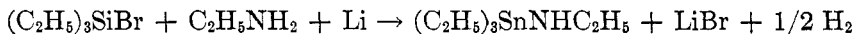
Triethyl-, tripropyl-, tributyl-, and triamyl-silicyl fluorides do not react with sodium in liquid ammonia at its boiling point (114).

Sodium triphenylgermanide has not been prepared by the action of the metal upon a triphenylgermanium halide, but only by the action of the metal upon hexaphenylgermanoethane. The reaction of sodium with diphenylgermanium dichloride must be carried on in an inactive solvent, since the chloride is ammonolyzed in liquid ammonia. Lithium in ethylamine solution acts upon diphenylgermanium dichloride to give a substance which retains ethylamine and which cannot be purified (192). Sodium does not act upon triethylgermanyl bromide in liquid ammonia, but instead reacts with the products of ammonolysis of the bromide:

$$2(C_2H_5)_3GeBr + 3NH_3 \rightarrow [(C_2H_5)_3Ge]_2NH + 2NH_4Br$$
$$2NH_4Br + 2Na \rightarrow 2NaBr + 2NH_3 + H_2$$
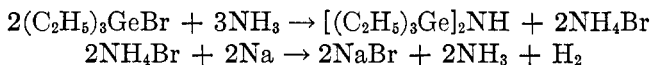
Similar reactions take place between lithium and triethylgermanyl chloride and bromide in ethylamine. Under the same conditions the fluoride has less tendency to ammonolyze and hence may be reduced,

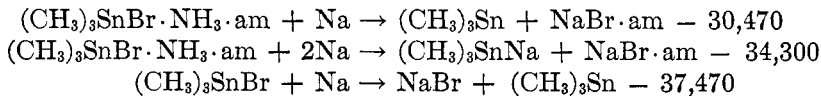$$2(C_2H_5)_3GeF + 2Li \rightarrow 2LiF + [(C_2H_5)_3Ge]_2$$
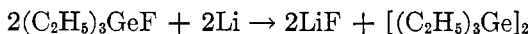
The reaction is unsatisfactory for the preparation of the digermane, however, since it seems to be complicated by the formation of lithium triethylgermanide (204).

Sodium in liquid ammonia reacts with triphenylstannyl bromide (61) and iodide (31, 32) to form sodium triphenylstannide. The trimethylstannide may be similarly prepared by the action of sodium on the corresponding bromide (32, 196, 223, 236) or chloride (206). If only one equivalent of sodium is used, this same reaction may be utilized to obtain a nearly quantitative yield of hexamethylstannoethane,

$$2(CH_3)_3SnBr + 2Na \rightarrow (CH_3)_3Sn \cdot Sn(CH_3)_3 + 2NaBr$$

Sodium also converts dimethylethylstannyl bromide into the corresponding stannide (33). From measurements of the heats of reaction in liquid ammonia solution the following energy equations may be written (235):

$$(CH_3)_3SnBr \cdot NH_3 \cdot am + Na \rightarrow (CH_3)_3Sn + NaBr \cdot am - 30{,}470$$
$$(CH_3)_3SnBr \cdot NH_3 \cdot am + 2Na \rightarrow (CH_3)_3SnNa + NaBr \cdot am - 34{,}300$$
$$(CH_3)_3SnBr + Na \rightarrow NaBr + (CH_3)_3Sn - 37{,}470$$

Diphenyltin dibromide (61) and diiodide (32) on treatment with sodium solution are converted into the free group diphenyltin, $(C_6H_5)_2Sn$, or the

salt, disodium diphenylstannide, $Na_2Sn(C_6H_5)_2$, depending upon the amount of sodium used. Similarly, dimethyltin dibromide is converted into the dimethyltin group, $(CH_3)_2Sn$, disodium dimethylstannide, $(CH_3)_2SnNa_2$ (32, 207), or disodium tetramethylstannoethane, $NaSn(CH_3)_2 \cdot Sn(CH_3)_2Na$ (222), depending upon the reacting ratios.

Dimethylgallium chloride, $(CH_3)_2GaCl$, is reduced to dimethylgallium when treated with one atomic equivalent of sodium in liquid ammonia. The free dimethylgallium combines with ammonia and may be obtained as a solid at $-33°C$., where an internal oxidation–reduction takes place slowly (rapidly at room temperature) according to the equation,

$$(CH_3)_2Ga \cdot NH_3 \rightarrow (CH_3)_2GaNH_2 + 1/2\ H_2$$

When dimethylgallium chloride is treated with two atomic equivalents of sodium, dimethylgallium is first formed, which reacts slowly with sodium, presumably according to the equation,

$$(CH_3)_2Ga \cdot NH_3 + Na \rightarrow (CH_3)_2Ga \cdot NaNH_2 + 1/2\ H_2$$
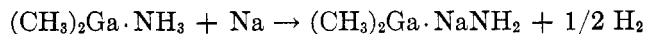
In this compound the amide ion is linked to gallium by a coördinate linkage (238).

Ethylmercuric chloride reacts slowly with sodium in liquid ammonia according to the following equation (219),

$$C_2H_5HgCl + 3Na + NH_3 \rightarrow NaCl + NaHg + C_2H_6 + NaNH_2$$
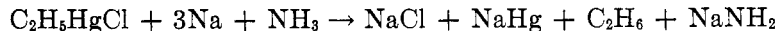
IV. ALCOHOLS AND PHENOLS

The alcohols react readily with the alkali metals in liquid ammonia with the evolution of hydrogen and the formation of alkoxides (44, 240). Secondary and tertiary alcohols react more slowly than primary alcohols. The resulting alkoxides are more soluble in the former cases (44). In many cases it seems that the alcohols do not react completely with sodium or potassium, but instead form compounds of the type $C_2H_5ONa \cdot C_2H_5OH$ (44, 379). The alkoxides of the alkaline-earth metals may also be prepared by reaction between solutions of these metals and alcohols (49). Salts of the polyhydric alcohols are formed in the same manner as salts of the monohydric alcohols. With but few exceptions only one of the hydrogen atoms is displaced by the metal (45, 52, 58). The preparation of salts of unsaturated alcohols is accompanied by reduction on the primary alcohol grouping (or the double bond) (47, 48, 58),

$$2CH_2:CH \cdot CH_2OH + 2Na \rightarrow$$
$$CH_2:CH \cdot CH_2ONa + NaOH + CH_2:CH \cdot CH_3$$

Phenols react with solutions of the alkali metals in the same manner as the aliphatic alcohols. The naphthols, on the other hand, are in part reduced

TABLE 11

Salts of alcohols, phenols, and naphthols prepared by reactions with solutions of metals in liquid ammonia

ALCOHOL	SALT FORMED	REFERENCES	NOTES
Monohydric saturated alcohols			
CH_3OH	CH_3OLi	58	
	CH_3ONa	58	
	CH_3OK	58	
	$(CH_3O)_2Ca$	50, 58	
	$(CH_3O)_2Sr$	58	
	$(CH_3O)_2Ba$	50, 58	
C_2H_5OH	C_2H_5OLi	58	
	C_2H_5ONa	58, 240, 379	White precipitate
	C_2H_5OK	58, 379	More soluble than C_2H_5ONa
	$(C_2H_5O)_2Ca$	50, 58	
	$(C_2H_5O)_2Sr$	50, 58	
	$(C_2H_5O)_2Ba$	50, 58	
$n\text{-}C_3H_7OH$	C_3H_7ONa	361	
$n\text{-}C_4H_9OH$	C_4H_9ONa	240, 361	Appreciably soluble
	C_4H_9OK	379	Insoluble
$iso\text{-}C_4H_9OH$	C_4H_9OLi	58	
	C_4H_9ONa	58	
	C_4H_9OK	58	
	$(C_4H_9O)_2Ca$	50	
$n\text{-}C_5H_{11}OH$	$C_5H_{11}ONa$	361	
	$(C_5H_{11}O)_2Ca$	50	
$iso\text{-}C_5H_{11}OH$	$C_5H_{11}OLi$	58	
	$C_5H_{11}ONa$	58	
	$C_5H_{11}OK$	58	
	$(C_5H_{11}O)_2Ca$	58	
Menthol: $C_{10}H_{19}OH$	$C_{10}H_{19}ONa$	45	
Borneol: $C_{10}H_{17}OH$	$C_{10}H_{17}ONa$	45	
Monohydric substituted alcohols			
Benzyl alcohol: $C_6H_5CH_2OH$	$C_6H_5CH_2OK$	379	
Phenylpropyl alcohol: $C_6H_5(CH_2)_2CH_2OH$	$C_6H_5(CH_2)_2CH_2ONa$	47	
Polyhydric saturated alcohols			
Glycol: $(CH_2OH)_2$	$CH_2OH \cdot CH_2OLi$	45, 52, 58	Stable in excess Na; insoluble $(CH_2OK)_2$ etc. by heating the solid
	$CH_2OH \cdot CH_2ONa$	45, 52, 58, 338, 379	
	$CH_2OH \cdot CH_2OK$	45, 52, 58	
Glycol	$(CH_2O)_2Ca$	52, 58	

233

TABLE 11—*Continued*

ALCOHOL	SALT FORMED	REFERENCES	NOTES
Polyhydric saturated alcohols—*Concluded*			
Glycerol: $CH_2OH \cdot CHOH \cdot$ CH_2OH	$CH_2OH \cdot CHOH \cdot$ CH_2ONa	45, 334, 338	
Erythritol: $CH_2OH \cdot (CHOH)_2 \cdot$ CH_2OH	Di-Li salt Mono-Na salt Ca salt 1:1	58 45, 58 58	
Mannitol: $CH_2OH \cdot (CHOH)_4 \cdot$ CH_2OH	Di-Li salt Mono-Na salt Mono-K salt	58 45, 58, 334 45, 58, 334	
Unsaturated primary alcohols			
Allyl alcohol: $CH_2:CHCH_2OH$	$CH_2:CHCH_2ONa$	47, 58	C_3H_6 (50 mole per cent of C_3H_5OH), no H_2, no reduction of C:C, NaOH
Citronellol: $(CH_3)_2C:CH(CH_2)_2-$ $CH(CH_3)CH_2-$ CH_2OH	Mono-Na salt	47	
Geraniool: $(CH_3)_2C:CH(CH_2)_2-$ $C(CH_3):CHCH_2OH..$	Mono-Na salt	58	$C_{10}H_{18}$, NaOH
Linalool: $(CH_3)_2C:CH(CH_2)_2-$ $C(CH_3)OHCH:CH_2..$	Na salt	58	$C_{10}H_{18}$, NaOH
Cinnamic alcohol: $C_6H_5CH:CHCH_2OH..$	$C_6H_5CH:CHCH_2ONa$ Some $C_6H_5(CH_2)_2-$ CH_2ONa	48, 58	Some $C_6H_5CH:-$ $CHCH_3$ and $C_6H_5(CH_2)_2CH_3$
Phenols			
Phenol: C_6H_5OH	C_6H_5ONa	210, 240, 379	Stable in excess Na
Resorcinol: $m-C_6H_4(OH)_2$........	$C_6H_4(OH)ONa$ $C_6H_4(ONa)_2$	379 379	Very soluble Rather insoluble (none of the disodium salts of dihydroxybenzenes is appreciably soluble (191))

TABLE 11—*Concluded*

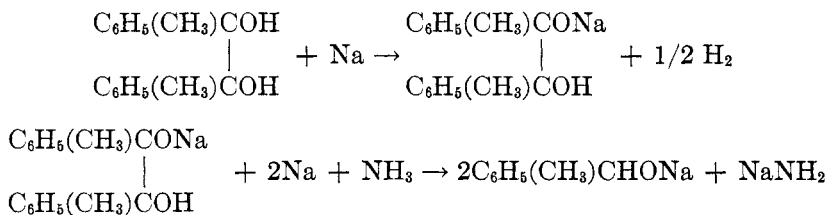| ALCOHOL	SALT FORMED		REFERENCES	NOTES
Naphthols (and tetrahydronaphthols)				
α-Naphthol:				
$C_{10}H_7OH$............. $\Big\{$	$C_{10}H_7ONa$		379	
	$C_{10}H_{11}ONa$	*ar*	379	
β-Naphthol:				
$C_{10}H_7OH$............. $\Big\{$	$C_{10}H_{11}ONa$	*ac*	379	
	$C_{10}H_{11}ONa$	*ar*	379	

to the tetrahydronaphthols, so that the preparation of the pure naphth-oxides requires the use of an alkali amide rather than the free metal.

The salts of alcohols, phenols, and naphthols which have been prepared by reaction with solutions of the alkali and alkaline-earth metals are assembled, together with references, in table 11. The alkali salts of this type have been utilized for the preparation of ethers (interaction with alkyl halides) (52, 240, 361, 379) and of lead and thallium (ous) alkoxides (metathesis between soluble alkoxides and soluble salts of lead and thallium) (50, 52, 58).

Sodium in liquid ammonia replaces only one of the hydrogen atoms of pinacol; it reacts extensively with acetophenone pinacol, first to replace one hydrogen and then to cleave a carbon–carbon bond (392),

$$
\begin{array}{ccc}
C_6H_5(CH_3)COH & & C_6H_5(CH_3)CONa \\
| & + Na \rightarrow & | \qquad + 1/2\ H_2 \\
C_6H_5(CH_3)COH & & C_6H_5(CH_3)COH
\end{array}
$$

$$
\begin{array}{c}
C_6H_5(CH_3)CONa \\
| \qquad + 2Na + NH_3 \rightarrow 2C_6H_5(CH_3)CHONa + NaNH_2 \\
C_6H_5(CH_3)COH
\end{array}
$$

Trimethylstannyl hydroxide reacts with sodium in liquid ammonia as follows (121):

$$(CH_3)_3SnOH + Na \rightarrow (CH_3)_3Sn + NaOH$$
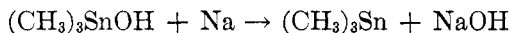
The complex hydroxybromide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$, reacts in some-what the same manner. At first trimethylstannyl precipitates, and then it goes into solution as more sodium is added to form sodium trimethyl-stannide, $NaSn(CH_3)_3$. As the reaction proceeds, gelatinous sodium hydroxide precipitates (197).

V. ETHERS AND OXIDES

The simple ethers, both aliphatic and aromatic,[8] are not acted upon by solutions of metals in liquid ammonia (242). Indeed, diethyl ether has been advantageously used as a diluent for carrying out liquid ammonia–metal reductions (70, 359, 400). When, however, the hydrocarbon portion of an ether contains a substituent normally reactive toward solutions of metals, reaction does occur. Thus, with sodium in liquid ammonia β-bromoethyl phenyl ether gives 1,4-diphenoxybutane and phenol, while γ-bromopropyl phenyl ether gives phenoxypropane, phenol, and 1,6-diphenoxyhexane (69).

While the bond between oxygen and carbon resists the action of metal solutions, the bonds between oxygen and such elements as germanium and tin are broken by the action of a solution of sodium. Thus triphenyl-germanium oxide reacts with sodium to form sodium triphenylgermanide and sodium triphenylgermanolate (254),

$$[(C_6H_5)_3Ge]_2O + 2Na \rightarrow (C_6H_5)_3GeNa + (C_6H_5)_3GeONa$$
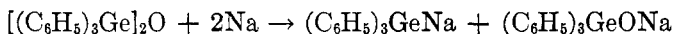
Triethylgermanium oxide reacts similarly with lithium in ethylamine (204). Sodium in liquid ammonia converts trimethylstannyl phenoxide, $(CH_3)_3SnOC_6H_5$, into sodium phenoxide and either trimethylstannyl or sodium trimethylstannide, depending upon the quantity of sodium used (222).

VI. AMINES

A few of the simple aliphatic amines dissolve some of the alkali metals (see part I, section II) and react with the dissolved metal to form substituted metal amides: CH_3NHCs (319), C_2H_5NHCs, and iso-C_4H_9NHCs (318). Usually, however, such reactions do not take place readily except at elevated temperatures (79), and most amines may be safely stored over sodium to insure complete dehydration.

Liquid ammonia is not a suitable medium for the preparation of salts of the aliphatic amines, since such substances are extensively ammonolyzed (318),

$$MNHR + NH_3 \rightarrow MNH_2 + H_2NR$$
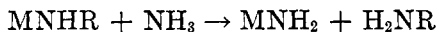
Tributylamine has been recommended as a diluent to increase the solubility of certain organic halogen compounds in the liquid ammonia–sodium
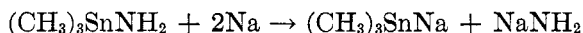
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[8] Since submitting this paper for publication, an important article (328a) has appeared which clearly demonstrates that diphenyl ether as well as its ortho and para mono- and di-substitution products are cleaved rapidly and quantitatively at the carbon–oxygen linkage by sodium in liquid ammonia,

$$ROR + 2e^- \rightarrow R^- + RO^-$$
$$R^- + NH_3 \rightarrow RH + NH_2^-$$
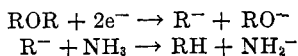
method of analysis for halogens (359). The monosodium salts of aniline, ethylaniline, o-toluidine, and diphenylamine have been formed by treating the amine with sodium in liquid ammonia in an autoclave at room temperature. These reactions did not occur readily at −40°C. Disodium anilide and sodium benzylamide could not be formed (312). Sodium diphenylamide has been prepared by the interaction of sodium and diphenylamine at −33°C. (168, 377). Sodium and potassium react with triphenylmethylamine to form an alkali triphenylmethide and the corresponding amide (233),

$$(C_6H_5)_3CNH_2 + 2K \rightarrow (C_6H_5)_3CK + KNH_2$$
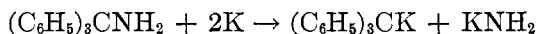
Trimethylstannylamine reacts similarly with sodium in ammonia (223),

$$(CH_3)_3SnNH_2 + 2Na \rightarrow (CH_3)_3SnNa + NaNH_2$$

VII. ALDEHYDES AND RELATED COMPOUNDS

Since the aldehydes are themselves reactive toward liquid ammonia, this medium is suitable only for reactions between aldehyde derivatives and solutions of metals. Acetaldehyde ammonia and sodium react (−33°C.) in the ratio of one mole of the former to one gram-atom of the latter to give one equivalent of hydrogen and a precipitate which was taken to be $CH_3CH(ONa)NH_2$ (242). Aldehyde ammonia, however, appears to be a hydrate of triethylidene triimine, $(CH_3CH:NH)_3 \cdot 3H_2O$ (353), so that the precipitate might well have been sodium hydroxide. Similarly, benzaldehyde reacts with liquid ammonia to form a precipitate which is acted upon by sodium (244).

The acetals are not very reactive toward liquid ammonia and are seemingly stable toward solutions of metals, since dimethylacetal has been recommended as a diluent in the liquid ammonia–sodium method of analysis for organic halogens (359).

Hexamethylenetetramine, $(CH_2)_6N_4$, and N, N, N, N-tetramethyl methylenediamine, $[(CH_3)_2N]_2CH_2$, are not acted upon by sodium in liquid ammonia. N-Ethylideneethylamine, $CH_3CH:NC_2H_5$, forms N,N-diethyl-2,3-butanediamine, $CH_3CH(NHC_2H_5)CH(NHC_2H_5)CH_3$, when treated with a sodium solution in an autoclave at room temperature. This reaction does not occur at −40°C. and is incomplete at −20°C. (311). Benzylideneimine, $C_6H_5CH:NH$, is reduced to benzylamine by sodium in liquid ammonia (351).

VIII. KETONES AND RELATED COMPOUNDS

The reactions of only a few ketones with solutions of metals have been studied. One mole of acetone reacts with one gram-equivalent of sodium without the formation of any gas, but the reaction product has not been
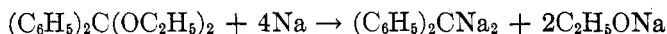
definitely characterized (244).   Benzophenone in ammonia solution reacts with one equivalent of sodium to form a monosodium ketyl, $(C_6H_5)_2CONa$, and with two equivalents to form a disodium ketyl, $(C_6H_5)_2CNaONa$ (190, 244, 331, 386, 387).   A salt of the composition $C_7H_8O_2K$ has been obtained by the action of a potassium solution on dimethylpyrone (331).

The reduction of two chlorine-substituted ketones has been studied, but the results are not entirely conclusive. α-Chloroacetophenone reacts in liquid ammonia with 2.2 atoms of sodium to give a nitrogen- and chlorine-free reddish oil (45 per cent by weight of original ketone) from which acetophenone (13 per cent), a colorless solid (1.3 per cent), and tar may be obtained. β-Chloropropiophenone similarly reacts with 1.53 atoms of sodium to give a nitrogen- and chlorine-free viscous oil (68.8 per cent), which solidifies to a hard resin (69).

Benzophenone diethylketal reacts with sodium and potassium solutions ($-33°C$.) to form sodium and potassium ethoxydiphenylmethides and the corresponding ethoxides (391),

$$(C_6H_5)_2C(OC_2H_5)_2 + 2Na \rightarrow (C_6H_5)_2C(Na)OC_2H_5 + C_2H_5ONa$$
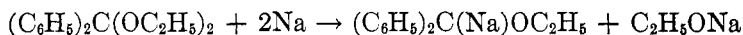
At the same time about 14.4 per cent of the acetal is doubly cleaved,

$$(C_6H_5)_2C(OC_2H_5)_2 + 4Na \rightarrow (C_6H_5)_2CNa_2 + 2C_2H_5ONa$$

By the action of one gram-atom of potassium in liquid ammonia upon one mole of benzil, one obtains a solution colored a deep blue-violet and, by the action of two gram-atoms of potassium, a deep red solution and precipitate.   Neither the monopotassium nor the dipotassium salt is pure, because even at low temperatures benzil reacts with ammonia to form high-melting, nitrogen-containing products (350).

Solutions of metallic potassium and sodium in liquid ammonia give with benzophenoneimine, $(C_6H_5)_2C:NH$, highly colored (red) and very soluble products, which cannot be freed from ammonia, and an excess of metal for analysis.   In each case, however, there is reduction (up to 50 per cent) to benzohydrylamine or the product of its reaction with benzophenoneimine, benzophenonebenzohydrylamine.   Other facts concerning the reaction indicate that this reduction takes place through the formation of the monosodium ketyl of benzophenoneimine, followed by ammonolysis to an equimolecular mixture of amine and imine together with sodium amide. Some disodium ketyl may be formed, but the amount is very small (346).

IX. CARBOHYDRATES

Schmid and coworkers (334, 338) have studied the reaction of carbohydrates with solutions of sodium and potassium in liquid ammonia, and report the rapid formation of monoalkali salts of glucose, fructose, α-

methylglucoside, glycogen, inulin, soluble starch, lichenin, and chitin. With excess of alkali metal further reaction is slow and proceeds in a different manner, since the products obtained contain nitrogen.

As intermediates in the synthesis of carbohydrate derivatives, Muskat and others (136, 274, 298, 299) have prepared ($-33°C.$) a number of potassium salts of carbohydrates (not isolated): tetrapotassium α-methylmannoside, tripotassium monoacetoneglucose, monopotassium diacetoneglucose, monopotassium acetone methylrhamnoside (γ), monopotassium 2,3-acetonemethylrhamnopyranoside, octapotassium sucrose (?), and monopotassium heptamethylisosucrose. Sugars with potential aldehyde or ketone groups react with liquid ammonia to form the corresponding amines. Methylation of fructose methylphenylosazone by the method of Muskat (alkali metal salt + methyl iodide) led to cleavage of the N–N linkages instead of methylation of the hydroxyl groups. The only crystalline product isolated was trimethylphenylammonium iodide (78). This technique of methylation has been applied to acetylstarch and to the Schardinger dextrins (104a).

Cellulose reacts rapidly with an ammonia solution of sodium to form the monosodium derivative. This product is in turn slowly converted into the trisodium derivative $[C_6H_7O_2(ONa)_3]_x$, which is stable toward an excess of the metal (330, 339).

X. ACIDS AND THEIR DERIVATIVES

A. Simple carboxylic acids

In liquid ammonia the carboxylic acids react to form ammonium salts. The reactions of ammonium salts have already been treated in section II of part I. While sodium acetate is inactive toward sodium in ammonia, sodium benzoate does react, although the resulting products have not been determined (245, 328a).

B. Acid amides, amidines, cyanamide, and dicyanodiamide

The acid amides react as monobasic acids with solutions of the alkali metals to liberate hydrogen and form salts. Sodium and potassium acetamide, CH_3CONHK, have been prepared in this manner (100), as well as the sodium salts of benzenesulfonamide, succinimide, benzoic sulfimide, and urea (99). Sodium in excess of one atom reacts slowly and incompletely with a very dilute solution of urea in liquid ammonia ($-33°C.$). Apparently the product is a mixture of mono- and di-sodium urea (137). Magnesium reacts similarly with acetamide, $(CH_3CONH)_2Mg \cdot 4NH_3$ (99,. 101), benzenesulfonamide, $(C_6H_5SO_2NH)_2Mg \cdot nNH_3$, (102), succinimide, benzoic sulfimide, urea (99), and cyanamide (102). Calcium and mag-

nesium form with dicyanodiamide the following salts: $Ca(H_3C_2N_4)_2 \cdot 4NH_3$ and $Mg(H_3C_2N_4)_2 \cdot 2NH_3$ (94).

In studying the reactions of acid amides with sodium in liquid ammonia ($-50°C.$), Chablay (51, 59) observed not only the formation of sodium salts but also the reduction of a part of the amide to the corresponding alcohol:

$$3RCONH_2 + 3Na \rightarrow 3RCONHNa + 3H$$
$$RCONH_2 + 3H + Na \rightarrow RCH_2ONa + NH_3$$
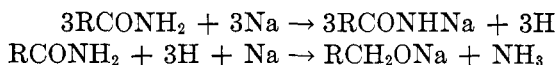
Acetamide, propionamide, butyramide, and isovaleramide react rapidly, while capronamide, caprylamide, and higher homologues react very slowly.

Diphenylmethylformamidine, $C_6H_5N:CH \cdot N(CH_3)C_6H_5$, reacts with sodium in ammonia (room temperature) to form a sodium salt (384).

C. Amino acids and proteins

Voss and Gutterman (369) prepared (low temperatures) the sodium salts of the following amino acids: glycine, $CH_2(NH_2)CO_2Na$, dl-alanine, $CH_3CH(NH_2)CO_2Na$, dl-leucine, $(CH_3)_2CHCH_2CH(NH_2)CO_2Na$, dl-phenylalanine, $C_6H_5CH_2CH(NH_2)CO_2Na$, sarcosine, $CH_3NHCH_2CO_2Na$, l-tyrosine, p-$NaOC_6H_4CH_2CH(NH_2)CO_2Na$, β-alanine, γ-amino-n-butyric acid, $H_2N(CH_2)_3CO_2Na$, and d-glutamic acid, $NaO_2CCH_2CH_2CH(NH_2)$-CO_2Na.

Miller and coworkers (280, 288, 289, 325) have examined the reactions of solutions of sodium in liquid ammonia ($-33°C.$) with amino acids, proteins, and related substances. Table 12 gives the ratio of the moles of hydrogen evolved to the moles of substance used when the various substances and mixtures are treated with a slight excess of sodium. Table 13 gives the ratio of the moles of hydrogen evolved to the moles of diketopiperazine used when various amounts of sodium are added. These results lead to the following conclusions: (1) Glycine and alanine react as monobasic acids. (2) The phenolic hydroxyl group of tyrosine is slightly acidic. (3) Some tyrosine seems to be reduced in the treatment. (4) Leucine liberates more hydrogen than does a monoaminomonocarboxylic acid. (5) Cystine is reduced by sodium acting directly on the disulfide bond (see below). (6) The peptide linkage in dipeptides is not acidic in liquid ammonia. (7) Diketopiperazine is reduced by sodium in liquid ammonia. (8) Mixtures of amino acids and of diketopiperazine do not liberate hydrogen, additively, as is to be expected (289). Proteins (silk fibroin, casein, edestin, and silk) are acidic in liquid ammonia and react readily with sodium and potassium to form hydrogen and ammonolytic products containing alkali metal. The reaction of glycyl-dl-alanine shows that the imide link of the peptide is not quantitatively reduced by sodium

in liquid ammonia. Glycine ethyl ester hydrochloride similarly treated yielded some of the glycine ester and an unidentified product, while *N*-methylacetamide was not completely reduced or decomposed (280). In general, the reactions of proteins with sodium in liquid ammonia occur more slowly than do similar reactions involving amino acids or dipeptides, and are sometimes complicated by the catalytic activity of the proteins

TABLE 12

Reaction of amino acids and related substances with sodium in liquid ammonia

SUBSTANCE	MOLES OF H₂/MOLES OF SUBSTANCE	
Glycine...	0.50	
Alanine...	0.48	0.48
Tyrosine..	0.65	0.67
Glycolic acid...	0.94	0.96
l-Cystine..	0.53	0.55
l-Leucine..	0.64	
Diketopiperazine...	0.32	
Glycylglycine...	0.51	
Glycyl-*dl*-alanine..	0.51	0.52
N-Methylacetamide...	0.53	0.54
Acetanilide...	0.05	0.06
Glycylglycine and diketopiperazine, mole ratio 1:1................	0.02	0.02
Glycylglycine, 2 moles, and diketopiperazine, 1 mole.............	0.05	0.05
Glycine and tyrosine, mole ratio 1:1.............................	0.39	
Glycine 53.3 per cent, alanine 31.1 per cent, tyrosine 15.6 per cent..	0.36	

TABLE 13

Action of sodium in liquid ammonia upon diketopiperazine

SUBSTANCE	ATOMIC WEIGHTS OF Na MOLES OF SUBSTANCE	MOLES OF H₂ MOLES OF SUBSTANCE
Diketopiperazine...........................	0.50	0.04
	1.00	0.06
	2.00	0.32
	3.00	0.32
	4.00	0.32

(notably hemoglobin and hematin) toward the reaction between sodium and ammonia (326). Parathyroid hormone behaves as a typical protein toward sodium and is apparently without catalytic activity (327).

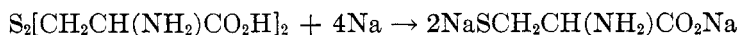Cystine has been shown to be reduced to cysteine by sodium in liquid ammonia (362, 366, 368),

$$S_2[CH_2CH(NH_2)CO_2H]_2 + 4Na \rightarrow 2NaSCH_2CH(NH_2)CO_2Na$$

TABLE 14

Behavior of amino acid derivatives toward solutions of sodium in liquid ammonia

SUBSTANCE	PRODUCTS	REFERENCES
Carbobenzoxy-β-alanine, $C_6H_5CH_2OCONHCH_2CH_2CO_2H$	β-Alanine (ca. quant.), bibenzyl, toluene	345

Carbobenzoxy-*l*-carnosine, $C_6H_5CH_2OCONHCH_2CH_2CONHCHCO_2H$
        CH_2
       $HNCH:NC:CH$
	l-Carnosine (β-alanyl-*l*-histidine)
	 $H_2NCH_2CH_2CONHCH(CO_2H)CH_2$
	               $HNHC:NC:CH$
		345

Carbobenzoxy-*d*-carnosine	*d*-Carnosine	365
Carbobenzoxycystine............	Na salt of cysteine	345
Dicarbobenzoxycystinyldiglycine............	Cystinyldiglycine (after oxidation)	278
Cystinyldiglycine............	Na salt of cysteinylglycine	278
Cysteinylglycine............	Na salt	278

N-Carbobenzoxy-γ-glutaminyl-*S*-benzylcysteinylglycine
     $CH_2SCH_2C_6H_5$
     ┌────────┐
 $NHCHCONHCH_2CO_2H$
     ┌────────┐
 $COCH_2CH_2CHCO_2H$
              $C_6H_5CH_2CO_2NH$
	Na salt of γ-glutaminylcysteinylglycine (gluta-thione by acidification)
	     CH_2SH
	 $NHCHCONHCH_2CO_2H$
	 $COCH_2CH_2CHCO_2H$
	            NH_2
		366a

*N*α-[β-(Benzylmercapto)-*N*-carbobenzoxyalanyl]glutamine
     $CH_2SC_7H_7$
 $CHNHOCOC_7H_7$
 $CONHCHCO_2H$
           $CH_2CH_2CONH_2$
	*N*α-(β-Mercaptoalanyl)glutamine, bibenzyl
	     CH_2SH
	 $CHNH_2$
	 $CONHCHCO_2H$
	          $CH_2CH_2CONH_2$ (74 per cent)
		122

Benzyl ester of β-(benzylmercapto)-N-(Nα-carbobenzoxy-glutaminyl)alanine $CH_2CH_2CONH_2$ | $CHNHCOC_7H_7$ | $CONHCHCO_2C_7H_7$ | $CH_2SC_7H_7$	N-glutaminylcysteine $CH_2CH_2CONH_2$ | $CHNH_2$ | $CONHCHCO_2H$ | CH_2SH (60 per cent)	122
Homocystine, $S_2[CH_2CH_2CH(NH_2)CO_2H]_2$.............	Na salt of homocysteine, $NaSCH_2CH_2CH(NH_2)$-CO_2Na	39, 363, 366, 367
S-Benzyl-N-methylhomocysteine..................	Na salt of cysteine	303a
S-Benzylcysteine................................	Na salt of cysteine	345
S-Benzyl-l-cysteine.............................	Na salt of l-cysteine	367
S-Benzyl-dl-homocysteine.......................	Na salt of homocysteine	324, 367
	Bibenzyl, some toluene	304
S-Benzyl-d-homocysteine........................	Sodium d-cysteinate	367
S-Benzyl-l-homocysteine........................	Sodium l-cysteinate	367
Pentocystine....................................	Sodium pentocysteinate	364
l-Histidine.....................................	Sodium salt	362a
p-Toluenesulfonyl-1-N-methyl-1(or 3)-benzyl-l-histidine.	l-Amino-N-methylhistidine	362a

Some sodium sulfide and alanine seem also to be formed in the reduction of cystine (107).

In connection with synthetic studies in the field of the amino acids and their derivatives, du Vigneaud and others have examined the conduct of a number of substances toward liquid ammonia solutions of sodium ($-33°$ to $-77°$C.). The results of these investigations are given in table 14. The sodium solution is a particularly valuable reagent in this field. In none of the reductions studied was racemization encountered. Hence optically active derivatives of active substances may be prepared readily by

TABLE 15

Reduction of esters by sodium in liquid ammonia

ESTER REDUCED	ALCOHOLS OBTAINED
Esters of monocarboxylic acids:	
Methyl *n*-butyrate	Butanol
Methyl isovalerate	Isoamyl alcohol
Ethyl caproate	Hexanol
Methyl heptylate	Heptanol
Methyl caprylate	Octanol
Methyl laurate	Dodecanol ($C_{12}H_{25}OH$)
Methyl myristate	Tetradecanol ($C_{14}H_{29}OH$)
Methyl palmitate	Hexadecanol ($C_{16}H_{33}OH$)
Esters of dicarboxylic acids:	
Methyl sebacate, $CH_3O_2C(CH_2)_8CO_2CH_3$	Decanediol-1,10
Dimethyl α, α'-dimethylglutarate,	
$CH_3O_2CC(CH_3)_2(CH_2)_2CO_2CH_3$	2,2-Dimethylpentanediol-1,5
Esters containing an aromatic radical:	
Ethyl phenylacetate, $C_6H_5CH_2CO_2C_2H_5$	Phenylethyl alcohol, $C_6H_5CH_2CH_2OH$
Methyl cinnamate, $C_6H_5CH:CHCO_2CH_3$	Phenylpropyl alcohol, $C_6H_5(CH_2)_2CH_2OH$

methylation or by hydrolysis (plus oxidation) of the intermediate sodium salts.

D. Esters

When esters of carboxylic acids are treated with sodium in liquid ammonia ($-50°$C.), two reactions occur,

$$RCOOR' + 2Na + NH_3 \rightarrow RCONHNa + R'ONa + H_2 \qquad (1)$$
$$RCOOR' + H_2 + 2Na \rightarrow RCH_2ONa + R'ONa \qquad (2)$$
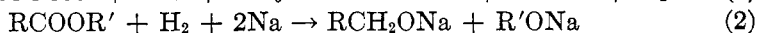
These reactions were observed using the following esters: ethyl acetate, methyl butyrate, methyl isovalerate, ethyl caproate, and methyl caprylate

(51, 60). Esters dissolved in absolute alcohol and added to sodium solutions ($-80°C.$) are reduced in the following manner:

$$RCOOR' + 2C_2H_5OH + 4Na \rightarrow RCH_2ONa + 2C_2H_5ONa + R'ONa$$

Esters so treated and the alcohols obtained are given in table 15. Methyl cinnamate did not give the expected cinnamic alcohol, $C_6H_5CH:CHCH_2OH$, but rather phenylpropyl alcohol, owing to the hydrogenation of the double bond (53).

E. Nitriles

Sodium in liquid ammonia reacts vigorously with α-tolunitrile to form a sodium salt,

$$C_6H_5CH_2CN + Na \rightarrow C_6H_5CHNaCN \text{ (or } C_6H_5CH:CNNa) + 1/2\ H_2$$
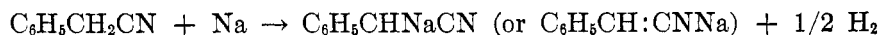
which, when treated with alkyl halides, reacts to form α-alkyl-α-tolunitriles. Some toluene (and presumably sodium cyanide) accompanies the formation of the sodium salt (3). Benzonitrile reacts rapidly with two atoms of sodium to give a wine-red solution and a white precipitate. The reaction products have not been determined, although only traces of cyanide are present (250).

XI. ORGANIC NITRO AND AZOXY COMPOUNDS. DERIVATIVES OF HYDRAZINE, HYDROXYLAMINE, AND DIIMIDE

White and Knight (378) have studied the products of reduction of nitrobenzene and related compounds with solutions of metals in liquid ammonia. Nitrobenzene yields with both sodium and potassium the dialkali phenylhydroxylamine according to the equation,
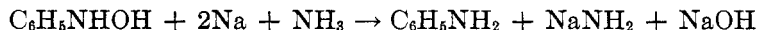
$$C_6H_5NO_2 + 4Na + NH_3 \rightarrow C_6H_5N(Na)ONa + NaNH_2 + NaOH$$

An excess of sodium completely reduced the nitrogen atom, probably to disodium anilide,

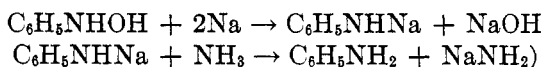$$C_6H_5N(Na)ONa + 2Na + NH_3 \rightarrow C_6H_5NNa_2 + NaNH_2 + NaOH$$
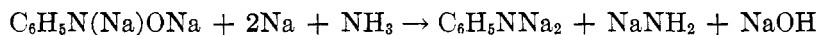
When water is added to partially reduced nitrobenzene and liquid ammonia, azoxybenzene and azobenzene result from the familiar reactions of phenylhydroxylamine in alkaline aqueous solution. Nitrosobenzene with sodium or potassium produces dialkali phenylhydroxylamine,
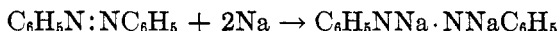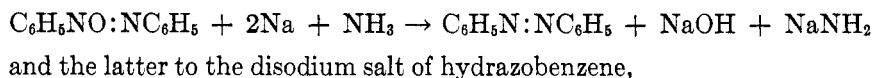
$$C_6H_5NO + 2Na \rightarrow C_6H_5N(Na)ONa$$
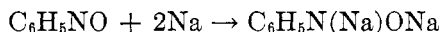
while phenylhydroxylamine itself is reduced directly to aniline by two atoms of sodium without the liberation of hydrogen,

$$C_6H_5NHOH + 2Na + NH_3 \rightarrow C_6H_5NH_2 + NaNH_2 + NaOH$$

(Perhaps the latter reaction proceeds thus,

$$C_6H_5NHOH + 2Na \rightarrow C_6H_5NHNa + NaOH$$
$$C_6H_5NHNa + NH_3 \rightarrow C_6H_5NH_2 + NaNH_2)$$

Azoxybenzene is reduced to azobenzene,

$$C_6H_5NO:NC_6H_5 + 2Na + NH_3 \rightarrow C_6H_5N:NC_6H_5 + NaOH + NaNH_2$$

and the latter to the disodium salt of hydrazobenzene,

$$C_6H_5N:NC_6H_5 + 2Na \rightarrow C_6H_5NNa \cdot NNaC_6H_5$$

The statement of White and Knight that the N–N bond in disodium benzhydrazide is ruptured by an excess of sodium has been disproved by Kraus and Bien (190).

Hydrazotriphenylmethane and hydrazophenylfluorene [s-bis(9-phenyl-9-fluoryl)hydrazine], $C_6H_5C_{13}H_8NHNHC_{13}H_8C_6H_5$, react vigorously with sodium in liquid ammonia at 0°C. to form products (probably sodium salts) which, upon treatment with water, yield triphenylmethane (90 per cent) and 9-phenylfluorene, $C_6H_5C_{13}H_9$, respectively (313).

XII. HETEROCYCLIC NITROGEN RING SYSTEMS

A. Five-membered rings

Franklin (93) has examined the reactions of metals with pyrrole, indole, and carbazole. Pyrrole discharges the blue color of a solution of potassium in liquid ammonia with the evolution of hydrogen, but the potassium salt so formed could not be brought to crystallization. Calcium and magnesium react similarly, and the solubility of the salts is such as to permit their isolation: $(C_4H_4N)_2Ca \cdot 4NH_3$ and $(C_4H_4N)_2Mg \cdot 2NH_3$. That there is little reduction of the pyrrole to tetrahydropyrrole is attested by the fact that 91.6 per cent of the theoretical amount of hydrogen was obtained from one reaction with calcium. The calcium and magnesium salts, $(C_8H_6N)_2M \cdot 4NH_3$, of indole may be prepared similarly. The failure to obtain much more than half of the expected amount of hydrogen from the reaction with calcium indicates that extensive reduction to dihydroindole accompanies these reactions. With carbazole and potassium reduction is so extensive that only a very small amount of hydrogen is liberated and the solution becomes strongly colored.

Imidazole, $HN{-}CH:N{-}CH:CH$, and magnesium react in liquid ammonia to form a magnesium salt, $(C_3H_3N_2)_2Mg$, and hydrogen (373). Benzimidazole,
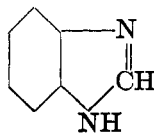
forms a monosodium salt and 0.92 equivalent of hydrogen by a similar reaction (385). The calcium and magnesium salts of lophine (2,4,5-triphenylimidazole) and 1,2,4-triazole, $\overline{HN—CH:N—CH:N}$, and the calcium salt of tetrazole, $\overline{HN—N:N—CH:N}$, are prepared in the same manner (352).

B. Six-membered rings

Pyridine and sodium in liquid ammonia (both at $-60°C$. and at room temperature) form a substance, $(C_5H_5NNa)_2 \cdot NH_3$, which reacts with various alkyl halides to form non-crystallizable, ether-soluble, basic products and yields a hydrate of tetrahydrodipyridyl, $(C_5H_6N)_2 \cdot H_2O$, upon decomposition with 95 per cent alcohol and small quantities of water in the presence of ether (272).

XIII. ORGANIC COMPOUNDS OF SULFUR

The reducing action of sodium in liquid ammonia upon certain organic sulfur compounds has been utilized for the analytical determination of sulfur in these substances. Sodium sulfide and sulfite so formed are then oxidized by sodium peroxide and precipitated as barium sulfate. This method has been found to be satisfactory for the following compounds: thiourea, benzoyl sulfimide, acetone diethyl sulfone, diphenyl sulfone, dinitrophenyl thiocyanate, benzenesulfonamide, benzenesulfonyl chloride, n-propyl p-toluenesulfonate, p-toluenesulfonic acid, and 2-naphthylamine-5,7-disulfonic acid (348).

Alkyl mercaptans (211, 380) and phenyl mercaptan (211, 242, 379) react with liquid ammonia to form ammonium salts, $RSNH_4$, which in turn react with sodium to form the corresponding sodium mercaptides.

Aliphatic sulfides (ethyl, n-propyl, and n-heptyl) react with sodium in liquid ammonia chiefly according to the equation,

$$R_2S + 2Na + NH_3 \rightarrow RSNa + RH + NaNH_2,$$

although the high ratio of sodium ethylmercaptide to sodium amide indicates some such concomitant reaction as (380)

$$2R_2S + 2Na \rightarrow 2RSNa + R—R$$
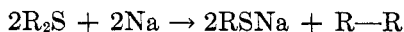
Diphenyl sulfide, while reacting with sodium in the same mole ratio, furnishes benzene, sodium sulfide, and a small amount of a water-insoluble gas (250). A particularly interesting reduction of a sulfide is that of (12-phenyl-12-β-benzoxanthylmercapto)acetic acid, which with sodium in liquid ammonia forms a deep orange-brown sodium triarylmethyl. After reaction with a slight excess of ammonium bromide, the resulting colorless

trisubstituted methane is found to be optically active, showing that the sodium salt (or ion) must also be active (1).

When treated with sodium in liquid ammonia, aliphatic disulfides (ethyl, *n*-propyl, and isoamyl) are reduced quantitatively to the corresponding mercaptides (380),

$$R_2S_2 + 2Na \rightarrow 2RSNa$$
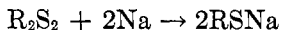
Advantage has been taken of the reactivity of ammonia solutions of metals (sodium, potassium, calcium, and barium) toward sulfur compounds in the purification of petroleum oil (64).

From the reaction products of sodium upon phenyl isothiocyanate, C_6H_5NCS, aniline, sodium sulfide (no cyanide), and a little biphenyl have been isolated. Sodium benzenesulfonate reacts with two atoms of sodium to furnish benzene (71 per cent), sodium sulfite, and a small amount of biphenyl (250).

The amidosulfonic acid derived from vitamin B_1 reacts with sodium in liquid ammonia to form low yields of 2,5-dimethyl-6-aminopyrimidine (65a, 381). For the reactions of benzenesulfonamide and benzoic sulfimide see section X, B; for those of amino acids containing sulfur see section X, C.

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REFERENCES

(1) ADAMS, F. H., AND WALLIS, E. S.: J. Am. Chem. Soc. **54**, 4753–4 (1932).
(2) BACHMAN, G. B.: J. Am. Chem. Soc. **57**, 1088–90 (1935).
(3) BALDINGER, L. H., AND NIEUWLAND, J. A.: J. Am. Chem. Soc. **55**, 2851–3 (1933).
(4) BAXTER, G. P., AND GREENE, C. H.: J. Am. Chem. Soc. **53**, 606–10 (1931).
(5) BERGSTROM, F. W.: J. Am. Chem. Soc. **45**, 2790 (1923).
(6) BERGSTROM, F. W.: J. Am. Chem. Soc. **45**, 2789–90 (1923); **46**, 1549 (1924).
(7) BERGSTROM, F. W.: J. Am. Chem. Soc. **46**, 1548 (1924).
(8) BERGSTROM, F. W.: J. Am. Chem. Soc. **46**, 1552 (1924).
(9) BERGSTROM, F. W.: J. Am. Chem. Soc. **47**, 1503–7 (1925).
(10) BERGSTROM, F. W.: J. Am. Chem. Soc. **47**, 1837 (1925).
(11) BERGSTROM, F. W.: J. Phys. Chem. **29**, 160–5 (1925).
(12) BERGSTROM, F. W.: J. Phys. Chem. **30**, 12–9 (1926).
(13) BERGSTROM, F. W.: J. Am. Chem. Soc. **48**, 146–51 (1926).
(14) BERGSTROM, F. W.: J. Am. Chem. Soc. **48**, 2849–51 (1926).
(15) BERGSTROM, F. W.: J. Am. Chem. Soc. **50**, 653 (1928).

(16) BERGSTROM, F. W.: J. Am. Chem. Soc. **50**, 653, 655 (1928).
(17) BERGSTROM, F. W.: J. Am. Chem. Soc. **53**, 3037-8 (1931).
(18) BERGSTROM, F. W., AND FERNELIUS, W. C.: Chem. Rev. **12**, 43-179 (1933).
(19) Reference 18, pp. 58-9.
(20) Reference 18, p. 90.
(21) Reference 18, pp. 92-3.
(22) BERGSTROM, F. W., AND FERNELIUS, W. C.: Forthcoming review.
(23) BILTZ, W.: Z. Elektrochem. **26**, 374-7 (1920).
(24) BILTZ, W., AND HÜTTIG, G. F.: Z. anorg. allgem. Chem. **114**, 241-65 (1920).
(25) BLAIR, J. S.: J. Am. Chem. Soc. **48**, 90-2 (1926).
(26) BOOTH, H. S., AND MERLUB-SOBEL, M.: J. Phys. Chem. **35**, 3308-13 (1931).
(27) BOSSUET, R., AND HACKSPILL, L.: Compt. rend. **157**, 720-1 (1913).
(28) BOURGUEL, M.: Ann. chim. [10] **3**, 205-8, 355-66 (1925).
(29) BRONN, J.: Tiede-Richter's Handbuch der Arbeitsmethoden in der anor-
        ganischen Chemie, II, 2, 1384-1405 (1925).
(30) BROWNE, A. W., AND HOULEHAN, A. E.: J. Am. Chem. Soc. **33**, 1742-52 (1911).
(31) BULLARD, R. H.: J. Am. Chem. Soc. **51**, 3065-7 (1929).
(32) BULLARD, R. H., AND ROBINSON, W. B.: J. Am. Chem. Soc. **49**, 1368-73 (1927).
(33) BULLARD, R. H., AND VINGEE, R. A.: J. Am. Chem. Soc. **51**, 892-4 (1929).
(33a) BURGESS, W. M., AND HOLDEN, F. R.: J. Am. Chem. Soc. **59**, 459-62, 462-3
        (1937).
(34) BURGESS, W. M., AND ROSE, A.: J. Am. Chem. Soc. **51**, 2127-31 (1929).
(35) Reference 34, p. 2128.
(36) BURGESS, W. M., AND SMOKER, E. H.: J. Am. Chem. Soc. **52**, 3573-5 (1930).
(37) BURGESS, W. M., AND SMOKER, E. H.: Chem. Rev. **8**, 265-72 (1931).
(38) Reference 37, pp. 267-71.
(39) BUTZ, L. W., AND VIGNEAUD, V. DU: J. Biol. Chem. **99**, 141 (1932-3).
(40) CALINGAERT, G., AND HITCHCOCK, L. B.: J. Am. Chem. Soc. **49**, 754 (1927).
(41) CARLI, F. DE: Gazz. chim. ital. **57**, 347-55 (1927).
(42) CHABLAY, E.: Compt. rend. **140**, 1262-4 (1905).
(43) Reference 42, pp. 1262-3.
(44) CHABLAY, E.: Compt. rend. **140**, 1343-4 (1905).
(45) CHABLAY, E.: Compt. rend. **140**, 1396-8 (1905).
(46) CHABLAY, E.: Compt. rend. **142**, 93-5 (1906).
(47) CHABLAY, E.: Compt. rend. **143**, 123-6 (1906).
(48) CHABLAY, E.: Compt. rend. **143**, 829-31 (1906).
(49) CHABLAY, E.: Compt. rend. **153**, 819-21 (1911).
(50) CHABLAY, E.: Compt. rend. **153**, 953-5 (1911).
(51) CHABLAY, E.: Compt. rend. **154**, 364-6 (1912).
(52) CHABLAY, E.: Compt. rend. **154**, 1507-9 (1912).
(53) CHABLAY, E.: Compt. rend. **156**, 1020-2 (1913).
(54) CHABLAY, E.: Ann. chim. [9] **1**, 469-501 (1914).
(55) Reference 54, pp. 478-9.
(56) CHABLAY, E.: Ann. chim. [9] **1**, 501-10 (1914).
(57) CHABLAY, E.: Ann. chim. [9] **1**, 510-9 (1914).
(58) CHABLAY, E.: Ann. chim. [9] **8**, 145-201 (1917).
(59) CHABLAY, E.: Ann. chim. [9] **8**, 201-4 (1917).
(60) CHABLAY, E.: Ann. chim. [9] **8**, 205-13 (1917).
(61) CHAMBERS, R. W., AND SCHERER, P. C.: J. Am. Chem. Soc. **48**, 1054-62 (1926).
(62) Reference 61, p. 1060.

(63) CHITTUM, J. F., AND HUNT, H.: J. Phys. Chem. **40**, 581-9 (1936).
(64) CLANCY, J. C.: U. S. patent 1,423,710; Chem. Abstracts **16**, 3202 (1922).
(65) CLIFFORD, C. W.: J. Am. Chem. Soc. **41**, 1051-60 (1919).
(65a) CLINE, J. K., WILLIAMS, R. R., RUEHLE, A. E., AND WATERMAN, R. E.: J. Am. Chem. Soc. **59**, 530-3 (1937).
(66) COTTRELL, F. G.: J. Phys. Chem. **18**, 85-100 (1914).
(67) DAINS, F. B., AND BREWSTER, R. Q.: J. Am. Chem. Soc. **42**, 1573-9 (1920).
(68) DAINS, F. B., VAUGHN, T. H., AND JANNEY, W. M.: J. Am. Chem. Soc. **40**, 936 (1918).
(69) DEAN, P. M., AND BERCHET, G.: J. Am. Chem. Soc. **52**, 2823-6 (1930).
(70) Reference 69, p. 2825.
(71) DEAN, P. M., BERCHET, G., AND BARNUM, L., JR.: J. Colo.-Wyo. Acad. Sci. **1**, No. 2, 43 (1930); Chem. Abstracts **26**, 3496 (1932).
(72) DENNIS, L. M., AND BROWNE, A. W.: J. Am. Chem. Soc. **26**, 587-600 (1904).
(73) DERMER, O. C.: Chem. Rev. **14**, 385-430 (1934).
(74) Reference 73, pp. 391-4.
(75) DIVERS, E.: Proc. Roy. Soc. London **21**, 110 (1872-3); Trans. Roy. Soc. London **163**, 368 (1873).
(76) ELLIOTT, L. D.: J. Phys. Chem. **28**, 615-9 (1924).
(77) ELLIOTT, N., AND YOST, D. M.: J. Am. Chem. Soc. **56**, 1058 (1934).
(78) ENGEL, L. L.: J. Am. Chem. Soc. **57**, 2420 (1935).
(79) ERDMANN, H., AND SMISSEN, H. VAN DER: Ann. **361**, 32-68 (1908).
(80) FARKAS, L.: Z. physik. Chem. **A161**, 355-61 (1932).
(81) FERNELIUS, W. C.: Unpublished observations.
(82) FERNELIUS, W. C., AND BERGSTROM, F. W.: J. Phys. Chem. **35**, 746 (1931), for bibliography.
(83) FERNELIUS, W. C., AND BERGSTROM, F. W.: J. Phys. Chem. **35**, 748 (1931).
(84) FERNELIUS, W. C., AND ROBEY, R. F.: J. Chem. Education **12**, 56-61 (1935).
(85) FERNELIUS, W. C., AND ROBEY, R. F.: J. Chem. Education **12**, 66-7 (1935).
(86) FITZGERALD, F. F.: J. Am. Chem. Soc. **29**, 661 (1907).
(87) FITZGERALD, F. F.: J. Phys. Chem. **16**, 657-9 (1912).
(88) FLOOD, E. A.: J. Am. Chem. Soc. **54**, 1667 (1932).
(89) FLOOD, E. A.: J. Am. Chem. Soc. **55**, 4937 (1933).
(90) FORBES, G. S., AND NORTON, C. E.: J. Am. Chem. Soc. **48**, 2278-85 (1926).
(91) FOSTER, L. S., AND HOOPER, G. S.: J. Am. Chem. Soc. **57**, 76 (1935).
(92) FRANK, H. H., AND FREITAG, C.: Z. angew. Chem. **39**, 1430-2 (1926).
(93) FRANKLIN, E. C.: J. Phys. Chem. **24**, 81-99 (1920).
(94) FRANKLIN, E. C.: J. Am. Chem. Soc. **44**, 502 (1922).
(95) FRANKLIN, E. C.: The Nitrogen System of Compounds, pp. 319-30. Reinhold Publishing Corp., New York (1935).
(96) FRANKLIN, E. C., AND CADY, H. P.: J. Am. Chem. Soc. **26**, 499-530 (1904).
(97) FRANKLIN, E. C., AND KRAUS, C. A.: Am. Chem. J. **20**, 820-36 (1898).
(98) FRANKLIN, E. C., AND KRAUS, C. A.: Am. Chem. J. **20**, 836-41 (1898).
(99) FRANKLIN, E. C., AND KRAUS, C. A.: Am. Chem. J. **23**, 304 (1900).
(100) FRANKLIN, E. C., AND STAFFORD, O. F.: Am. Chem. J. **28**, 83-107 (1902).
(101) Reference 100, p. 104.
(102) Reference 100, p. 105.
(103) FREDENHAGEN, K.: Z. anorg. allgem. Chem. **186**, 1-37 (1930).
(104) FREED, S., AND THODE, H. G.: Nature **134**, 774-5 (1934).
(104a) FREUDENBERG, K., AND RAPP, W.: Ber. **69B**, 2043-4 (1936).

(105) FULTON, R. A., AND BERGSTROM, F. W.: J. Am. Chem. Soc. **56**, 167 (1934).
(106) GARNER, W. E., AND GILBE, H. F.: J. Chem. Soc. **1928**, 2895–8.
(107) GEBAUER-FUELNEGG, E.: J. Am. Chem. Soc. **52**, 4610–1 (1930).
(108) GIBSON, G. E., AND ARGO, W. L.: Phys. Rev. [2] **7**, 33 (1916).
(109) GIBSON, G. E., AND ARGO, W. L.: J. Am. Chem. Soc. **40**, 1327–61 (1918).
(110) Reference 109, pp. 1328–38.
(111) Reference 109, pp. 1345–61.
(112) Reference 109, p. 1360.
(113) GIBSON, G. E., AND PHIPPS, T. E.: J. Am. Chem. Soc. **48**, 312–26 (1926).
(114) GIERUT, J. A., SOWA, F. J., AND NIEUWLAND, J. A.: J. Am. Chem. Soc. **58**, 898 (1936).
(115) GILBERT, H. N., SCOTT, N. D., ZIMMERLI, W. F., AND HANSLEY, V. L.: Ind. Eng. Chem. **25**, 739–40 (1933).
(116) GORE, G.: Proc. Roy. Soc. London **21**, 140–7 (1872–3).
(117) GOVAERT, F.: Proc. Acad. Sci. Amsterdam **37**, 157 (1934).
(118) GRIENGL, F., STEYSKAL, F., AND STEYSKAL, K.: Monatsh. **63**, 394–426 (1933).
(119) GUNTZ, A., AND BENOIT, F.: Bull. soc. chim. [4] **41**, 436 (1927).
(120) GUNTZ AND MENTREL: Bull. soc. chim. [3] **29**, 585–7 (1903).
(121) HARADA, T.: Bull. Chem. Soc. Japan **4**, 266–70 (1929).
(122) HARINGTON, C. R., AND MEAD, T. H.: Biochem. J. **30**, 1598–1611 (1936).
(123) HESS, K., AND MUNDERLOH, H.: Ber. **51**, 377–84 (1918).
(124) HOTH, W., AND PYL, G.: Z. angew. Chem. **42**, 888–91 (1929).
(125) HUGOT, C.: Compt. rend. **121**, 206–8 (1895).
(126) HUGOT, C.: Compt. rend. **126**, 1719–22 (1898).
(127) HUGOT, C.: Compt. rend. **127**, 553–5 (1898).
(128) HUGOT, C.: Compt. rend. **129**, 299–302 (1899).
(129) HUGOT, C.: Compt. rend. **129**, 388–90 (1899).
(130) HUGOT, C.: Compt. rend. **129**, 603–5 (1899).
(131) HUGOT, C.: Ann. chim. phys. [7] **21**, 5–87 (1900).
(132) Reference 131, pp. 37–41.
(133) HUNT, H.: J. Am. Chem. Soc. **54**, 3509–10 (1932).
(134) HUNT, H., and LARSEN, W. E.: J. Phys. Chem. **38**, 801–4 (1934).
(135) HURD, C. D., AND MEINERT, R. N.: J. Am. Chem. Soc. **53**, 291 (1931).
(135a) INGOLD, C. K., AND MARSHALL, P. G.: J. Chem. Soc. **1926**, 3084.
(136) IRVINE, J C., AND ROUTLEDGE, D.: Nature **134**, 143 (1934); J. Am. Chem. Soc. **57**, 1413 (1935).
(137) JACOBSON, R. A.: J. Am. Chem. Soc. **58**, 1985 (1936).
(138) JOANNIS, A.: Compt. rend. **113**, 795–8 (1891).
(139) JOANNIS, A.: Compt. rend. **114**, 585–7 (1892).
(140) JOANNIS, A.: Compt. rend. **116**, 1370–3 (1893).
(141) JOANNIS, A.: Compt. rend. **116**, 1518–21 (1893).
(142) JOANNIS, A.: Compt. rend. **118**, 713–6 (1894).
(143) JOANNIS, A.: Compt. rend. **119**, 557–9 (1894).
(144) JOANNIS, A.: Ann. chim. phys. [8] **7**, 53–6 (1906).
(145) JOANNIS, A.: Am. chim. phys. [8] **7**, 64–84 (1906).
(146) JOANNIS, A.: Am. chim. phys. [8] **7**, 84–101 (1906).
(147) JOANNIS, A.: Am. chim. phys. [8] **7**, 101–7 (1906).
(148) JOANNIS, A.: Ann. chim. phys. [8] **7**, 107–13 (1906).
(149) JOHNSON, W. C.: J. Phys. Chem. **36**, 2590 (1932).
(150) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **6**, 20–33 (1929).

(151) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **6**, 33–5 (1929); **7**, 983–95, 2604–7 (1930).
(152) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **6**, 441–7 (1929).
(153) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **6**, 443–4 (1929).
(154) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **6**, 447–50 (1929).
(155) JOHNSON, W. C., AND FERNELIUS, W. C.: J. Chem. Education **7**, 981–99 (1930).
(156) JOHNSON, W. C., AND KRUMBOLTZ, O. F.: Z. physik. Chem. **A167**, 249–59 (1933).
(157) Reference 156, pp. 250–4.
(158) JOHNSON, W. C., AND MARTENS, R. I.: J. Am. Chem. Soc. **58**, 15–7 (1936).
(159) JOHNSON, W. C., AND MEYER, A. W.: J. Phys. Chem. **33**, 1922–30 (1929).
(160) JOHNSON, W. C., AND MEYER, A. W.: Chem. Rev. **8**, 273–301 (1931).
(161) JOHNSON, W. C., AND MEYER, A. W.: J. Am. Chem. Soc. **54**, 3621–8 (1932).
(162) Reference 161, pp. 3621–2.
(163) JOHNSON, W. C., MOREY, G. H., AND KOTT, A. E.: J. Am. Chem. Soc. **54**, 4280–1 (1932).
(164) Reference 163, p. 4281.
(165) JOHNSON, W. C., AND PISKUR, M. M.: J. Phys. Chem. **37**, 93–9 (1933).
(166) JOHNSON, W. C., AND SIDWELL, A. E.: J. Am. Chem. Soc. **55**, 1884–9 (1933).
(166a) JOHNSON, W. C., AND WHEATLEY, A. C.: Z. anorg. allgem. Chem. **216**, 273–7 (1934).
(167) JOHNSON, W. C., AND WHEATLEY, A. C.: Z. anorg. allgem. Chem. **216**, 279–80 (1934).
(168) JONES, P. C.: U. S. patent 2,046,876.
(169) KAHLER, H. L., JR.: Dissertation, University of Cincinnati, 1934.
(170) KILLIAN, D. B., HENNION, G. F., AND NIEUWLAND, J. A.: J. Am. Chem. Soc. **56**, 1384–5 (1934).
(171) KRAUS, C. A.: J. Am. Chem. Soc. **29**, 1557–71 (1907).
(172) Reference 171, p. 1561.
(173) Reference 171, pp. 1561–2.
(174) KRAUS, C. A.: J. Am. Chem. Soc. **30**, 660–7 (1908).
(175) KRAUS, C. A.: J. Am. Chem. Soc. **30**, 1200–18 (1908).
(176) KRAUS, C. A.: J. Am. Chem. Soc. **35**, 1735 (1913).
(177) KRAUS, C. A.: J. Am. Chem. Soc. **36**, 866–8 (1914).
(178) KRAUS, C. A.: J. Am. Chem. Soc. **36**, 871–2 (1914).
(179) KRAUS, C. A.: The Properties of Electrically Conducting Systems, pp. 366–83. Chemical Catalog Co., New York (1922).
(180) KRAUS, C. A.: J. Am. Chem. Soc. **44**, 1220–35 (1922).
(181) KRAUS, C. A.: Rec. trav. chim. **42**, 588–93 (1923).
(182) KRAUS, C. A.: Trans. Am. Electrochem. Soc. **45**, 175–86 (1924).
(183) KRAUS, C. A.: J. Am. Chem. Soc. **46**, 2196–204 (1924).
(184) Reference 183, p. 2200.
(185) KRAUS, C. A.: Contemporary Developments in Chemistry. Columbia University Press, New York (1927).
(186) KRAUS, C. A.: Chem. Rev. **8**, 251–64 (1931).
(187) KRAUS, C. A.: J. Chem. Education **8**, 2128–30 (1931).
(188) KRAUS, C. A.: J. Franklin Inst. **212**, 537–62 (1931).
(189) KRAUS, C. A.: Lectures at The Ohio State University, August, 1932.
(190) KRAUS, C. A., AND BIEN, P. B.: J. Am. Chem. Soc. **55**, 3609–14 (1933).
(191) Reference 190, p. 3611.
(192) KRAUS, C. A., AND BROWN, C. L.: J. Am. Chem. Soc. **52**, 4031–5 (1930).

(193) KRAUS, C. A., AND BROWN, E. H.: J. Am. Chem. Soc. **51**, 2690–6 (1929).
(194) KRAUS, C. A., AND BROWN, E. H.: J. Am. Chem. Soc. **52**, 4414–8 (1930).
(195) Reference 194, pp. 4414–6.
(196) KRAUS, C. A., AND BULLARD, R. H.: J. Am. Chem. Soc. **48**, 2131–6 (1926).
(197) KRAUS, C. A., AND BULLARD, R. H.: J. Am. Chem. Soc. **52**, 4057–8 (1930).
(198) KRAUS, C. A., AND CARNEY, E. S.: J. Am. Chem. Soc. **56**, 765–8 (1934).
(199) Reference 198, pp. 765–7.
(200) KRAUS, C. A., CARNEY, E. S., AND JOHNSON, W. C.: J. Am. Chem. Soc. **49**, 2206–9 (1927).
(201) KRAUS, C. A., AND CHIU, C. Y.: J. Am. Chem. Soc. **44**, 1999–2008 (1922).
(202) Reference 201, pp. 2002–4.
(203) KRAUS, C. A., AND EATOUGH, H.: J. Am. Chem. Soc. **55**, 5008–14 (1933).
(204) KRAUS, C. A., AND FLOOD, E. A.: J. Am. Chem. Soc. **54**, 1635–44 (1932).
(205) KRAUS, C. A., AND FOSTER, L. S.: J. Am. Chem. Soc. **49**, 457–67 (1927).
(206) KRAUS, C. A., AND GREER, W. M.: J. Am. Chem. Soc. **44**, 2629–33 (1922).
(207) KRAUS, C. A., AND GREER, W. M.: J. Am. Chem. Soc. **47**, 2568–75 (1925).
(208) KRAUS, C. A., AND GLASS, S. W.: J. Phys. Chem. **33**, 984–94 (1929).
(209) KRAUS, C. A., AND HAWES, W. W.: J. Am. Chem. Soc. **55**, 2779–80 (1933).
(210) KRAUS, C. A., AND JOHNSON, E. G.: J. Am. Chem. Soc. **55**, 3542–7 (1933).
(211) Reference 210, p. 3543.
(212) KRAUS, C. A., AND JOHNSON, W. C.: J. Am. Chem. Soc. **47**, 727–9 (1925).
(213) KRAUS, C. A., AND KAHLER, W. H.: J. Am. Chem. Soc. **55**, 3537–42 (1933).
(214) Reference 213, pp. 3538–9.
(215) KRAUS, C. A., AND KAWAMURA, T.: J. Am. Chem. Soc. **45**, 2756–63 (1923).
(216) Reference 215, p. 2758.
(217) KRAUS, C. A., AND KURTZ, H. F.: J. Am. Chem. Soc. **47**, 43–60 (1925).
(218) Reference 217, p. 52.
(219) Reference 217, pp. 57–9.
(220) KRAUS, C. A., AND LUCASSE, W. W.: J. Am. Chem. Soc. **43**, 2535–6 (1921).
(221) KRAUS, C. A., AND LUCASSE, W. W.: J. Am. Chem. Soc. **44**, 1942–3 (1922); **45**, 2551 (1923).
(222) KRAUS, C. A., AND NEAL, A. M.: J. Am. Chem. Soc. **51**, 2403–7 (1929).
(223) KRAUS, C. A., AND NEAL, A. M.: J. Am. Chem. Soc. **52**, 695–701 (1930).
(224) KRAUS, C. A., AND NEAL, A. M.: J. Am. Chem. Soc. **52**, 4426–33 (1930).
(225) KRAUS, C. A., AND NELSON, W. K.: J. Am. Chem. Soc. **56**, 195–202 (1934).
(226) Reference 225, pp. 196–7.
(227) KRAUS, C. A., AND NUTTING, H. S.: J. Am. Chem. Soc. **54**, 1622–30 (1932).
(228) Reference 227, pp. 1623–4.
(229) KRAUS, C. A., AND PARMENTER, E. F.: J. Am. Chem. Soc. **56**, 2384–8 (1934).
(230) KRAUS, C. A., AND PRESCOTT, R. F.: J. Am. Chem. Soc. **56**, 86–8 (1934).
(231) KRAUS, C. A., AND RIDDERHOF, J. A.: J. Am. Chem. Soc. **56**, 79–86 (1934).
(232) KRAUS, C. A., AND ROSEN, R.: J. Am. Chem. Soc. **47**, 2739 (1925).
(233) KRAUS, C. A., AND ROSEN, R.: J. Am. Chem. Soc. **47**, 2745–6 (1925).
(234) KRAUS, C. A., AND ROSEN, R.: J. Am. Chem. Soc. **47**, 2746–7 (1925).
(235) KRAUS, C. A., AND SCHMIDT, F. C.: J. Am. Chem. Soc. **56**, 2297–2300 (1934).
(236) KRAUS, C. A., AND SESSIONS, W. V.: J. Am. Chem. Soc. **47**, 2361–8 (1925).
(237) KRAUS, C. A., AND SHERMAN, C. S.: J. Am. Chem. Soc. **55**, 4694–7 (1933).
(238) KRAUS, C. A., AND TOONDER, F. E.: J. Am. Chem. Soc. **55**, 3547–54 (1933).
(239) Reference 238, pp. 3548–9.
(240) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 769–70 (1923).

(241) Reference 240, p. 769.
(242) Reference 240, p. 770.
(243) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 770-1 (1923).
(244) Reference 243, p. 771.
(245) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 771-2 (1923).
(246) Reference 245, p. 772.
(247) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 773 (1923).
(248) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 773-4 (1923).
(249) Reference 248, p. 774.
(250) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 775 (1923).
(251) KRAUS, C. A., AND WHITE, G. F.: J. Am. Chem. Soc. **45**, 776 (1923).
(252) KRAUS, C. A., AND WHYTE, E. F.: J. Am. Chem. Soc. **48**, 1781-90 (1926).
(253) Reference 252, pp. 1783, 1786.
(254) KRAUS, C. A., AND WOOSTER, C. B.: J. Am. Chem. Soc. **52**, 372-6 (1930).   81
(255) KRAUS, C. A., AND ZEITFUCHS, E. H.: J. Am. Chem. Soc. **44**, 1250-2, 2716-9
      (1922).
(256) KRAUS, C. A., AND ZEITFUCHS, E. H.: J. Am. Chem. Soc. **44**, 2714-28 (1922).
(257) LAI, T. Y.: Bull. soc. chim. [4] **53**, 687-92 (1933).
(258) LEBEAU, P.: Compt. rend. **130**, 502-5 (1900).
(259) LEBEAU, P.: Compt. rend. **134**, 284-6 (1902).
(260) LEBEAU, P.: Bull. soc. chim. [3] **27**, 163 (1902).
(261) LEBEAU, P.: Bull. Soc. chim. [3] **27**, 256-60 (1902).
(262) LEBEAU, P.: Compt. rend. **140**, 1042-4 (1905).
(263) LEBEAU, P.: Compt. rend. **140**, 1264-6 (1905).
(264) LEBEAU, P., AND PICON, M.: Compt. rend. **156**, 1077-9 (1913).
(265) LEBEAU, P., AND PICON, M.: Compt. rend. **157**, 137-9 (1913).
(266) LEBEAU, P., AND PICON, M.: Compt. rend. **157**, 223-4 (1913).
(267) LEBEAU, P., AND PICON, M.: Compt. rend. **158**, 1514-7 (1914); **175**, 223-5 (1922).
(268) LEBEAU, P., AND PICON, M.: Compt. rend. **159**, 70-2 (1914); **173**, 84-6 (1921).
(269) LEBEAU, P., AND PICON, M.: Compt. rend. **159**, 70-2 (1914).
(270) Reference 269, p. 71.
(271) LEBEAU, P., AND PICON, M.: Compt. rend. **173**, 84-6 (1921).
(272) LEBEAU, P., AND PICON, M.: Compt. rend. **173**, 1178-80 (1921).
(273) LEBEAU, P., AND PICON, M.: Compt. rend. **175**, 223-5 (1922).
(274) LEVENE, P. A., AND MUSKAT, I. E.: J. Biol. Chem. **105**, 435-6 (1934).
(275) LINHARD, M., AND STEPHAN, M.: Z. physik. Chem. **A163**, 185-95 (1933); **A167**,
      87-102 (1933).
(276) LOANE, C. M.: J. Phys. Chem. **37**, 617-9 (1933).
(277) Reference 276; cf. reference 360.
(277a) LOOMIS, A. G., J. Am. Chem. Soc. **44**, 8-19 (1922).
(278) LORING, H. S., AND VIGNEAUD, V. DU: J. Biol. Chem. **111**, 385-92 (1935).
(279) MAXTED, E. B.: J. Chem. Soc. **111**, 1016-9 (1917).
(280) McCHESNEY, E. W., AND MILLER, C. O.: J. Am. Chem. Soc. **53**, 3888-96 (1931).
(280a) McCUSKER, P. A., AND KROEGER, J. W.: J. Am. Chem. Soc. **59**, 213-4
      (1937).
(281) McCLEARY, R. L., AND FERNELIUS, W. C.: J. Am. Chem. Soc. **56**, 803-4 (1934).
(282) McKELVY, E. C., AND TAYLOR, C. S.: Scientific Papers of the Bureau of Stand-
      ards, No. 465 (1923).
(283) MEINERT, R. N., AND HURD, C. D.: J. Am. Chem. Soc. **52**, 4544 (1930).
(284) MENTREL: Compt. rend. **135**, 740-2 (1902).
(285) Reference 284, p. 741.

(286) MENTREL: Bull. soc. chim. [3] 29, 493–503 (1903).
(287) MIDGLEY, T., JR., AND HENNE, A. L.: J. Am. Chem. Soc. 51, 1293–4 (1929).
(288) MILLER, C. O., AND ROBERTS, R. G.: Proc. Soc. Exptl. Biol. Med. 29, 533 (1932).
(289) MILLER, C. O., AND ROBERTS, R. G.: J. Am. Chem. Soc. 56, 935–7 (1934).
(290) MILLER, H. F., AND BACHMAN, G. B.: J. Am. Chem. Soc. 57, 768 (1935).
(291) MOISSAN, H.: Compt. rend. 127, 911–17 (1898).
(292) MOISSAN, H.: Compt. rend. 128, 26–30 (1899).
(293) Reference 292, p. 26.
(294) MOISSAN, H.: Compt. rend. 132, 516–7 (1901).
(295) MOISSAN, H.: Compt. rend. 133, 715–7 (1901).
(296) MOISSAN, H.: Compt. rend. 133, 771–4 (1901).
(297) MOISSAN, H.: Compt. rend. 136, 1217–22 (1903).
(298) MUSKAT, I. E.: J. Am. Chem. Soc. 56, 693–5 (1934).
(299) MUSKAT, I. E.: J. Am. Chem. Soc. 56, 2449–54 (1934).
(300) OGG, R. A., JR., LEIGHTON, P. A., AND BERGSTROM, F. W.: J. Am. Chem. Soc. 55, 1754–66 (1933).
(301) OSTWALD, Wo.: Kolloidchem. Beihefte 2, 437–40 (1910–11).
(302) PALMAER, W.: Z. Elektrochem. 8, 729–31 (1902).
(303) PATSCHEKE, G.: Z. physik. Chem. A163, 340–50 (1933).
(303a) PATTERSON, W. I., DYER, H. M., AND VIGNEAUD, V. DU: J. Biol. Chem. 116, 280–2 (1936).
(304) PATTERSON, W. I., AND VIGNEAUD, V. DU: J. Biol. Chem. 111, 393–8 (1935).
(305) PEARSON, T. G.: Nature 131, 166–7 (1933).
(306) PECK, E. B.: J. Am. Chem. Soc. 40, 335 (1918).
(307) PICON, M.: Compt. rend. 158, 1184–7 (1914).
(308) PICON, M.: Compt. rend. 158, 1346–9 (1914).
(309) PICON, M.: Compt. rend. 169, 32–4 (1919).
(310) PICON, M.: Compt. rend. 173, 155–8 (1921); Bull. soc. chim. [4] 29, 709–13 (1921).
(311) PICON, M.: Compt. rend. 175, 695–8 (1922).
(312) PICON, M.: Compt. rend. 175, 1213–6 (1922).
(313) PINCK, L. A.: J. Am. Chem. Soc. 55, 1714 (1933).
(314) PLESKOV, V. A., AND MONOSZON, A. M.: J. Phys. Chem. U. S. S. R. 4, 696 (1933); Acta Physicochim. U. R. S. S. 1, 715–6 (1935).
(315) PLESKOV, V. A., AND MONOSZON, A. M.: Acta Physicochim. U. R. S. S. 1, 872–4 (1935); 2, 615–20, 623–5 (1935).
(316) PLESKOV, V. A., AND MONOSZON, A. M.: Acta. Physicochim. U. R. S. S. 2, 615–20, 621–32 (1935).
(317) RENGADE, E.: Compt. rend. 138, 629–31 (1904).
(318) RENGADE, E.: Compt. rend. 141, 196–8 (1905).
(319) RENGADE, E.: Compt. rend. 140, 246–8 (1905).
(320) RENGADE, E.: Compt. rend. 140, 1536–8 (1905).
(321) RENGADE, E.: Bull. soc. chim. [3] 35, 769–75 (1906).
(322) RENGADE, E.: Bull. soc. chim. [3] 35, 775–8 (1906).
(323) REYNOLDS, H. H., BIGELOW, L. A., AND KRAUS, C. A.: J. Am. Chem. Soc. 51, 3067–72 (1929).
(324) RIEGEL, B., AND VIGNEAUD, V. DU: J. Biol. Chem. 112, 149–54 (1935).
(325) ROBERTS, R. G., AND MILLER, C. O.: Proc. Soc. Exptl. Biol. Med. 30, 821 (1933).
(326) ROBERTS, R. G., AND MILLER, C. O.: Proc. Soc. Exptl. Biol. Med. 31, 522–4 (1934); J. Am. Chem. Soc. 58, 309–10 (1936).

(327) ROBERTS, R. G., TWEEDY, W. R., AND SMULLEN, G. H.: J. Biol. Chem. **112,** 209–14 (1935).

(328) ROEDERER: Compt. rend. **140,** 1252–3 (1905).

(328a) SARTORETTO, P. A., AND SORVA, F. J., J. Am. Chem. Soc. **59,** 603–6 (1937).

(329) SCHERER, P. C., JR.: J. Am. Chem. Soc. **53,** 3694–6 (1931).

(330) SCHERER, P. C., JR., AND HUSSEY, R. E.: J. Am. Chem. Soc. **53,** 2344–7 (1931).

(331) SCHLUBACH, H.: Ber. **48,** 12–4 (1915).

(332) SCHLUBACH, H. H.: Ber. **53B,** 1689–93 (1920).

(333) SCHLUBACH, H. H., AND BALLAUF, F.: Ber. **54B,** 2811–25 (1921).

(334) SCHMID, L., AND BECKER, B.: Ber. **58B,** 1966–8 (1925).

(335) SCHMID, L., AND BECKER, B.: Ber. **58B,** 1968–71 (1925).

(336) SCHMID, L., AND FALKE, R.: Monatsh. **59,** 376–80 (1932).

(337) SCHMID, L., AND HASCHEK, L.: Monatsh. **59,** 328–34 (1932).

(338) SCHMID, L., WASCHKAU, A., AND LUDWIG, E.: Monatsh. **49,** 107–10 (1928).

(338a) SCHMIDT, F. C., SOTTYSIAK, J., AND KLUGE, H. D.: J. Am. Chem. Soc. **58,** 2509–10 (1936).

(339) SCHORIGIN, P., AND MAKAROWA-SEMLJANSKAJA, N. N.: Ber. **69B,** 1713–21 (1936).

(340) SHATENSHTEIN, A. I.: Acta Physicochim. U. R. S. S. **3,** 53–60 (1935).

(341) SHATENSHTEIN, A. I., AND MONOSZON, A. M.: Z. anorg. allgem. Chem. **207,** 204–8 (1932).

(342) SHATENSHTEIN, A. I., AND MONOSZON, A. M.: Z. physik. Chem. **A165,** 147–53 (1933).

(343) SHATENSHTEIN, A. I., AND USKOVA, L. S.: Acta Physicochim. U. R. S. S. **2,** 337–44 (1935).

(344) SHERRY, R. H.: J. Phys. Chem. **11,** 560–1 (1907).

(345) SIFFERD, R. H., AND VIGNEAUD, V. DU: J. Biol. Chem. **108,** 753–61 (1935).

(346) SMITH, G. E. P., JR., AND BERGSTROM, F. W.: J. Am. Chem. Soc. **56,** 2095–8 (1934).

(347) SMYTH, F. H.: J. Am. Chem. Soc. **39,** 1299–312 (1917).

(348) SOWA, F. J., ARCADI, V. G., AND NIEUWLAND, J. A.: Ind. Eng. Chem., Anal. Ed. **8,** 49–50 (1936)

(349) STAKELBECK, H.: Z. ges. Kälte-Ind. **40,** 33–40 (1933).

(350) STAUDINGER, H., AND BINKERT, A.: Helv. Chim. Acta **5,** 704 (1922).

(351) STRAIN, H. H.: J. Am. Chem. Soc. **49,** 1558–71 (1927).

(352) STRAIN, H. H.: J. Am. Chem. Soc. **49,** 1995–2000 (1927).

(353) STRAIN, H. H.: J. Am. Chem. Soc. **54,** 1224–5 (1932).

(354) STRAIN, H. H., AND SMITH, J. H. C.: J. Am. Chem. Soc. **52,** 5291–3 (1930).

(355) TAFT, R., AND BARHAM, H.: J. Phys. Chem. **34,** 930–2 (1930).

(356) TAYLOR, N. W.: J. Am. Chem. Soc. **48,** 858–9 (1926).

(357) VAUGHN, T. H.: J. Am. Chem. Soc. **56,** 2064–5 (1934).

(358) VAUGHN, T. H., AND DANEHY, J. P.: Proc. Indiana Acad. Sci. **44,** 144–8 (1934).

(359) VAUGHN, T. H., AND NIEUWLAND, J. A.: Ind. Eng. Chem., Anal. Ed. **3,** 274–5 (1931).

(360) VAUGHN, T. H., VOGT, R. R., AND NIEUWLAND, J. A.: J. Am. Chem. Soc. **56,** 2120–2 (1934).

(361) VAUGHN, T. H., VOGT, R. R., AND NIEUWLAND, J. A.: J. Am. Chem. Soc. **57,** 510–2 (1935).

(362) VIGNEAUD, V. DU, AUDRIETH, L. F., AND LORING, H. S.: J. Am. Chem. Soc. **52,** 4500–4 (1930).

(362a) VIGNEAUD, V. DU, AND BEHRENS, O. K.: J. Biol. Chem. **117**, 27–36 (1937).
(363) VIGNEAUD, V. DU, DYER, H. M., AND HARMON, J., JR.: J. Biol. Chem. **101**, 719–20 (1933).
(364) VIGNEAUD, V. DU, DYER, H. M., JONES, C. B., AND PATTERSON, W. I.: J. Biol. Chem. **106**, 401–7 (1934).
(365) VIGNEAUD, V. DU, AND HUNT, M.: J. Biol. Chem. **115**, 98 (1936).
(366) VIGNEAUD, V. DU, LORING, H. S., AND CRAFT, H. A.: J. Biol. Chem. **105**, 481–8 (1934).
(366a) VIGNEAUD, V. DU, AND MILLER, G. L.: J. Biol. Chem. **116**, 469–76 (1936).
(367) VIGNEAUD, V. DU, and PATTERSON, W. I.: J. Biol. Chem. **109**, 97–103 (1935).
(368) VIGNEAUD, V. DU, AND PATTERSON, W. I.: J. Biol. Chem. **114**, 533–8 (1936).
(369) VOSS, W., AND GUTTERMAN, R.: Ber. **63B**, 1726–31 (1930).
(370) WATT, G. W.: Dissertation, The Ohio State University, 1935.
(371) WELSH, T. W. B.: J. Am. Chem. Soc. **37**, 501–2 (1915).
(372) WELSH, T. W. B., AND BRODERSON, H. J.: J. Am. Chem. Soc. **37**, 818–24 (1915).
(373) WENZEL, R. N.: Dissertation, Stanford University, 1928.
(374) WHITE, G. F.: J. Am. Chem. Soc. **45**, 779–84 (1923).
(375) Reference 374, pp. 780–1.
(376) Reference 374, pp. 783–4.
(377) Reference 374, p. 784.
(378) WHITE, G. F., AND KNIGHT, K. H.: J. Am. Chem. Soc. **45**, 1780–7 (1923).
(379) WHITE, G. F., MORRISON, A. B., AND ANDERSON, E. G. E.: J. Am. Chem. Soc. **46**, 961–8 (1924).
(380) WILLIAMS, F. E., WITH GEBAUER-FUELNEGG, E.: J. Am. Chem. Soc. **53**, 352–6 (1931).
(381) WILLIAMS, R. R., AND CLINE, J. K.: J. Am. Chem. Soc. **58**, 1063–4 (1936).
(382) WISLICENUS, W.: Ber. **25**, 2084–7 (1892).
(383) WOLTHORN, H. J., AND FERNELIUS, W. C.: J. Am. Chem. Soc. **56**, 1551 (1934).
(384) WOOD, D., JR., AND BERGSTROM, F. W.: J. Am. Chem. Soc. **55**, 3314–9 (1933).
(385) Reference 384, p. 3317.
(386) WOOSTER, C. B.: J. Am. Chem. Soc. **50**, 1388–94 (1928).
(387) WOOSTER, C. B.: J. Am. Chem. Soc. **51**, 1856–60 (1929).
(388) WOOSTER, C. B.: Chem. Rev. **11**, 1–91 (1932).
(389) Reference 388, pp. 10–11.
(390) Reference 388, p. 12.
(391) WOOSTER, C. B., AND DEAN, J. G.: J. Am. Chem. Soc. **57**, 112–4 (1935).
(391a) WOOSTER, C. B., AND GODFREY, K. L.: J. Am. Chem. Soc. **59**, 596–7 (1937).
(392) WOOSTER, C. B., AND LATHAM, D. S.: J. Am. Chem. Soc. **58**, 76–8 (1936).
(393) WOOSTER, C. B., AND MITCHELL, N. W.: J. Am. Chem. Soc. **52**, 688–94 (1930).
(394) Reference 393, p. 691.
(395) WOOSTER, C. B., AND MITCHELL, N. W.: J. Am. Chem. Soc. **52**, 1042–8 (1930).
(396) WOOSTER, C. B., AND MORSE, R. A.: J. Am. Chem. Soc. **56**, 1735–7 (1934).
(397) WOOSTER, C. B., AND RYAN, J. F.: J. Am. Chem. Soc. **54**, 2419–24 (1932).
(398) WOOSTER, C. B., AND RYAN, J. F.: J. Am. Chem. Soc. **56**, 1133–6 (1934).
(399) Reference 398, p. 1133.
(400) Reference 398, p. 1134.
(401) WOOSTER, C. B., AND SMITH, F. B.: J. Am. Chem. Soc. **53**, 179–87 (1931).
(402) Reference 401, p. 181.
(403) YOUNG, R. C.: J. Am. Chem. Soc. **57**, 1195–6 (1935).
(404) ZEIGLER, K., COLONIUS, H., AND SCHÄFER, O.: Ann. **473**, 54–6 (1929).
(405) ZINTL, E., AND DULLENKOPF, W.: Z. physik. Chem. **B16**, 183–94 (1932).

(406) ZINTL, E., GOUBEAU, J., AND DULLENKOPF, W.: Z. physik. Chem. **A154**, 1–46 (1931).

(407) Reference 406, pp. 18–26.

(408) ZINTL, E., AND HARDER, A.: Z. physik. Chem. **A154**, 47–91 (1931); **B34**, 238–54 (1936).

(409) Reference 408, pp. 86–7.

(410) Reference 408, pp. 87–8.

(411) ZINTL, E., AND HARDER, A.: Ber. **66B**, 760–1 (1933).

(411a) ZINTL, E., AND HARDER, A.: Z. physik. Chem **B34**, 238–54 (1936).

(412) ZINTL, E., AND KAISER, H.: Z. anorg. allgem. Chem. **211**, 113–31 (1933).

(413) Reference 412, pp. 116–7.

(414) ZINTL, E., AND KOHN, O.: Ber. **61B**, 189–99, 2063 (1928).

(415) ZINTL, E., AND NEUMAYR, S.: Ber. **63B**, 237–43 (1930).