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HYDRIDES OF GROUPS IV AND V

William L. Jolly and Arlan D. Norman

August, 1967

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Submitted as part of the book Preparative Inorganic Reactions published by Interscience a subsidiary of John Wiley & Sons.

UCRL-17760
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Hydrides of Groups IV and V

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OUTLINE

I. Introduction

II. Synthetic Procedures

- A. Synthesis Using Lithium Aluminum Hydride
- B. Synthesis Using Hydroborates
- C. Reactions of Metal Salts of Hydrides with Halo Hydrides
- D. Solvolysis of "ide" Salts
- E. Electrolytic and Active Metal Reduction in Protonic Solvents
- F. Coupling Reactions
  1. Oxidative Coupling
  2. Reductive Coupling (Würtz-Fittig)
- G. Electric Discharge Synthesis
- H. Synthesis by Pyrolysis of Binary Hydrides
- I. Disproportionation Reactions
- J. Miscellaneous

III. Recommended Procedures

IV. Physical Properties

I. Introduction

In this chapter we discuss methods for preparing the hydrides of the elements of Groups IV and V, exclusive of carbon and nitrogen. We consider not only binary hydrides such as Si_3H_8, but also ternary hydrides such as Si_2PH_7. However we exclude from consideration all derivatives involving other elements, such as CH_3AsH_2, $(SiH_3)_3N$, and GeH_2Cl_2. The kinetic and thermodynamic stabilities of the hydrides decrease so markedly upon going from silicon to lead and from phosphorus to bismuth that the hydrides of lead and bismuth are only laboratory curiosities. Consequently this chapter is concerned principally with the hydrides of silicon, germanium, tin, phosphorus, arsenic and antimony.

Usually a given hydride can be prepared by several different methods, and there are many methods each of which is applicable to several different hydrides. Our aim is to describe the important methods which have been used, emphasizing, when possible, the generality of their application. Specific synthetic methods are recommended for particular hydrides, but, inasmuch as new methods are being developed constantly, it is obvious that some of these recommendations may soon be obsolete. Indeed, we make several suggestions for future synthetic research, particularly for higher hydrides and ternary hydrides.

Finally, we list those physical properties of the hydrides which are pertinent to their manipulation and identification in the laboratory.

II. Synthetic Procedures

A. Synthesis Using Lithium Aluminum Hydride

Lithium aluminum hydride (lithium tetrahydroaluminate) has been an important, versatile reducing agent for both inorganic and organic compounds ever since its first commercial availability around 1948. Its use in the conversion of the halides of elements of Groups IV and V into the corresponding hydrides was first reported by Schlesinger and his coworkers.[1,2,3] These reactions are generally carried out in an ether solvent, and may be represented by the following general equations.

$$LiAlH_4 + MX_4 \rightarrow LiX + AlX_3 + MH_4$$

$$3LiAlH_4 + 4MX_3 \rightarrow 3LiX + 3AlX_3 + 4MH_3$$

The driving force for these reactions is readily explicable in terms of electronegativities. It is a general rule that the most stable combination of a group of elements is that in which the most electronegative atoms are bonded to the most electropositive atoms.[4] It will be noted that this combination is achieved in the above reactions. (The electronegativities increase in the order: Li, Al, Si-Sn, H, halogens.) The electronegativity rule must be used with caution, however, for it is apparently violated by the alkyls of the elements of Groups IV and V, which are inert toward lithium aluminum hydride, and by the alkyls of the

elements of Groups I and II, which are converted to hydrides.[3] (The electronegativities of carbon and hydrogen are 2.5 and 2.1, respectively.[4]) Toward explaining the behavior of the alkyls, we can point out the facts that carbon is only slightly more electronegative than hydrogen (indeed in its inductive effect,[5] hydrogen is more electron-attracting than carbon) and that the hydrides of Groups I and II have high lattice energies.

Lithium aluminum hydride is only effective as a reducing agent when a Lewis base (such as an ether or an alkoxide) is present, either as a solvent or as one of the reactants.[6] Probably the Lewis base facilitates the dissociation of $LiAlH_4$ into the ions Li^+ and AlH_4^-, principally by solvating the lithium ion. It is believed that the AlH_4^- ion acts as a nucleophile and effects displacement reactions. In the reduction of organic compounds, it seems likely that a series of S_N2 reactions involving the nucleophiles of general formula $(AlH_nX_{4-n})^-$ are involved.[7] Similar reactions may be involved with inorganic halides such as $GeCl_4$, but 4-center reactions may also be possible in such cases.

Silane may be obtained in essentially quantitative yields by the reaction of silicon tetrachloride with a slight excess of lithium aluminum hydride in diethyl ether[1,8] or tetraethylene glycol dimethyl ether.[9] The preparation of

disilane in 87% yield by the reaction of Si_2Cl_6 with lithium aluminum hydride has been reported,[1] but Ward and MacDiarmid warn that considerable cleavage of the Si-Si bond occurs, with consequent formation of SiH_4, if particular care is not taken to use appropriate concentrations of reagents, etc.[10] Presumably the method could be extended to Si_3Cl_8 and higher perchlorosilanes for the preparation of trisilane and higher silanes.

Silicon-oxygen bonds are converted to Si-H bonds by treatment with lithium or sodium aluminum hydride. Thus disiloxane[11] ($(H_3Si)_2O$), hexachlorodisiloxane[11,12] ($(Cl_3Si)_2O$) hexaalkoxydisiloxane[12] ($(RO)_3Si)_2O$), and tetraalkoxysilanes[12,13] ($Si(OR)_4$) are reduced to silane. Silane has been obtained in 93% yield by the reduction of triethoxysilane $[(EtO)_3SiH]$ with sodium and potassium aluminum hydride.[13] Even quartz sand[12] and silica gel[14] yield silane when heated with lithium aluminum hydride. Thus yields averaging 10% (based on $LiAlH_4$) have been obtained[14] by heating silica gel and $LiAlH_4$, in a 4:1 mole ratio, to 200°. It has been reported that dialkylaminosilazanes can be reduced to SiH_4 in 90% yield with lithium aluminum hydride.[15]

The reaction of germanium tetrachloride with lithium aluminum hydride in ethers has been reported to yield germane in yields ranging from 10 to 40%.[1,16,17] Sujishi and Keith[16] and Macklen[17] studied the effects of changing various conditions on the yield of germane. Both sets of investigators agreed

that the principal side-reaction causing the low yield of germane was the reduction of the tetrachloride to $GeCl_2$, with possible subsequent conversion of the $GeCl_2$ to polymeric GeH_2. Sujishi and Keith found that lithium tri-t-butoxy-hydroaluminate, $LiAlH(OC_4H_9)_3$, is a much more effective reagent than lithium aluminum hydride for the preparation of germane. This reagent may be prepared by the reaction of $LiAlH_4$ with t-butyl alcohol.

$$LiAlH_4 + 3\ HOC_4H_9 \rightarrow 3H_2 + LiAlH(OC_4H_9)_3$$

By using a ratio of $LiAlH(OC_4H_9)_3$ to $GeCl_4$ of about 4.2:1 and a reaction time of 30 hours, yields of 80% were obtained.

$$GeCl_4 + 4LiAlH(OC_4H_9)_3 \rightarrow GeH_4 + 4LiCl + 4Al(OC_4H_9)_3$$

Although it is known that lithium tri-t-butoxyhydroaluminate is a much milder reducing agent than lithium aluminum hydride, it is not understood why the yield of germane is affected so markedly on going from the one reducing agent to the other.

Stannane was obtained in 20% yield (based on $SnCl_4$) by Finholt et al.[1] by using a 4:1 ratio of lithium aluminum hydride to stannic chloride with diethyl ether. It was not stated whether the yield suffered by using a lower ratio of $LiAlH_4$ to $SnCl_4$. Using the same ratio of reagents, Emeléus and Kettle[18] increased the yield to 80-90% by passing a stream of nitrogen containing 0.1% of oxygen through the reaction

vessel during the reaction. The oxygen inhibited the decomposition of stannane to tin metal and hydrogen. The principal by-product of the synthetic reaction is finely divided tin. Wiberg and Bauer[19] observed a white precipitate in the reaction of $LiAlH_4$ and $SnCl_4$ at -60° in ether. This precipitate, for which they proposed the formulation $Sn(AlH_4)_4$, decomposed above -40° to give SnH_4 and AlH_3, together with tin metal and hydrogen.

In an attempt to prepare plumbane by the reduction of lead tetrachloride with lithium aluminum hydride, Emeléus and Kettle obtained only a powder of metallic lead.[18]

In the reaction of PCl_3 with lithium aluminum hydride in ether solution, part of the PCl_3 is converted to phosphine, and the remainder to a polymeric, yellow hydride of composition $(PH)_x$. Paddock[6] and Müller-Schiedmayer[20] observed that the relative amounts of these products is strongly influenced by temperature; the higher the temperature, the lower the yield of PH_3. In three experiments with a PCl_3:$LiAlH_4$ mole ratio of 4:3, at the temperatures -115°, -30°, and 20°, the percentage yields of phosphine were 79%, 27% and 22%, respectively.

Wiberg and Mödritzer[21] obtained arsine and stibine in yields of 83% and 82%, respectively, from the reactions of arsenic trichloride and antimony trichloride with $LiAlH_4$ at -90°. These yields are based on the following equations.

$$3LiAlH_4 + AsCl_3 \rightarrow AsH_3 + 3AlH_3 + 3LiCl$$

$$3LiAlH_4 + SbCl_3 \rightarrow SbH_3 + 3AlH_3 + 3LiCl$$

By using a special vacuum apparatus in which even the connecting tubing and stopcocks were cooled to -50°, Amberger[22] was able to obtain only traces (less than 1% yields) of bismuthine from the reaction of bismuth trihalides with $LiAlH_4$ at temperatures around -100°.

Wiberg and Mödritzer[23,24] attempted to prepare the pentahydrides PH_5 and SbH_5 by reaction of the corresponding chlorides in diethyl ether with $LiAlH_4$ at -100° and -120°, respectively. However, neither of the sought compounds was obtained - only equimolar amounts of hydrogen and the trihydrides.

It should be recognized that the hydrides of Groups IV and V are protonic acids and that they are reactive toward hydridic species such as the AlH_4^- ion. For example, in diglyme and tetrahydrofuran, phosphine reacts with lithium aluminum hydride to form a soluble product of composition $LiAl(PH_2)_4$.[25]

$$LiAlH_4 + 4PH_3 \rightarrow LiAl(PH_2)_4 + 4H_2$$

(Arsine reacts similarly.)

In diethyl ether almost three moles of hydrogen are evolved per mole of consumed phosphine, and an insoluble product forms. It is clear that in hydride syntheses involving

lithium aluminum hydride, provision should be made to remove the hydrides from the reaction mixture as rapidly as possible in order to avoid reactions of this type.

Two general procedures have been used in the preparation of hydrides using lithium aluminum hydride in a solvent. In one procedure, an ether solution of lithium aluminum hydride is placed in a reaction vessel attached to a vacuum line, and the halide or alkoxy compound is then condensed into the vessel after cooling the latter with liquid nitrogen. The mixture is allowed to warm slowly to a suitable temperature at which reaction takes place. The volatile hydride is collected in liquid nitrogen traps. This type of procedure was used by Finholt et al.[1] for the preparation of silane, germane and stannane, and by Emeléus and Kettle[18] for the preparation of stannane.

In the second general procedure, an ether solution of lithium aluminum hydride is stirred in a reaction flask equipped with a dropping funnel containing an ether solution of the halide and a gas outlet leading to a series of cold traps on a vacuum line. In some cases the positions of the reagents are switched. As the solution in the dropping funnel is slowly added to the stirred solution in the flask, the evolved hydride is collected in liquid nitrogen traps. This type of procedure was used by Finholt et al.[1] for the preparation of disilane, and by Peake et al.[8] for the preparation of silane.

The first general procedure, in which the reagents are warmed up from liquid nitrogen temperature to the reaction temperature, is simple and satsifactory for syntheses involving less than about 10 mmoles (0.38 g.) of lithium aluminum hydride. However, when larger amounts of $LiAlH_4$ are involved, the procedure is potentially dangerous because of the possibility of local overheating during the warm-up, and an uncontrollable fast evolution of gas. With the second procedure, the rate of reaction is readily controlled by the rate of addition of reagent from the dropping funnel, and the danger of a runaway reaction is considerably diminished.

Diethyl ether is the usual solvent employed in lithium aluminum hydride reductions because it is readily available in a high state of purity (i.e., essentially free of water and peroxides). However high molecular weight ethers (such as di-n-propyl ether, di-n-butyl ether, and diglyme) are occasionally used because of their relatively low vapor pressures. Such ethers are used when the hydride being prepared has a volatility comparable to that of diethyl ether and when the separation of the hydride from diethyl ether would consequently be very difficult.

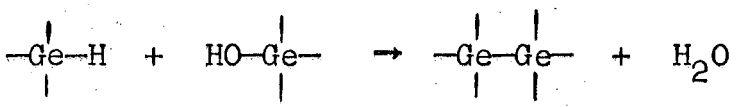
B. Synthesis Using Hydroborates

The alkali metal hydroborates (strictly, tetrahydroborates, and colloquially, borohydrides) are powerful reducing agents which have certain advantages over lithium aluminum hydride. The hydroborates are somewhat easier to handle than $LiAlH_4$ because of their relative inertness toward moist air. ($LiAlH_4$ must be carefully protected from moist air during storage, whereas KBH_4 is stable indefinitely at ordinary temperatures in moist air.) Whereas only thoroughly dry non-protonic solvents may be used with $LiAlH_4$, the hydroborates can be used in both protonic solvents such as water and non-protonic solvents such as 1,2-dimethoxyethane. Hydroborates are rapidly hydrolyzed in acidic aqueous solutions, but are very slowly hydrolyzed in alkaline aqueous solutions.

Schaeffer and Emilius[26] were the first to employ an aqueous hydroborate solution for the preparation of a hydride. They added an aqueous $NaBH_4$ solution to an aqueous solution of hydrochloric acid and stannous chloride. It was observed that the yield of stannane (based on the stannous chloride) increased with decreasing concentration of stannous chloride. They obtained their best yield (84%) when a 57-fold excess of aqueous $NaBH_4$ was added to a solution 0.0092 M in $SnCl_2$ and 0.6 M in HCl. Using analogous procedures, other hydrides of Groups IV and V have been prepared. Germane has been

obtained in yields of 75%,[27] 79%,[28] and 100%;[29] stibine has been prepared in yields of 35%[30] and 95%,[31] bismuthine has been prepared in "small but significant yields,"[26] and both diarsine (As_2H_4) and distibine (Sb_2H_4) have been prepared in unreported yields.[32]

The percentage yields quoted above are based on the element converted to the hydride. However, in all the syntheses except that of germane, by far the most expensive reagent was the alkali metal hydroborate. Therefore the percentage yield with respect to hydroborate is more significant, and in most of the above cases, this yield was very low. Improvement of the yield with respect to hydroborate can be effected by adding a concentrated alkaline solution of both hydroborate and an oxy-anion of the element whose hydride is desired to an excess of acid.[33,34] Thus stannane, arsine, and stibine can be obtained in yields (based on hydroborate) of 2.7%, 59% and 51%, respectively.[34] Small yields of digermane[34] (Ge_2H_6), trigermane[34] (Ge_3H_8), and distannane[35] (Sn_2H_6), have been prepared by this same general method. It appears that the yield of these higher hydrides increases with increasing concentration of the oxy-anion (germanate and stannite) in the alkaline solution. This suggests that the higher hydrides are formed by some sort of condensation reaction, perhaps of the following type.



It is noteworthy that aqueous silicic acid, phosphoric acid, and hypophosphorous acid are inert toward the hydroborate ion.[33] This inertness is surely a kinetic effect, inasmuch as the hydroborate ion has more than enough reducing power to reduce these acids to the corresponding hydrides, silane and phosphine. Probably in these oxyacids the central atoms (Si and P) are so crowded that it is difficult for an attacking BH_4^- ion to get close enough to cause a displacement of an hydroxide ion by a hydride ion. In accord with this theory, sulfate and nitrate are inert toward hydroborate, whereas sulfurous acid and nitrous acid are reduced to H_2S and NH_4^+, respectively.

It is assumed that in aqueous solutions all four hydrogen atoms of the hydroborate ion are available for hydride formation. Even though the best reported yield (based on hydroborate) is only 59%, there is no obvious reason why this yield could not be pushed closer to 100%. However, in an ether solvent, it appears that only one of the hydrogen atoms of the hydroborate ion is available for hydride formation. The other three hydrogens remain with the boron in the form of diborane or borane etherate. Thus ether solutions of $LiBH_4$ react with $AsCl_3$ at -80° and with $SbCl_3$ at -70° as follows.[21]

$$AsCl_3 + 3LiBH_4 \rightarrow AsH_3 + 3/2\ B_2H_6 + 3LiCl$$

$$SbCl_3 + 3LiBH_3 \rightarrow SbH_3 + 3/2\ B_2H_6 + 3LiCl$$

Based on these reactions, arsine is formed in 93% yield, and stibine in 89% yield. When these same reactions are carried out in ether at room temperature, the $AsCl_3$ and $SbCl_3$ are reduced principally to the corresponding elements.

C. Reactions of Metal Salts of Hydrides with Halo Hydrides

One of the most useful methods for forming bonds between two elements, allowing the synthesis of complex molecules, involves the use of condensation-type reactions which take place between strongly basic, nucleophilic reagents and halo-compounds. Several reactions of this type between alkali metal derivatives of Group IV or V hydrides and germyl- or silyl halides have been used effectively to prepare ternary or "higher" hydrides of Group IV and V elements. The reactions can be represented by the following general equation,

$$M:^- + M' - X \rightarrow M - M' + X:^-$$

in which $M:^-$ represents the anion of an alkali metal hydride salt such as PH_2^-, $M' - X$ represents a halo-hydride, and $M-M'$ represent a ternary or "higher" hydride product. It seems likely that these reactions are of the S_N2 type, in which the $M-M'$ bond is formed as a result of direct nucleophilic attack by $M:^-$ on the halo-hydride; although the mechanisms have not been experimentally verified. In some cases the $M'-X$ bond which must be broken in the reaction is stronger than the $M-M'$ bond which is subsequently formed, e.g. E_{Si-Cl} = 91 Kcal/mole[36] and E_{Si-Si} = 46.4 Kcal/mole.[37] However, because of the high lattice energies of the alkali

metal halides which are also formed in the reactions, condensation reactions of this type are generally thermodynamically favorable.

Trisilyl derivatives of phosphorus, arsenic, and antimony may be synthesized using the above method. Potassium dihydrogen phosphide (KPH_2) and potassium dihydrogen arsenide ($KAsH_2$) react with silyl halides at low temperature to form trisilylphosphine[38,39,40] and trisilylarsine,[39,41] respectively, as shown below:

$$3KPH_2 + 3SiH_3X \xrightarrow[22\ hr.]{-120\ to\ -40^\circ} 3KX + 2PH_3 + (SiH_3)_3P$$

(where X = Cl, Br)

$$3KAsH_2 + 3SiH_3Br \xrightarrow[2\ hr.]{-122\ to\ -30^\circ} 3KBr + 2PH_3 + (SiH_3)_3As$$

Yields of $(SiH_3)_3P$ and $(SiH_3)_3As$ (based on SiH_3X) as high as 55% and 49%, respectively, have been reported. However, regardless of the reactant proportions, no evidence has been obtained for the formation of mono- or bis- silyl derivatives in these reactions.

Potassium dihydrogen antimonide ($KSbH_2$) and SiH_3Br have been reported not to react, even under carefully controlled conditions, to product $(SiH_3)_3Sb$.[39] However, K_3Sb reacts with SiH_3Br at low temperatures to form $(SiH_3)_3Sb$ in a 76% yield.[39,42]

$$K_3Sb + 3SiH_3Br \rightarrow 3KBr + (SiH_3)_3Sb$$

Also, evidence has been presented for the formation of small quantities of $(SiH_3)_3As$ from ambient-temperature reactions of K_3As and SiH_3I.[43] Unfortunately, the low yield reported for this reaction (ca. 0.8% based on SiH_3I) would seem to preclude its usefulness in most synthetic work.

Recently, the successful application of the reaction of metal salts of hydrides (e.g. $KSiH_3$) with halo hydrides (e.g. GeH_3Cl) to the synthesis of Group IV hydrides has been reported. Germylsilane, GeH_3SiH_3, can be prepared in the ~~room-temp the~~ room-temperature reaction between potassium silyl and germyl chloride in yields as high as 20%.[44]

$$KSiH_3 + GeH_3Cl \rightarrow KCl + GeH_3SiH_3$$

Although this reaction gives considerably less than quantitative yields of GeH_3SiH_3, the ease of product separation and the simplicity of the reaction apparatus make this method superior to others (e.g. ozonizer discharge preparation, photochemical synthesis, or "ide" salt solvolysis) for the preparation of GeH_3SiH_3. Similarly, under carefully controlled conditions, disilane and trisilane are formed in reactions between $KSiH_3$ and SiH_3Br and Si_2H_5Br in 1,2-dimethoxyethane,[45] respectively.

$$KSiH_3 + SiH_3Br \rightarrow KBr + Si_2H_6$$

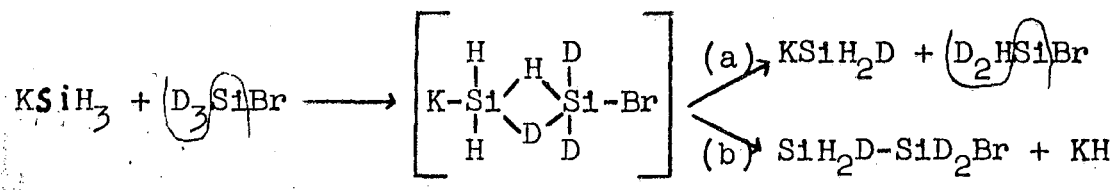
$$KSiH_3 + Si_2H_5Br \rightarrow KBr + Si_3H_8$$

Silane and small quantities of Si_3H_8 are formed with the disilane, and SiH_4 and Si_2H_6 are formed with the trisilane, suggesting that disproportionation processes may occur during the reactions. It is also reported that the products form rapidly in the reactions, but are destroyed upon prolonged exposure to the reaction medium. If they are immediately removed from the reaction mixture as the mixture warms from -196° to room temperature, yields of Si_2H_6 and Si_3H_6, up to 35% and 18%, respectively, can be achieved.

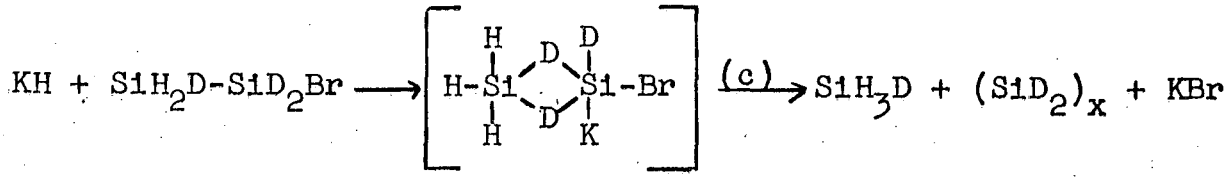
Some recent work with organogermanes[46] serves as a warning of the types of side-reactions that can complicate otherwise straightforward attempts to build up chains of germanium atoms. When trimethylchlorogermane is added to a solution of potassium triethylgermyl, a 55% yield of hexaethyldigermane is obtained. Reversing the order of addition gives an 83% yield. It was suggested that this unusual product is a consequence of a nucleophilic attack of $KGeEt_3$ on a Ge-Ge bond.

In principle, reactions of metal salts of hydrides and halo derivatives should also be applicable to the synthesis of various types of deuterium-labeled hydrides. Using the proper combinations of starting materials, per-deuterio ternary hydrides, e.g. $(SiD_3)_3P$, and specifically-labeled hydrides, e.g. SiH_3SiD_3 and SiH_3GeD_3, might be ex-

pected. An example of the former type has recently been reported. Cleanly-labeled trisilylphosphine-d_9, $(SiD_3)_3P$, can be obtained from the reaction of KPH_2 and SiD_3Cl, ~~analogous to that in eq. 21~~, with no apparent exchange of H for D atoms of the silyl groups.[47] Unfortunately, attempts to prepare specifically-labeled Group IV hydrides have so far been unsuccessful. When $KSiH_3$ and SiD_3Br were allowed to react, with the expectation of obtaining SiH_3SiD_3, a mixture of products consisting of deuteriosilanes, deuteriodisilanes, and partially protonated deuteriobromosilanes was obtained.[48] In their original report on this work,[48] Ring and Ritter suggested that the products might be accounted for by a series of reactions involving bridge-bonded transition states (I and II):



I.



II.

Processes a, b, and c would give rise to the observed products. However, it appears that alkali metal salt cleavage reactions of disilane,[45,49]

$$x\ SiH_3SiD_3 \xrightarrow{MX} x\ SiH_3D + (1/x)\ (SiD_2)_x, \text{etc.}$$

(where MX = alkali metal salt, e.g. LiCl)

and equilibrium reactions of the type,

$$SiH_3^- + SiH_3SiD_3 \rightleftharpoons SiH_3D + SiH_3SiD_2^-$$

may also be important processes in the reaction scheme. Therefore, until further studies of these systems have been carried out, it is pointless to speculate on the general applicability of these methods to the synthesis of labeled hydrides.

A general procedure for the preparation of ternary or "higher" hydrides from reactions of metal salts of hydrides and halo-hydrides can be outlined. The metal-hydride salt is prepared *in vacuo* by reaction of the appropriate Group IV or V hydride with a strong base. For example, $KGeH_3$, KPH_2, $KAsH_2$ or $KSbH_2$ can be conveniently prepared by reaction of GeH_4,[50] PH_3,[51,52] AsH_3,[53] or SbH_3,[39] respectively, with potassium metal in liquid ammonia, *e.g.*

$$K + GeH_4 \xrightarrow{\text{liq. } NH_3} KGeH_3 + 1/2\ H_2$$

$$K + PH_3 \xrightarrow{\text{liq. } NH_3} KPH_2 + 1/2\ H_2$$

The sodium or potassium salts of silane and germane are readily prepared by the reaction of silane and germane with sodium or potassium in 1,2-dimethoxyethane[48] or hexamethylphosphoramide.[54] Potassium germyl may be prepared in a non-hydroxylic solvent such as 1,2-dimethoxyethane or dimethyl sulfoxide by the reaction of germane with excess potassium hydroxide.[55] Generally, the appropriate halohydride is condensed (together with an aprotic solvent, if not already present) into the reaction vessel containing the hydride salt, and reaction is allowed to proceed. In the syntheses of $(SiH_3)_3P$, $(SiH_3)_3As$, and $(SiH_3)_3Sb$ it is necessary to maintain the reactants at low temperatures (-120 to -90°) for several hours in order to achieve maximum product yields. However, in the Si_2H_6, SiH_3GeH_3, and Si_3H_8 syntheses a short reaction period followed by immediate removal of the products from the reaction mixture is preferred. Upon completion of the reaction the products are separated by fractional condensation and identified by customary methods.

D. Solvolysis of "ide" Salts

The classical method for the preparation of the hydrides of an element of Group IV or V is the acid hydrolysis of a compound of the element and an electropositive metal such as magnesium or calcium. Thus Besson[56] and Stock and Somieski[57,58] prepared silicon hydrides by adding "magnesium silicide" (obtained by heating magnesium with silica) to hydrochloric acid. The so-called magnesium silicide was not a homogeneous silicide of magnesium--it probably contained magnesium oxide, lower oxides of silicon and silicates. The products of the hydrolysis included both non-volatile hydridic substances such as $(Si_2H_2O_3)_x$ and volatile hydrides. By fractional condensation on the vacuum line, Stock and Somieski separated the volatile materials into SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, and a mixture of Si_5H_{12} and Si_6H_{14}.[59] About 25% of the silicon in the "silicide" was converted to hydrides, of which 40% was SiH_4, 30% was Si_2H_6, 15% was Si_3H_8, 10% was Si_4H_{10}, and 5% were higher hydrides. More recently, gas chromatography has been used to separate the silanes formed by the acid hydrolysis of magnesium silicide. Twenty-six chromatographic peaks have been observed, corresponding to the silanes up through Si_8H_{18}, including the various structural isomers. In general the larger peaks corresponded to the supposed straight-chain silanes. Enough of the pentasilane isomers could be isolated such that they

could be identified by their proton magnetic resonance spectra.[60]

The method of preparation of the magnesium silicide has been found to markedly affect both the over-all yield and relative amounts of the silanes formed in the hydrolysis.[61,62] When the silicide is prepared by heating a mixture of powdered magnesium and silicon (containing 10% excess magnesium over the composition Mg_2Si) in a hydrogen atmosphere for 24 hours, the best yields (based on silicon conversion) are obtained when the heating is carried out around 650°. The higher the temperature used in the silicide preparation, the greater the fraction of higher silanes in the volatile product. This latter effect has been attributed to the formation of Mg_2Si (which yields SiH_4) at the lower temperatures and other silicides such as MgSi or Mg_3Si_2 (which yield higher silanes) at the higher temperatures.

When a solution of ammonium bromide in liquid ammonia is used in the hydrolysis instead of aqueous acid, the percentage conversion of silicon to silanes rises to 70-80%, but only silane and disilane are formed.[62,63] Depending on the temperature at which the magnesium silicide is prepared, the Si_2H_6/SiH_4 ratio varies from about zero to 0.12. Silane also has been prepared by the reaction of magnesium silicide with ammonium chloride in ammonia in a pressure

vessel at room temperature,[64] but this procedure seems to offer no advantages.

Dennis, Corey and Moore[65] added hydrochloric acid to magnesium germanide (prepared by heating magnesium with germanium), and obtained germane, digermane, and trigermane. About 23% of the germanium in the magnesium germanide was converted to the hydrides, and of this 74% appeared as GeH_4, 22% as Ge_2H_6 and 1% as Ge_3H_8. By using a solution of ammonium bromide in liquid ammonia instead of aqueous acid, Kraus and Carney[66] obtained 70% conversion to germanes, in which GeH_4 predominated. Fehér and Cremer[67] went to the extent of using a solution of hydrazine hydrochloride in anhydrous hydrazine, and thereby obtained 70-80% conversion to germanes (principally GeH_4). By subjecting the products of the aqueous hydrolysis to careful fractionation on the vacuum line and gas chromatography, germanes as high as Ge_5H_{12} have been identified.[60,68] By the use of heavy water and magnesium germanide, GeD_4, Ge_2D_6, and Ge_3D_8 have been prepared.[69]

Plumbane has been prepared by the dropwise addition of 0.8 M HCl to a metallic mixture corresponding to the composition Mg_2Pb.[70] The yield was very low, and the PbH_4 was identified only by its mass spectrum.

By the reaction of aqueous acid or water with phosphides such as aluminum phosphide[71] and calcium phosphide,[72] phosphine can be prepared in fairly good yields. Diphosphine

is a by-product of these hydrolyses, and Evers and Street recommend the use of calcium phosphide for preparing the latter hydride. They obtained 10 g. of P_2H_4 from 200 g. of commercial Ca_3P_2.

By treating zinc arsenide with aqueous sulfuric acid, arsine is readily prepared.[73] Nast[74] used an Mg-Al-As alloy, and obtained, in addition to AsH_3, very small yields of As_2H_4. By dissolving arsenic in a solution of sodium in liquid ammonia, it is possible to prepare a solution of Na_3As--or possibly ammonolysis products such as $NaNH_2$ + Na_2AsH. When such a solution is treated with ammonium bromide, 60-90% yields of arsine, based on sodium, are obtained.[53]

Stibine may be prepared by adding a pulverized alloy of magnesium and antimony (containing at least 60% Mg) to dilute hydrochloric acid.[73,78] About 10 g. of stibine can be obtained from 250 g. of alloy.

Bismuthine has been prepared by adding dilute hydrochloric acid to a mixture of magnesium and bismuth corresponding to Mg_3Bi_2. The yield was very low, and identification was made mass-spectrometrically.[70] Decomposition was so rapid that only 10-15 min. of observation time in the spectrometer was available.

It has been reported that calcium monosilicide (CaSi), when treated with alcoholic HCl, gives an amorphous light brown solid of composition $(SiH_2)_x$ which is spontaneously

inflammable,[76] and that treatment of calcium monogermanide (CaGe) with acid yields the amorphous yellow compound $(GeH_2)_x$.[77] However, more recent studies[78] of the solvolysis of CaGe, Ca_2Ge, CaSi and Ca_2Si indicate that these polymeric hydrides should be formulated as $GeH_{0.9-1.2}$ and $SiH_{0.7-0.9}$.

Ternary hydrides can be prepared by the acid hydrolysis of ternary alloys or intimate mixtures of two binary compounds. Thus Timms et al.[79] added Mg-Ge-Si alloys to 10% hydrofluoric acid and obtained a mixture of silanes, germanes, and silicon-germanium hydrides. These were separated by gas chromatography.[79,80] Silicon-rich hydrides were prepared from an alloy of nominal composition $Mg_{20}Si_9Ge$. The following yields (based on germanium conversion) of ternary hydrides were typical: Si_2GeH_8 (3%); n-Si_3GeH_{10} (1.5%); n-Si_4GeH_{12} (0.3%); n-Si_5GeH_{14} (0.07%). Hydrides relatively rich in germanium were best made from an alloy of composition Mg_4SiGe. The following yields (based on germanium conversion) of ternary hydrides were typical: $SiGeH_6$ (0.6%); $SiGe_2H_8$ (0.4%); n-$SiGe_3H_{10}$ (0.03%); n-$Si_2Ge_2H_{10}$ (0.5%); n-$Si_3Ge_2H_{12}$ (0.02%). The ratios of the straight-chain isomers to the branched isomers were: Si_3GeH_{10}, 7.5:1; $Si_2Ge_2H_{10}$, 3.5:1; $SiGe_3H_{10}$, 1.0:1; Si_4GeH_{12}, 1.5:1; Si_5GeH_{14}, 1.0:1. Royen and Rocktäschel have reported a similar, less extensive, study of hydrides formed by the hydrolysis of Ca-Si-Ge alloys.[81]

Royen *et al.*[82,83] have reported the mass-spectrometric identification of a variety of binary and ternary hydrides prepared by the acid hydrolysis of ternary alloys and compressed mixtures of binary compounds. Among the species identified were P_3H_5, As_3H_5, and AsH_2PH_2 (from Mg_3P_2/Mg_3As_2), P_3H_5 and GeH_3PH_2 (from $CaGe/Ca_3P_2$), As_3H_5 and GeH_3AsH_2 (from $CaGe/Ca_3As_2$).

E. Electrolytic and Active Metal Reduction in Protonic Solvents

It has long been recognized that the dissolution of an active metal in acid is fundamentally an electrolytic process.[84] The metal acts as a set of short-circuited galvanic cells, in which the bulk metal is the common anode (with a high overvoltage for hydrogen evolution) and impurity sites are the cathodes (with relatively low hydrogen overvoltages). In the process of dissolution, metal ions leave the bulk metal surface while hydrogen gas is evolved from the impurity sites. If other reducible species are in the solution in addition to hydrogen ions, they can also undergo reduction in the cathodic regions. Thus acidic solutions of salts or oxyacids of germanium, tin, lead, arsenic, antimony and bismuth react with metals such as zinc to form the volatile hydrides, just as these hydrides are formed by cathodic reduction of similar solutions. Because of the fundamental similarity of the two processes, they are discussed together in this section.

The electrolytic and active metal reduction processes are very seldom used as synthetic methods for volatile hydrides - the processes are generally considered too cumbersome, or the yields are too low. Certain of the electrolytic processes may be of commercial significance, however, and it is possible that electrolytic methods may be useful

in the laboratory when it is desired to generate a hydride at a steady, slow rate over a long period of time.

Voegelen[85] first obtained germane, by the reduction of germanium(IV) in aqueous sulfuric acid with sodium amalgam and zinc metal, but the amount of germanium available was so small that only a minute amount of the hydride was prepared, and imperfectly characterized. Later Paneth and Schmidt-Hebbel[86] prepared somewhat larger amounts of germane by similar reductions using zinc and magnesium. Green and Robinson[87] studied the electrolysis of alkaline solutions of sodium germanate using a mercury cathode. Under the conditions of electrolysis, the cathode became a sodium amalgam, and then three cathodic processes occurred simultaneously: hydrogen evolution, germane evolution and germanium deposition. Germane current efficiences as high as 40% were obtained.

The reaction of magnesium powder with solutions of tin in sulfuric acid[88] and the electrolysis of tin solutions using lead electrodes[89,90] were among the first methods used for the preparation of stannane. Only a few milligrams of stannane was formed in each experiment. Plumbane has been obtained by the "spark-electrolysis" of a sulfuric acid solution using lead electrodes.[91] The yields of plumbane were so small, however, that it was necessary to detect its formation by using radioactive lead in the synthesis and by detecting the volatile plumbane by its radio-

activity.

When arsenic(III) is in very low concentrations in aqueous solutions, it can be quantitatively reduced to arsine either electrolytically or by active metals dissolving in acid. The reduction of arsenious acid to arsine by zinc is the basis of the Marsh test for traces of arsenic.[92] A fairly good preparative procedure for arsine involves the addition of a solution of arsenious oxide in aqueous hydrochloric acid to an excess of magnesium turnings.[75] About 8 g. of arsine is formed per 20 g. of arsenious oxide. Quantitative studies have been made of the reduction of As(III) solutions with mercury cathodes,[93,94] arsenic cathodes,[95], zinc amalgams,[96,97] and sodium amalgams.[98] As the concentration of arsenic(III) is increased, the fraction of the arsenic which is reduced to arsine decreases. At higher arsenic(III) concentrations, good yields of a brownish-black solid hydride of composition AsH_x (where x varies from 0.001 to 0.26) can be obtained.[99]

Like arsine, stibine may be prepared by the reduction of aqueous Sb(III) by zinc[92] and sodium amalgam,[100] and many studies have been made of the electrolytic generation of stibine.[101,102,103,104,105]

F. Coupling Reactions

1. Oxidative Coupling. Teal and Kraus[106] studied the electrolysis of solutions of sodium germyl ($NaGeH_3$) in liquid ammonia, using a platinum anode and a mercury cathode. They expected to obtain digermane, according to the reaction

$$2\ GeH_3^- = Ge_2H_6 + 2e^-.$$

However, they observed that germane and nitrogen were evolved in a 6:1 ratio, in accord with the following anode process.

$$6\ GeH_3^- + 2\ NH_3 = 6\ GeH_4 + N_2 + 6e^-$$

Actually this latter process, and the 6:1 stoichiometry, are the results of the coupling of the following two processes:

$$8\ NH_3 = N_2 + 6\ NH_4^+ + 6e$$

$$6\ NH_4^+ + 6\ GeH_3^- = 6\ GeH_4 + 6\ NH_3$$

The anodic process involves the formation of six moles of ammonium ion per mole of nitrogen, and these six moles of ammonium ion cause the simultaneous release of six moles of germane. A similar phenomenon occurs in the electrolysis of a liquid ammonia solution of $NaPH_2$.[107] Here the anode reaction is

$$6\ PH_2^- + 2\ NH_3 = N_2 + 6\ PH_3 + 6e^-$$

From the above results, it appears that anodic coupling of hydride anions cannot readily be accomplished in a protonic solvent such as ammonia. Perhaps the desired coupling reaction could be accomplished in an aprotic solvent in which the anodic oxidation of the solvent might have a much higher overvoltage than the anodic coupling reaction. However, a recent attempt to anodically oxidize potassium germyl dissolved in dimethyl sulfoxide yielded principally germane and a polymeric germanium hydride, GeH_x.[108] It appears that digermane undergoes a base-catalyzed disproportionation analogous to that of disilane.[49]

It may be that the coupling of hydride anions can be accomplished better by use of a dissolved oxidizing agent, rather than electrolytically.

$$Ox + 2\ GeH_3^- \rightarrow Red + Ge_2H_6$$

A variety of organometallic anions have been coupled in this way. For example, lithium triphenylgermyl[109] and lithium triphenylstannyl[110] react with ethyl carbonate to form hexaphenyldigermane and hexaphenyldistannane, respectively.

$$2\ Li\overset{\frown}{M}Ph_3 + (EtO)_2CO \rightarrow M_2\overset{\frown}{Ph}_6 + 2\ LiOEt + CO$$

Similar oxidative coupling of the triphenylstannyl ion may

be accomplished with carbon dioxide or benzophenone.[111]

$$2\ LiSnPh_3 + 2CO_2 \rightarrow Sn_2Ph_6 + Li_2C_2O_4$$

$$2\ LiSnPh_3 + Ph_2CO \rightarrow Sn_2Ph_6 + 2\ Ph_2CO^-Li^+$$

Other organic and organometallic couplings have employed the following oxidizing agents: iron(III) chloride, hexacyanoferrate(III), permanganate, metal carbonyls, silver salts, and lead(IV) acetate. The analogous reactions with hydride anions such as GeH_3^- and PH_2^- clearly constitute an area for future research.

2. Würtz-Fittig Coupling Reaction. A large variety of organopolysilanes and organopolygermanes can be prepared from the coupling of organosilicon or organogermanium halides by active metals, an extension of the familiar Würtz-Fittig reaction in organic chemistry.[112] Using this technique, disilane can be prepared in up to 67% yield from the room-temperature reaction of silyl iodide with sodium amalgam.[113]

$$2SiH_3I + 2Na \longrightarrow Si_2H_6 + 2NaI$$

Small quantities of SiH_4 and H_2 are also produced as a result of secondary reactions.

Coupling reactions have not been used to prepare unsubstituted Group IV hydrides other than disilane. Also, the method has been unsuccessful when other monohalosilanes or metals are substituted for silyl iodide or sodium in the reaction. Thus the reactions of silyl chloride with sodium[114] and silyl bromide with magnesium[115] are reported to yield only silane, hydrogen and polymeric ($(SiH_x)_m$) silicon-containing residues.

The difficulties encountered in obtaining compounds containing silicon-silicon bonds may in part be a result of the apparent instability of the silicon-silicon bond to alkali metals or alkali metal salts. Ring and Ritter reported that potassium reacts with disilane to form a variety of products which include substantial quantities

of SiH_4 and H_2.[48] More recently, it has also been shown that disilane is converted to SiH_4 and polymeric silicon-containing hydrides in the presence of catalytic amounts of lithium chloride, fluoride, or iodide,[45,49] ie.,

$$XSi_2H_6 \xrightarrow{LiCl} XSiH_4 + (1/X)\ (-SiH_2)_x$$

Thus a combination of complex reactions of the above types may account for the products of the unsuccessful coupling reactions.

G. Ozonizer-Type Silent Electric Discharge Syntheses

Ozonizer-type silent electric discharge reactions provide the most general technique available for the preparation of "higher" ~~or~~ and ternary Group IV and V hydrides. Using this method it is possible to prepare compounds which are thermodynamically unstable or difficult to prepare by more conventional chemical reactions. The discharge reactions are carried out by subjecting a hydride or a mixture of hydrides to a high-voltage electrodeless electrical discharge, under which conditions a variety of highly energetic processes occur that ultimately lead to the formation of products. For example, the general reaction of Group IV monohydrides is shown below:

$$xMH_4 \longrightarrow M_2H_6,\ M_3H_8,\ M_4H_{10},\ M_5H_{12},\ \text{etc.} + H_2 + \text{polymeric subhydrides.}$$

The ozonizer discharge technique was first applied successfully by Schwartz and Heinrich[76] to the synthesis of disilane and trisilane from monosilane. Since that time it has been used to prepare "higher" hydrides of silicon, germanium, phosphorus, and arsenic, ternary silicon-germanium hydrides, and ternary hydrides containing elements of both Group IV and V.

The processes which take place in an electrical discharge reaction and which are involved in the formation of products are generally of complex and varied types. When high-voltage (5-50 kv) alternating current is applied to a

gaseous reactant hydride(s) in an ozonizer tube, a silent electric discharge is established. Interaction of the resulting electron flux with other species in the system leads to the formation of ionic, metastable, atomic, and radical species. These species can, in turn, initiate and propagate chemical reactions. The general processes which can occur have been discussed previously by Glockler and Lind[116] and Jolly[117] and are briefly summarized below.

(1) Ionization Impacts - Reactions of this type occur when high-energy electrons collide with molecules (M) to form positive ions:

$$e^- \text{ (fast)} + M \longrightarrow M^+ + 2e^- \text{ (slow)}$$

These positive ions may then collide with neutral molecules to form ion clusters,

$$M^+ + M \longrightarrow (MM)^+$$

which upon neutralization by electrons can yield new chemical species: ~~liberate sufficient energy to activate chemical reactions.~~

$$(MM)^+ + e^- \longrightarrow M\text{-}M$$

(2) Electron Addition - This process takes place when electrons are captured by molecules resulting in the formation of negative ions:

$$M + e^- \longrightarrow M^-$$

If these negative ions collide with a positively charged species in the system, products can result, i.e.,

$$M^- + M^+ \longrightarrow M\text{-}M$$

However, processes of this type may be of minor importance since the probability of ion collisions is relatively low.

(3) Excitation Impacts - In the presence of the electron flux, reactions of the type

$$e^- \text{ (fast)} + M \longrightarrow M^* + e^- \text{ (slow)}$$

also occur. If these "excited" molecules (M^*) return to their ground states through simple energy radiation no chemical reaction will occur:

$$M^* \longrightarrow M + h\nu$$

However, if they dissociate into radical species, e.g.

$$SiH_4{}^* \longrightarrow SiH_3 + H \text{ , etc.,}$$

subsequent radical reactions can be initiated and propagated.

In view of the complex processes which can occur in a discharge reaction it is pointless to predict, without more data than ~~is~~ are currently available, which reactions are the most important in Group IV and V hydride syntheses. However, it is not unreasonable to assume that the products arise as a result of both ionic and radical processes.

In practice an ozonizer discharge synthesis is carried out in an apparatus of the type shown in Figure 1. A gas circulating system is generally used instead of a static system so that reasonable quantities of products can be prepared in a given experiment. In this apparatus the reactant hydride or hydride mixture is circulated by means of a Toepler pump (A) through the discharge tube (B) at some predetermined rate and the resulting products, which are of lower volatility than the reactants, are preferentially condensed in an appropriately cooled U-trap (C). A complete description of the ozonizer apparatus and the procedures involved in its use are discussed in more detail later in this section.

The overall yields and distribution of products from the discharge reactions are influenced by several factors: 1) the frequency and potential of the discharge current, 2) the rate of gas circulation, 3) the total pressure of gas(es) in the system, 4) the temperature of the ozonizer, 5) the time of the discharge reaction and 6) the temperature of the product collecting traps. The effect of each of these conditions on hydride synthesis reactions have not been fully determined although all conditions except the current frequency are easily varied. In general, the most efficient conversions of mono-hydrides or hydride mixtures to higher or ternary hydrides are obtained when 7.5 - 25 kv. 60 c.p.s. alternating current is applied to the dis-

charge tube, the total gas pressure in the system is between 0.25-0.5 atm, and the gas is circulated at rates of 200-500 ml./min. The distribution of products from a reaction is most significantly controlled by the choice of the product collection trap (C). For example, in a reaction involving the conversion of a Group IV monohydride (MH_4) to higher hydrides (ie. M_2H_6, M_3H_8, M_4H_{10}, etc.), the use of a product trap which will condense the first-formed product of the reaction, M_2H_6, and still allow the circulation of MH_4 will result in the highest relative yield of M_2H_6. However, if a higher-temperature trap is used which allows products to recirculate through the ozonizer, further reaction and relatively higher yields of M_3H_8, M_4H_{10}, etc., will result.

Several reports of the conversion of silane to "higher" silanes using ozonizer discharge reactions have been made.[76,118,119,120] According to Spanier and MacDiarmid,[118] SiH_4 can be converted in 63% yield during a 5 hr. reaction in a 7.5 kv. ozonizer to a mixture of hydrides containing Si_2H_6 (66%), Si_3H_8 (23%), and higher hydrides (11%). In this reaction, products were condensed from the system in a -134° trap as they formed; however, higher relative yields of Si_3H_8, Si_4H_{10}, etc., can be obtained if this trap is replaced by a trap of higher temperature. Thus it is reported that maximum yields of Si_3H_8 are obtained using a -95° product trap whereas for

optimum yields of silanes higher than Si_3H_8, a -78° trap is most effective.[119] By means of gas chromatographic techniques it is possible to separate the mixtures of high molecular weight silanes (ie. Si_4H_{10} and higher) into their respective components and in this way it has been shown that low yields of the various isomers of hydrides up to Si_8H_{18} can be obtained.[119] In the case of tetrasilane, sufficient product was obtained to allow the separation and characterization of the two possible isomers, n-Si_4H_{10} and iso-Si_4H_{10}.[120]

The decomposition of monogermane (GeH_4) in an ozonizer discharge apparatus results in the formation of higher germanes ranging from digermane (Ge_2H_6) to nonagermane (Ge_9H_{20}).[119,121] Drake and Jolly have examined this reaction under varied conditions of voltage, pressure and time and have determined what appear to be optimum conditions for "higher" germane syntheses. ~~Thus~~ During a 5.5-hr. reaction in a 15 kv. ozonizer apparatus, in which products were trapped at -78°, GeH_4 initially at 400 mm. Hg. pressure, was 90% decomposed and a mixture of Ge_2H_6 (39%, based on GeH_4 decomposed), Ge_3H_8 (32%), Ge_4H_{10} (12%), and higher hydrides was formed.[121] As expected, relatively higher yields of Ge_2H_6 can be obtained if products are trapped at -95° instead of -78°. Digermane and germane can be separated from the product mixture using conventional fractional

condensation techniques. Hydrides higher than Ge_3H_8 are most effectively separated by gas-liquid chromatography, and a technique for preparative-scale separation of these mixtures and mixtures of higher silanes has been described.[119]

A synthesis intended specifically for diphosphine (P_2H_4) or higher phosphines has not been reported; however, P_2H_4 has been recognized as a major product in the discharge reactions of germane-phosphine and silane-phosphine mixtures.[122] On the basis of these observations and other unpublished data dealing with phosphine discharge reactions[123] it appears that the ozonizer discharge method is effective for the preparation of P_2H_4 and higher molecular weight volatile phosphines. Diarsine (As_2H_4) is reported to form during the ozonizer discharge decomposition of arsine.[99,124] The reaction has been examined under various conditions and it has been found that optimum yields of As_2H_4 are obtained when hydrogen-arsine or helium-arsine mixtures are passed through the discharge instead of arsine alone.[124] However, owing to the thermal instability of As_2H_4 and the necessity of using special techniques of sample trapping and manipulation, further studies of higher arsine syntheses have not been carried out.

A variety of interesting ternary hydrides containing Group IV or V elements can be prepared by subjecting mixtures of Group IV or V hydrides to ozonizer electric dis-

charges. Spanier and MacDiarmid have reported that germylsilane (GeH_3SiH_3) along with higher-molecular weight hydrides can be prepared from a silane-germane mixture in this way.[125] The yield of products from their reaction was not high; as a result of circulating a mixture of 44.7 and 47.5 mmoles of GeH_4 and SiH_4, respectively, through a 7.5 kv. ozonizer for 28 hours, 0.9 mmoles of GeH_3SiH_3 and an undetermined amount of the higher hydrides were prepared. Owing to the complexity of the product mixtures obtained from ternary hydride syntheses, it is difficult to isolate other silicon-germanium hydrides higher than GeH_3SiH_3 using "conventional" separation techniques. However, Andrews and Phillips have recently shown that mixtures from similar discharge reactions can be effectively separated using gas chromatographic techniques,[126] and on the basis of their data, these authors provisionally identified several new hydrides of the type $Si_xGe_yH_{2x+2y+2}$.

The ozonizer discharge method can also be applied to the synthesis of silyl phosphines, germyl phosphines, silyl arsines, and germyl arsines.[127] These syntheses are carried out by passing equimolar silane-phosphine, silane-arsine, germane-phosphine, and germane-arsine mixtures, respectively, at a pressure of 0.25 - 0.5 atm. through a -78° cooled, 15 kv. ozonizer discharge tube.

Of the products of the latter three reactions, only the first members of each ternary hydride series have been conclusively characterized, i.e. GeH_3PH_2, SiH_3AsH_2, and GeH_3AsH_2. However, mass spectrometric evidence for the existence of Ge_2PH_7, Ge_3PH_9, GeP_2H_6, Si_2AsH_7, and possibly $SiAs_2H_6$ has been obtained. The silane-phosphine reaction has been examined in greater detail and it has been shown that both SiH_3PH_2 and Si_2PH_7 can be isolated from the mixture of reaction products. Also, as a result of a careful examination of Si_2PH_7 it has been found that the material is a mixture of the two possible isomers, disilyl phosphine ($(SiH_3)_2PH$) and disilanylphosphine, ($Si_2H_5PH_2$).[122]

Ozonizer discharge reactions are not restricted to systems involving only monohydrides or mixtures of monohydrides as reactants. Since complex molecules do not undergo complete fragmentation when passed through an ozonizer tube, it is possible to "tailor-make" certain isomeric ternary hydrides by a suitable ~~selection~~ choice of complex hydride starting materials. Thus, it has been shown that the reaction of a disilane-phosphine mixture results in the isomer-specific synthesis of $Si_2H_5PH_2$.[128] No evidence for the formation of $(SiH_3)_2PH$ was obtained. Similarly, $(SiH_3)_2PH$ is the only Si_2PH_7 hydride produced in the reactions of silane-silylphosphine (SiH_3PH_2) mixtures.[128] These reactions are particularly interesting because they suggest

that certain mechanistic processes do not take place, eg. insertion of phosphine fragments into Si-Si bonds. Also, they suggest that a variety of complex, isomeric hydrides can be "tailor-made" from carefully selected reactant systems. However, until more of these reactions have been examined it is pointless to speculate on the generality of this approach to Group IV and V hydride syntheses.

In spite of the versatility and adaptability of the ozonizer discharge technique, there are several disadvantages which should be pointed out. Foremost of these is the problem of separating complex product mixtures that are sometimes formed, particularly in cases of ternary hydride syntheses. Fortunately, this problem becomes less significant when advanced separation techniques such as low-temperature column distillation and gas-phase chromatography are available. The remaining consideration is that discharge reactions require the use of high-voltage electricity and large quantities of gaseous, toxic or flammable, reactants. Therefore, in order to minimize any dangers associated with these factors, proper shielding of the electrical system and the reaction apparatus from the surroundings is necessary. A detailed description of the construction and use of a typical ozonizer discharge apparatus has been given elsewhere by Gokhale, Drake, and Jolly.[119]

H. Synthesis by Pyrolysis of Binary Hydrides

Group IV and V hydrides can be prepared by thermal decomposition or pyrolysis of a variety of hydrides or hydride mixtures. In some cases processes of this type have been classified as disproportionation reactions, and are discussed in the next section (I). However, since pyrolysis reactions that take place at relatively high temperatures may possibly proceed by mechanisms which are quite different from the disproportionation reactions discussed in Section I, we discuss them separately.

Higher silanes can be prepared from monosilane under carefully controlled pyrolysis conditions. At temperatures above 400° silane undergoes decomposition to form Si_2H_6, Si_3H_8, small quantities of higher hydrides, nonvolatile polymeric $(SiH_x)_y$ solids, and hydrogen.[129,130,131] Small quantities of disilane and trisilane are also produced in the pyrolysis of SiH_4 - ethylene mixtures at 450-510°.[132] According to Fritz, optimum pyrolytic conditions for the synthesis of Si_2H_6 involve repeated passage of SiH_4 at around 4 mm. pressure through a 470-500° reactor.[131] Under these conditions Si_2H_6 and H_2 are the primary products; however, small quantities of other silanes are also formed.

The pyrolytic decompositions of Si_2H_6,[133] Si_3H_8,[133] Si_4H_{10}[61] and Si_5H_{12}[59] have also been studied. For the most part these reactions yield lower hydrides, hydrogen, and

silicon-hydrogen polymers. Since the higher hydrides are the most difficult to prepare, reactions involving their decomposition are not synthetically useful.

The mechanism(s) by which silanes undergo decomposition to yield higher hydrides has been the subject of several investigations. While it is generally agreed that radicals (i.e. SiH_3 , SiH_2:, etc.) must be involved in the reactions, the exact nature of the radical species has not been determined. Based on the fact that the decomposition of Si_2H_6 and Si_3H_8 in the presence of hydrogen gas yields a higher percentage of SiH_4 than in the absence of hydrogen, Emeléus and Reid concluded that SiH_3 radicals are involved.[133] Evidence obtained by Stokland on the pyrolysis of Si_2H_6,[130] by White and Rockow on the SiH_4-C_2H_4 system,[132] and by Fritz on SiH_4,[131] has been used in support of this theory. However, as pointed out previously[130] if a process of the type shown below occurs,

$$Si_2H_6 \longrightarrow SiH_4 + SiH_2$$

in which a silene (SiH_2) is formed, the addition of hydrogen to the pyrolysis could also cause increased yields of SiH_4. Recently, the kinetics of the pyrolysis of SiH_4 in the temperature range 375-430° has been examined, and on the basis of the data obtained, the presence of SiH_2: as a reaction intermediate was postulated.[134] It is apparent, therefore,

that further studies of these reaction systems are necessary in order to elucidate the mechanisms of silane pyrolysis processes.

Germane decomposes rapidly at temperatures above 280° to form hydrogen, germanium, and in some cases solid germanium hydrides.[135,136,137] Similarly Ge_2H_6 undergoes pyrolysis at 195-220° to produce GeH_4, hydrogen and solid germanium hydride according to[137]

$$Ge_2H_6 \longrightarrow 1.18GeH_4 + 0.49H_2 + 0.82GeH_{0.3}$$

Only one example of the synthesis of higher germanes from GeH_4 pyrolysis has appeared. According to Drake and Jolly, less than 3% yields of Ge_2H_6 and Ge_3H_8 are obtained when GeH_4 is pyrolyzed at ca. 10-40 cm. pressure in a gas circulating system. Slightly higher yields were obtained at lower GeH_4 pressures; however, product yields were still less than half that obtained using the ozonizer discharge technique[121] (see Section G).

Shriver and Jolly have reported that diarsine (As_2H_4) can be prepared by the passage of AsH_3 over a 60-watt tungsten light-bulb filament.[124] Using this method As_2H_4 can be produced in a single passage over the filament (filament voltage = 60 V), in about 3.2% yield (based on the AsH_3 consumed).

The relatively low-temperature thermal decompositions

of P_2H_4 and As_2H_4 are discussed in the following section.

In a few cases ternary hydrides can be prepared by the pyrolytic reaction of selected binary-hydride mixtures. An excellent example of this has been reported by Timms, et al, who have shown that a large variety of ternary silicon-germanium hydrides can be prepared from the pyrolysis of silane-germane mixtures.[79] The general technique used in the syntheses is to quickly pass mixtures of selected silanes and germanes in a hydrogen stream through a 350-370° glass-wool-packed reactor (reactor residence times of 0.3-0.6 sec. were found to be optimum). Using this method of synthesis and gas phase chromatography to separate the product mixtures, the hydrides shown in Table I can be prepared.

Table I

Ternary Hydrides Prepared by Pyrolysis

Major Ternary Hydride Product	Pyrolysis Mixture
Si_2GeH_8	Ge_2H_6 + Si_2H_6
$SiGe_2H_8$	$SiGeH_6$ + Ge_2H_6
iso- and n-Si_3GeH_{10}	Si_3H_8 + Ge_2H_6 or
	Si_3H_8 + Ge_3H_8
iso- and n-$SiGe_3H_{10}$	$SiGeH_6$ or $SiGe_2H_8$ + Ge_2H_6 or Ge_3H_8
iso-Si_4GeH_{12}	n-Si_4H_{10} and i-Si_4H_{10} + Ge_3H_8
n-Si_4GeH_{12}	n-Si_4H_{10} + Ge_3H_8
iso- and n-Si_3Ge_{12}	Si_3H_8 + Ge_2H_6 or
	Si_3GeH_{10} + Ge_3H_8

The product yields in these syntheses are fairly low. From a single passage of an equimolar Si_2H_6-Ge_2H_6 mixture through the reactor, Si_2GeH_8 was obtained in an approximately 10% yield (based on Si_2H_6). However, in the other syntheses, yields were less than 5% per passage.

The mechanisms of the pyrolytic reactions are interesting since it appears that GeH_2:, not $GeH_3\cdot$ radicals are involved in the reaction processes. This conclusion is consistent with the fact that in all pyrolyses higher homologs of germanium are formed, but no changes in silicon-chain length occur in going from the reactant to the product.

Thus formation of products would be expected to involve bond cleavage and radical formation according to

$$-SiH_2SiH_2GeH_3 \longrightarrow -SiH_2SiH_3 + GeH_2:$$

instead of

$$-SiH_2SiH_2GeH_3 \longrightarrow -SiH_2SiH_2\cdot + GeH_3\cdot$$

Silyl phosphine, SiH_3PH_2, can be prepared from the pyrolytic reaction of monosilane and phosphine.[138,139] According to Fritz, the passage of about eight liquid milliliters of an equimolar SiH_4-PH_3 mixture through a 60-cm. reaction tube held at 500° results in the formation of one ml. of liquid product. Silylphosphine can be separated as a major component from this mixture of products.[138]

A possible mechanism for the formation of SiH_3PH_2 from SiH_4 and PH_3 at 500°, which has been described by Fritz, is shown below.[140]

$$SiH_4 \longrightarrow SiH_3\cdot + H\cdot$$

$$H\cdot + PH_3 \longrightarrow PH_2\cdot + H_2$$

$$SiH_3\cdot + PH_2\cdot \longrightarrow SiH_3PH_2$$

This mechanism is preferred because at temperatures $\leq 500°$ PH_3 decomposition is negligible. However, in view of the recent suggestion by Purnell and Walsh that silene radicals

(SiH_2:) may be involved in the thermal decomposition of SiH_4,[134] processes involving the SiH_2: species cannot be precluded.

I. Disproportionation Reactions

Group IV and V hydrides can in many cases be efficiently prepared from disproportionation reactions. In fact several of the more classical methods of hydride synthesis, such as the preparation of phosphine from the reaction of elemental phosphorus with hot alkaline solution, involve reactions of this type.

The disproportionation reactions are of two basically different types and are discussed in the sections which follow. The first reactions are those which are thermally induced. The reactions in the second section are those in which disproportionation occurs as a result of interaction with some other reagent. It should be emphasized that Group IV or V hydrides are produced in a large variety of disproportionation reactions of hydride derivatives.[141,142] For example, silane is produced in the disproportionation of silyl halides, according to

$$2SiH_3X \longrightarrow SiH_4 + SiH_2X_2$$

(where X = F, Cl, Br, I)

However, since these reactions are not generally useful for the synthesis of hydrides, they are not included in the following discussion. Also, thermal decomposition reactions of silanes and germanes are omitted from this section primarily because of the apparent similarity be-

tween these reactions and hydrocarbon "cracking" reactions. Instead, they are discussed separately in Section H.

Numerous reports of the preparation of phosphine from the thermal disproportionation of phosphorous acid (H_3PO_3), hypophosphorous acid (H_3PO_2), phosphites or hypophosphites have been made.[143,144,145] The reactions of the acids can be represented as

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

$$4H_3PO_2 \xrightarrow{\Delta} 2H_3PO_4 + 2PH_3,$$

in which orthophosphoric acid and phosphine are formed as the principal disproportionation products in each case. However, in the H_3PO_2 reaction small quantities of red phosphorus, phosphorous acid and hydrogen are also formed as disproportionation products.

The disproportionation of H_3PO_3 has been shown to be a particularly useful reaction for the synthesis of laboratory quantities of PH_3.[146,147] This method is highly desirable because of the simplicity of the reaction apparatus, the ready availability of pure, crystalline H_3PO_3, and the high purity of the product. By simply heating crystalline H_3PO_3 at 205-210° for about thirty minutes, greater than 95% yields of PH_3 (based on the equation in the preceding paragraph) can be obtained.[146] A trace of P_2H_4 is also formed in the reaction; however, this is easily

removed from the PH_3 by routine fractionation techniques.

"Higher" phosphorus hydrides can be prepared from the thermal disproportionation of diphosphine (P_2H_4). Diphosphine decomposes in either the gaseous or condensed phase above -78° to form phosphine and a variety of higher hydrides, i.e.,

$$xP_2H_4 \longrightarrow yPH_3 + \text{higher hydrides}$$

The composition of these hydrides or hydride mixtures depends primarily on the temperature and duration of the disproportionation reactions. Thus under mild reaction conditions in which the products are removed from the reaction mixture as soon as they are formed, volatile hydrides of discrete molecular types can be obtained. It has been reported that the flow-pyrolysis of P_2H_4 in a tubular flow reactor at 127° results in the formation of phosphine, P_2H_2, and small quantities of higher molecular weight hydrides.[148] In a reaction more suitable for general synthetic use, Fehlner[149] has reported that P_2H_4 can be converted in nearly 50% yield during a 1 hr. reaction in a hot-cold reactor[150] (hot wall at 70° - cold wall at -63°) to a mixture of triphosphine (P_3H_5) and phosphine. Although not specifically established, it appears that this reaction may be represented as

$$2P_2H_4 \longrightarrow P_3H_5 + PH_3$$

Triphosphine is thermally less stable than P_2H_4, decomposing above -23° to form phosphine and an uncharacterized solid residue. Baudler and co-workers[151,152,153] have also examined the disproportionation of P_2H_4 and they have obtained mass spectrometric evidence for the existence of extensive series of new hydrides of the types P_nH_{n+2} (n = 3-7), P_nH_n (n = 3-10), P_nH_{n-2} (n = 4-8), P_nH_{n-4} (n = 6-9) and several others. At the time of this writing the experimental details of these syntheses have not been reported.

If diphosphine is allowed to undergo disproportionation under conditions which are relatively more vigorous than those in the above cases, solid higher phosphorus hydrides can be synthesized. Stock et al.[154] reported that yellow $(P_2H)_x$, which Schenk and Buck[155] formulated as $P_{12}H_6$, and phosphine are the final products of the room temperature disproportionation of liquid P_2H_4, i.e.,

$$5P_2H_4 \longrightarrow 6PH_3 + 2/x(P_2H)_x$$

However, Evers and Street in a more recent report[72] have found that a hydride of composition $P_{12}H_6$ is obtained only if water vapor is present during the disproportionation. Under strictly anhydrous conditions the hydride which forms has a higher P:H ratio, approaching a limiting composition of P_9H_4.

Solid phosphorus hydrides having P:H ratios greater than $P_{12}H_6$ (2:1) or P_9H_4 (2.25:1) can be obtained upon mild heating of $P_{12}H_6$ or P_9H_4. According to Stock et al.,[156] the thermal decompsition of $P_{12}H_6$ at 100°-230° results in formation of a red hydride of composition P_9H_2 (P:H ratio = 4.5:1) and phosphine according to

$$5P_{12}H_6 \longrightarrow 6P_9H_2 + 6PH_3$$

At a slightly lower temperature, 80°, Hackspill[157] prepared a solid hydride of composition P_5H_2 from Stock's $P_{12}H_6$. Although several workers have offered explanations which attempt to rationalize the composition of the lower phosphorus hydrides,[158,159] the work by Evers and Street[72] seems to suggest that hydrides of nearly any composition can be obtained depending on the temperature and duration of the decomposition reactions.

Since the solid phosphorus hydrides are amorphous, polymeric and generally intractable, they are of limited usefulness to the synthetic inorganic chemist. For a more complete review of the chemistry of these hydrides and a discussion of the structures and bonding which must exist, the reader is referred elsewhere.[72,143]

Diarsine (As_2H_4) undergoes rapid disproportionation in the liquid phase at temperatures above -100°. Nast[74] and Jolly et al.[99] reported that warming As_2H_4 to room

temperature results in the formation of arsine and a solid, polymeric arsenic hydride which appears to be $(As_2H)_x$.

$$5xAs_2H_4 \longrightarrow 6AsH_3 + 2/x(As_2H)_x$$

No evidence for the formation of higher, volatile arsenic hydrides in these reactions was obtained. Upon heating above 150°, $(As_2H)_x$ disproportionates further to form arsine, hydrogen and elemental arsenic as the final products.

Bismuthine can be readily prepared from the thermal disproportionation of methyl bismuthines. According to Amberger,[22] $(CH_3)_2BiH$ and CH_3BiH_2 disproportionate above -15° and -45°, respectively, to form BiH_3 and $(CH_3)_3Bi$ as

$$3(CH_3)_2BiH \xrightarrow{-15°} 2(CH_3)_3Bi + BiH_3$$

$$3CH_3BiH_2 \xrightarrow{-45°} (CH_3)_3Bi + 2BiH_3$$

Amberger has also reported that plumbane is formed in the thermal disproportionation of methyl plumbanes.[160] At room temperature $(CH_3)_3PbH$ and $(CH_3)_2PbH_2$ decompose, presumably according to

$$4(CH_3)_3PbH \longrightarrow 3(CH_3)_4Pb + PbH_4$$

$$2(CH_3)_2PbH_2 \longrightarrow (CH_3)_4Pb + PbH_4$$

Since these reactions proceed at temperatures at which PbH_4 undergoes rapid decomposition, the reactions are not generally suitable for the synthesis of PbH_4.

Since the chemistry of ternary Group IV and V hydrides has not been studied extensively, only limited information concerning their thermal disproportionation reactions is available. However, it has been observed that SiH_3PH_2 and GeH_3PH_2 decompose, forming PH_3 and other uncharacterized products.[123] In the case of SiH_3PH_2, no appreciable decomposition is observed below 200° C; however, GeH_3PH_2 which is much less stable has been found to decompose slowly at room temperature both in the gas and liquid phase.

Chemical disproportionation reactions can sometimes be used to prepare Group IV and V hydrides. One of the foremost examples of a reaction of this type is the synthesis of phosphine from the reaction of elemental phosphorus (P_4) with hot alkaline solutions.[143,144,145] The principal reaction which takes place and which yields phosphine can be written as

$$P_4 + 4OH^- + 2H_2O \longrightarrow 2HPO_3^{2-} + 2PH_3$$

Hydrogen is also formed during the reaction as a result of a competing process,

$$P_4 + 4OH^- + 4H_2O \longrightarrow 4H_2PO_2^- + 2H_2$$

and to a lesser extent as a result of decomposition of hypophosphite by the alkaline solution,[143] i.e.,

$$H_2PO_2^- + OH^- \longrightarrow HPO_3^{2-} + H_2$$

The greater the concentration of the alkaline solution, the higher the PH_3/H_2 ratio will be. Traces of P_2H_4 are also formed in the P_4-hydroxide reaction. However, its presence does not constitute a serious disadvantage since it can be easily separated from PH_3 by fractional condensation.

A procedure for phosphine synthesis based on the above reaction has been described.[73] It is claimed that a high yield of PH_3 can be obtained from the reaction of P_4 with a concentrated KOH solution at 60°, although the exact yield is not reported. In view of the relative complexity of this synthesis, it is less desirable for most general laboratory syntheses than the previously described H_3PO_3-disproportionation method.[146]

Phosphine can also be prepared from reactions of dry alkaline earth hydroxides ($Mg(OH))_2$, $Ca(OH)_2$, and $Ba(OH)_2$) with red phosphorus at elevated temperatures. According to Datta,[161] phosphine is formed in high yields (exact yields not reported) when 1:2 to 1:10 mixtures of phosphorus and the appropriate hydroxide are heated at temperatures up to 300°. Highest product yields are obtained

with $Mg(OH)_2$ and no P_2H_4 is formed in the reaction. However, with $Ca(OH)_2$ and $Ba(OH)_2$, lower PH_3 yields and traces of P_2H_4 are observed.

Tris-substituted silyl phosphines can be efficiently prepared from unusual boron trifluoride-promoted disproportionation reactions of mono-substituted silyl phosphines.[162,163] These reactions can be represented as

$$3 \geqslant Si\text{-}PH_2 \xrightarrow{BF_3} (\geqslant Si)_3P + 2PH_3$$

$$(\geqslant Si\text{-} = H_3Si\text{-} \text{ or } H_5Si_2\text{-})$$

Trisilylphosphine ($(SiH_3)_3P$) can be prepared in up to 90% yields from the BF_3- promoted disproportionation of SiH_3PH_2 during an 8 hr. reaction at -78°.[162] Under similar conditions, 9 hr. at -78° followed by 2.3 hr. at -45°, $Si_2H_5PH_2$ can be converted in greater than 90% yield to tris(disilanyl)phosphine ($(Si_2H_5)_3P$).[162] In these reactions small quantities of what are probably intermediate disproportionation products, i.e., $(SiH_3)_2PH$ and $(Si_2H_5)_2PH$, respectively, can be detected.

Mixed tris-substituted silyl phosphines can also be prepared using the BF_3- promoted disproportionation method.[162] Co-disproportionation of a SiH_3PH_2 - $Si_2H_5PH_2$ mixture during a 17 hr. reaction at -78° yields $(SiH_3)_3P$,

$(SiH_3)_2PSi_2H_5$, $SiH_3P(Si_2H_5)_2$ and $(Si_2H_5)_3P$. Disilyl(disilanyl)phosphine ($(SiH_3)_2PSi_2H_5$) can be separated from the reaction mixture by low temperature column distillation. However, attempts to obtain pure $SiH_3P(Si_2H_5)_2$ have been unsuccessful and the compound has not been adequately characterized.

Several experiments aimed at determining the mechanism of the silyl phosphine disproportionation reactions and the role of the Lewis acid therein, have been carried out.[162] Reactions in which BCl_3 or BBr_3 were substituted for BF_3, indicated that the presence of both uncoordinated and coordinated silyl phosphine (i.e., $>Si-PH_2$ and $>SiPH_2\ BX_3$) is necessary for disproportionation to occur. Disproportionation of specifically deuterium labeled silylphosphine (SiH_3PD_2) yielded only isotopically pure $(SiH_3)_3P$ and PD_3, ruling out the existence of divalent reaction intermediates. A reaction scheme, consistent with these observations can be written (for clarity SiH_3PH_2 is used as the example):

$$SiH_3PH_2 + BX_3 \rightleftharpoons SiH_3PH_2BX_3 \qquad (1)$$

$$SiH_3PH_2 + SiH_3PH_2BX_3 \longrightarrow (SiH_3)_2PH + PH_3 + BX_3 \qquad (2)$$

$$(SiH_3)_2PH + SiH_3PH_2BX_3 \longrightarrow (SiH_3)_3P + PH_3 + BX_3 \qquad (3)$$

Disproportionation occurs in steps (2) and (3) in processes which probably involve the elimination of PH_3 (assisted by

BX_3) simultaneous with the transfer of SiH_3 groups.

Since it is not unreasonable to expect that other tris-substituted ternary Group IV and V hydrides could also be prepared using Lewis acid-promoted disproportionation reactions, future studies in this area of ternary hydride chemistry could prove interesting.

J. Miscellaneous Methods

Group IV and V hydrides have been prepared by several methods which do not properly belong in any of the above categories. In some cases these methods are interesting because of the unique chemistry involved. Others are significant because they represent the only ways known to prepare certain hydrides. The following sections are devoted to a discussion of several of these miscellaneous reaction types.

1. Exchange Reactions. Recently Craddock *et al.* reported the preparation of trigermylphosphine, $(GeH_3)_3P$, from an exchange-type reaction between $(SiH_3)_3P$ and GeH_3Br.[164] The product was described as being a relatively stable, low-volatility liquid at room temperature. Although a detailed account of the work was not given, the following equation for the reaction was suggested.

$$(SiH_3)_3P + 3GeH_3Br \longrightarrow 3SiH_3Br + (GeH_3)_3P$$

It is interesting that Ge-P bonds can be formed in a reaction of this type since it indicates that (neglecting entropy effects, which should be small) the bond energy difference between the Si-P and Ge-P bonds is less than that of the Si-Br and Ge-Br bonds, *i.e.*, 8 kcal./mole.[36] Application of this method to the preparation of other germyl phosphine systems will undoubtedly be the subject of further investi-

gations.

2. Amine-Induced Reactions. Evidence has been reported which suggests that silylphosphine and trisilylphosphine can be prepared in low yields from reactions of phosphine and a trialkylamine silyl iodide complex, $R_3N \cdot SiH_3I$, (where R = CH_3- or C_2H_5-).[43] These reactions are particularly interesting since phosphine and silyl iodide by themselves do not react to any appreciable extent. However, in the presence of a tertiary amine reaction proceeds and products are formed.

Unfortunately, it is difficult to discuss the mechanisms of these amine-induced reactions in detail for two reasons: 1) insufficient data are available to establish the reaction stoichiometry, and 2) the structure of the trialkylamine silyl iodide complex, $R_3N \cdot SiH_3I$, has not been firmly established.[141] It seems possible that the principal role of the amine in these reactions is to remove HI from the reaction system

$$SiH_3I + PH_3 \longrightarrow SiH_3PH_2 + HI$$

$$R_3N + HI \longrightarrow R_3NHI$$

thereby preventing HI from reacting with SiH_3PH_2 and simply reforming the starting materials. Uncoordinated SiH_3I could result either from partial dissociation of the complex $R_3N \cdot SiH_3I$ or from a disproportionation of the type

$$2\ R_3N \cdot SiH_3I \longrightarrow SiH_3I2NR_3 + SiH_3I$$

described recently by Campbell-Ferguson and Ebsworth.[165] It also seems possible that if $R_3N \cdot SiH_3I$ has the quaternary amine-type structure, $R_3NSiH_3{}^+I^-$, the SiH_3 group may have greater Lewis acidic character than uncoordinated SiH_3I, thereby facilitating reaction with phosphine. Future studies of these amine-induced reactions will undoubtedly prove interesting.

3. <u>Cleavage of Silicon-Phosphorous Bonds.</u> Phosphine can be prepared in high yields from reactions between silyl phosphines and water[122] or hydrogen halides.[138,128] Recently, it has been found that partial hydrolysis of trisilylphosphine, $(SiH_3)_3P$, also yields disilylphosphine, $(SiH_3)_2PH$, and silylphosphine, SiH_3PH_2.[166] These cleavage reactions can be represented by the following general equation.

$$\geq Si\text{-}P < + \; H\text{-}X \longrightarrow \geq Si\text{-}X + > P\text{-}H$$

(where H-X = H-OH, H-Cl, H-Br)

The advantage of the above reactions to synthetic work lies not in the large-scale preparation of phosphines and silyl phosphines but in the synthesis of specifically isotopically-labeled products. For example, cleanly-labeled silylphosphine-P-d_2, SiH_3PD_2, can be prepared by the controlled deuterolysis of $(SiH_3)_3P$. Although $(SiH_3)_2PD$ from this reaction was not fully characterized, it undoubtedly forms prior to SiH_3PD_2 in a stepwise deuterolysis scheme:

$$2(SiH_3)_3P + D_2O \longrightarrow (SiH_3)_2O + 2(SiH_3)_2PD$$

$$2(SiH_3)_2PD + D_2O \longrightarrow (SiH_3)_2O + 2SiH_3PD_2$$

$$2SiH_3PD_2 + D_2O \longrightarrow (SiH_3)_2O + 2PD_3$$

Cleavage reactions of this type may also be useful for the

synthesis of specifically-labeled phosphines, e.g., PH_2D, PHD_2, etc. Thus, hydrolysis or deuterolysis of the appropriately substituted silyl phosphine,

$$2SiH_3PH + D_2O \longrightarrow (SiH_3)_2O + 2PH_2D$$

$$2(SiH_3)_2PH + D_2O \longrightarrow (SiH_3)_2O + 2PHD_2$$

would yield the desired products.

4. Photochemical Reactions. Several Group IV hydrides have been prepared using a mercury-sensitized photochemical technique. A sensitizer is necessary to promote the reactions because simple hydrides are generally insufficiently "excited" through the absorption of ultraviolet light to dissociate into radical species. Using this method the hydride or hydride mixture containing the sensitizer (Hg), is irradiated with 2537 A° (Hg source) light. Absorption of energy by mercury results in the formation of "excited" atoms which in turn decompose the reactant(s) to radicals through collision processes. Subsequently, through various combination and/or abstraction reactions of these radicals, the final products are formed. The over-all photolysis reaction can be represented as

$$Hg(^1S_0) + h\nu \longrightarrow Hg^*(^3P_1)$$

$$Hg^*(^3P_1) + MH_4 \longrightarrow Hg(^1S_0) + MH_3\bullet + H\bullet$$

$$MH_3\bullet + MH_3\bullet \longrightarrow M_2H_6$$

$$H\bullet + M_2H_6 \longrightarrow M_2H_5\bullet + H_2$$

$$MH_3\bullet + M_2H_5\bullet \longrightarrow M_3H_8$$

Silane, germane, and germane-silane mixtures may be converted in low yields ($<10\%$) to disilane,[167,168] digermane,[169] and germylsilane,[170] respectively. Hydrogen,

small amounts of volatile higher hydrides, and polymeric residues are also formed in the reactions. Small amounts of higher silanes are also produced from mercury-sensitized irradiation of SiH_4-hydrocarbon mixtures.[132] In the example reported, the hydrides were irradiated in static reaction systems and steady-state concentrations of products were obtained with irradiation times of one minute or less. Therefore, it has been suggested[170] that the use of a flow system reactor might result in increased product yields and make the mercury-sensitized photolysis technique more practical for general laboratory synthetic work.

5. Alkali and Alkaline Earth Metal Hydride Reductions.

Several reports of the syntheses of Group IV and V hydrides by the reduction of halo compounds by alkali- or alkaline earth metal hydrides have appeared. According to Finholt, *et al.*,[1] SiH_4 can be prepared in up to 89% yields from the room-temperature reaction of $SiCl_4$ with LiH in diethyl ether. For optimum yields a three to four-fold excess of hydride is required. Silane has also been prepared from the reaction at 250° of SiF_4 with CaH_2 in the absence of solvents.[172,278] Finholt *et al.* also prepared SnH_4 from the reaction of LiH with $SnCl_4$. In this case less than a 1% yield was obtained.[1]

Phosphorus tribromide can be reduced in 100% yields by LiH in diethyl ether to yield a solid phosphorus hydride, $(PH)_x$ according to,

$$PBr_3 + 3LiH \xrightarrow[0°]{Et_2O} (PH)_x + H_2 + 3LiBr$$

However, with PCl_3, small quantities of PH_3 were also obtained.[20]

6. "Active" Phosphorus. It has been reported that phosphine can be prepared from reactions of "active" phosphorus with hydrogen-containing compounds[173] in reactions analogous to those observed for "active" nitrogen.[174] The "active" phosphorus is obtained by passing phosphorus (P_4) in a carrier gas (argon) through a condensed discharge apparatus. When this mixture is allowed to react with hydrocarbons, ammonia, or hydrazine, phosphine is produced as the major product. The yield of products from these reactions was not reported although it might be expected that the over-all yields are relatively low. Since the exact nature of the "active" phosphorus species is not known, a detailed discussion of the reactions is not possible. However, the reaction system is interesting and will undoubtedly be further investigated.

7. Active Metals in Non-Protonic Solvents. Active metals, in the absence of protonic solvents, have been shown to react with silyl halides to form a variety of silicon hydrides. The most useful reaction of this type, namely the Wurtz-Fittig coupling of SiH_3I to yield disilane,[113] has been discussed in a previous section. The remaining reactions of these types yield silane and/or solid, polymeric silicon hydrides as the principal products. Thus, the reactions of SiH_3Cl,[114] SiH_2Cl_2,[175] and $SiHCl_3$[176] with alkali metals (sodium) yield silane, in some cases hydrogen, and solid silicon hydrides having compositions intermediate between $(SiH)_x$ and $(SiH_2)_x$. Similarly, magnesium reacts with SiH_3Br[115] or SiH_3I[113] in isoamyl ether to form silane, hydrogen and varying quantities of polymeric hydrides. Recently, it has been found that a solid silicon hydride of discrete composition, $(SiH)_x$, can be quantitatively prepared from the room temperature reaction of $SiHBr_3$ with magnesium in diethyl ether, i.e.,

$$2SiHBr_3 + 3Mg \xrightarrow{Et_2O} 3MgBr + 2/n\ (SiH)_n$$

It is reported that $SiHCl_3$ reacts similarly, but much slower to yield $(SiH)_x$.[177] These latter reactions are particularly interesting because they appear to be unique syntheses for pure, $(SiH)_x$ silicon hydride.

8. Hydrolysis of Phosphonium Halides. Phosphine can be conveniently prepared from the alkaline hydrolysis of phosphonium bromide (PH_4Br) or iodide (PH_4I).[144,178]

$$PH_4X + KOH \longrightarrow PH_3 + KX + H_2O$$

(where X = Br or I)

A reliable synthesis based on the hydrolysis of the latter halide, PH_4I, has been reported.[73] According to this procedure a 33% (by weight) solution of KOH is added dropwise to solid PH_4I at room temperature, producing PH_3 in greater than 95% yield. The main advantage of this procedure over most others which can be used for PH_3 synthesis is that if the reaction is carried out by adding the KOH solution at a dropwise rate, the product is formed free of P_2H_4 contamination. However, if the KOH is added rapidly, it is reported that small quantities of P_2H_4 are formed.

9. Synthesis in a Molten Salt Electrolysis Cell. One of the most technically interesting methods of carrying out a lithium hydride reduction of $SiCl_4$, in order to prepare SiH_4, has been reported by Sundermeyer and Glemser.[179] This method involves the synthesis of silane in a molten salt electrolysis cell, in which the hydride reducing agent (LiH) can be regenerated after reduction of the $SiCl_4$. Using this process SiH_4 can be continuously prepared in the same reaction apparatus. In the first step of the synthesis, LiH is dissolved in a molten salt LiCl-KCl eutectic mixture (58.3% LiCl) which is contained in a specially constructed electrolysis cell. Silicon tetrachloride is then introduced into the cathode chamber of the cell and formation of SiH_4, according to

$$4LiH + SiCl_4 \longrightarrow SiH_4 + 4LiCl$$

occurs. Upon completion of this reaction, current (ca. 4 V., 32 A.) is passed through the cell for several minutes causing the processes

$$Li^+ + e^- \longrightarrow Li^\circ \quad \text{and}$$

$$Cl^- \longrightarrow e^- + \tfrac{1}{2}Cl_2$$

to take place at the cathode and anode, respectively. During this electrolysis chlorine is removed continuously from the anode chamber. Hydrogen gas is then passed into

the cathode chamber, bringing about the reaction

$$2Li + H_2 \longrightarrow 2LiH,$$

in which LiH, required in the original synthetic reaction is regenerated. According to the authors, by simply repeating the above sequence of reactions, a semicontinuous process of SiH_4 production can be achieved. Using this method silane can be produced in greater than 70% yields (based on $SiCl_4$ consumed).

10. Reduction of Silica with Hydrogen and Aluminum. It will be noted from Table IV that the hydrides which are under consideration in this chapter are thermodynamically unstable with respect to the elements. Thus it is impossible to prepare any of the hydrides directly from the elements (e.g., silicon and hydrogen) under ordinary conditions. Because of the great stability of the oxides of the elements of Groups IV and V, it is even less possible to prepare the hydrides by reduction with hydrogen of the corresponding oxides. However, when an electropositive metal such as aluminum can enter into the reaction, the conversion of an oxide to a hydride is possible. Thus Jackson et al.[180] have prepared silane in conversions up to 80% from silica and silicates by treatment with super-atmospheric-pressure hydrogen in the presence of aluminum and aluminum chloride. Aluminum and hydrogen alone do not hydrogenate silica; an aluminum halide must be present for the over-all reaction.

$$3\ SiO_2 + 4\ Al + 2\ AlX_3 + 6H_2 \longrightarrow \frac{6}{n}\ (Al\ OX)_n + 3\ SiH_4$$

To provide a liquid reaction medium, a molten salt mixture (m.p. 120°) composed of 63 mole % $AlCl_3$ and 37 mole % NaCl is used. The reaction rate is negligible below 800° at atmospheric pressure, and above 800° silane decomposes too fast. However, the rate is strongly dependent on the hydrogen pressure. Thus, using reaction times around 10 hr., silicon conversion rises from 0% at 1 atm. to 10% at 100 atm. to 76% at 900 atm.

It is believed that the reaction mechanism of this silane synthesis involves the formation of a volatile aluminum chlorohydride intermediate, $AlCl_nH_{3-n}$. For example,

$$H_2 + \frac{1}{3}\,AlCl_3 + \frac{2}{3}\,Al \rightleftarrows AlClH_2$$

The $AlCl_nH_{3-n}$ intermediate is the active hydrogenating agent:

$$2\,AlClH_2 + SiO_2 \longrightarrow SiH_4 + \frac{2}{X}(AlOCl)_x$$

Although the above reaction results in the efficient synthesis of high-purity silane, the high-pressure equipment which is required tends to preclude its usefulness for small-scale laboratory preparations. The method appears to be most useful for large-scale laboratory or industrial applications. Presumably it can be extended to the synthesis of other hydrides of Groups IV and V.

11. Atomic Hydrogen Reactions. Reactions of atomic hydrogen with Group IV or V elements (or compounds) can in many cases be used to prepare Group IV or V hydrides. The reaction type is general and at least one example of hydride formation for each of the elements can be found. However, in spite of the generality of the method it should be emphasized that in most cases these reactions are impractical for routine laboratory syntheses. This is due to the generally low yields and the fact that the reaction apparatus is often not simple.

Atomic hydrogen reactions are usually carried out by bombarding an appropriate Group IV or V target surface with a stream of hydrogen atoms. If the product is volatile it may then be swept from the reactor by the hydrogen stream into an appropriate product trap. On the other hand, if the product is a non-volatile, polymeric hydride it is left at the target surface until the end of the reaction.

Atomic hydrogen can be produced by many techniques. ~~however~~. For the reactions cited below, it has been produced from molecular hydrogen in one of the following ways.

(a) Discharge Method: A stream of hydrogen at low pressure is passed through a high voltage discharge tube (either silent electric discharge or electrode type, *ca.* 3-10 kv) in which case fractions of the H_2 molecules are dissociated to hydrogen atoms. This method was first reported by Wendt and Landauer[181,182] who erroneously characterized the active hydrogen species as triatomic hydrogen (H_3).[181,182,183] However in later work,

Wood[184] and Bonhoeffer[185] demonstrated that the active species in this reaction is indeed atomic hydrogen (H'). The discharge apparatuses used in most reactions are basically modifications of the original units, and are often referred to as Wood-Bonhoeffer discharge tubes.

(b) High-Temperature Dissociation: In this method a stream of molecular hydrogen is passed through a hot zone (e.g. a high density arc)[186] at a temperature greater than 1000°, at which point significant dissociation of hydrogen molecules to atoms occurs.[187] Based on a heat of dissociation value of 98 kcal./mole for the dissociation of H_2 into H atoms, Langmuir has shown that at 5000° K, H_2 should be greater than 94% dissociated.[188] Although the heat of dissociation of H_2 is now known to be slightly greater than 98 kcal./mole, it is clear that at high temperatures hydrogen streams containing fairly high concentrations of H atoms can be obtained.

(c) Photochemical Dissociation: If molecular hydrogen is irradiated with 2537 Å light in the presence of mercury vapor, significant dissociation of H_2 into H atoms can be effected.[189,190] This technique, often called mercury-sensitized photolysis, has been used in several instances to produce hydrogen atoms for hydride synthesis. For additional discussion of mercury-sensitized reactions see the section in this chapter entitled Photochemical Synthesis.

Several examples of the formation of phosphorus hydrides using atomic hydrogen reactions have been reported. Phosphine

has been prepared by the action of hydrogen atoms on elemental phosphorus[187,191,192,193] and phosphorus pentoxide.[192,194] Traces of P_2H_4 were observed among the products of the reaction of atomic and molecular H_2 with red phosphorus.[193] A solid polymeric phosphorus hydride was reported from the reaction of atomic hydrogen with PH_3;[195] however, more recent work indicates that red phosphorus and H_2 are the actual products which form.[193]

The formation of arsine from reactions of atomic H with arsenic has been reported in several cases.[187,192,196,197] Also, atomic hydrogen reacts with arsenic pentoxide to form a volatile product[198] which is probably arsine.[279] In all cases the product yields were low, clearly making the reactions unsuitable for general synthetic use.

Two reports of the preparation of stibine from the reaction of atomic hydrogen with antimony have appeared although neither investigator adequately characterized the product.[187,199] However, it is reasonable to accept their assumptions since stibine is the only volatile antimony hydride stable enough to be handled under their reaction conditions.

There is evidence which suggests that bismuthine is formed in the reactions of atomic hydrogen with bismuth.[187,194,197,200,201] However, since the hydride has not been isolated and characterized in any of the reactions, the exact nature of the species produced may be subject to question.

Of the Group IV hydrides described in this section, the hydrides of silicon and germanium are known to be the most stable. However, relatively little information concerning the

synthesis of these hydrides has been reported. Hiedemann has presented evidence for the formation of a silane(s) (silane or disilane) as a result of the reaction of atomic H with what appears to be the glass walls of the electrical discharge tube.[202,203] Volatile hydrides of germanium are reportedly formed from atomic hydrogen - germanium reactions, but again, as with the silanes, no definite hydride was identified. In view of the lack of information concerning the formation of silanes and germanes in atomic hydrogen reactions, it is clear that additional studies of these reactions would be interesting.

It seems certain that stannane is produced in reactions of atomic hydrogen with tin[187,204] and it has been proved that SnH_4 is formed in reactions of atomic hydrogen with stannous chloride[205] and stannic chloride.[206] The latter case represents one of the few examples where the product yield from an atomic hydrogen reaction has been reported. As a result of a 1-hr. reaction of atomic hydrogen with 1.5 g of $SnCl_4$ ($SnCl_4$ maintained at -195° during the reaction), 30 to 90 micrograms of SnH_4 could be obtained.

Evidence for the formation of a volatile lead hydride, probably PbH_4, during reactions of atomic hydrogen with lead[200,207,208] and lead chloride[208] has been presented. However, in a more recent study Wells and Roberts have shown that a solid hydride of composition $PbH_{0.19}$ is the only product of the atomic hydrogen - lead reaction.[209] In view of this more recent data, the conclusions of the early workers must be accepted with some reservations.

12. Solvolysis of Lower Oxides. Timms and Phillips[209a] observed that when silicon monoxide was treated with 10% aqueous hydrofluoric acid it dissolved completely with evolution of hydrogen and volatile silanes. Mono-, di-, tri-, iso- and n-tetra-, iso- and n-penta-, and iso- and n-hexasilane were identified in the mixture of silanes. Yields of 9-24% were observed. Germanium monoxide was found to be almost insoluble in 10% HF. However, by condensing the vapors of SiO and GeO together on a cold finger, a solid was obtained which gave silanes, silicon-germanium hydrides, and germanes with 10% HF.

Table II

Recommended Synthetic Methods for Binary Hydrides

(References given in parentheses)

Hydride	Large-Scale Synthesis		Small-Scale (one-shot) Synthesis	
SiH_4	$LiAlH_4 + SiCl_4$	(210)	$LiAlH_4 + SiO_2$	(14)
Si_2H_6	SiH_4 + silent discharge or $LiAlH_4 + Si_2Cl_6$	(118,119) (1)	$LiAlH_4 + Si_2Cl_6$	(1)
Si_3H_8, Si_4H_{10}, etc.	SiH_4 + silent discharge or $Mg_2Si + H^+$	(118,119) (59,61)	$Mg_2Si + H^+$	(59,61)
GeH_4	$H_2GeO_3 + BH_4^- + H^+$	(29,34)	$LiAlH_4 + GeO_2$	(213)
Ge_2H_6	GeH_4 + silent discharge or $Mg_2Ge + H^+$	(119,121) (65)	$H_2GeO_3 + BH_4^- + H^+$	(34)
Ge_3H_8, Ge_4H_{10}, etc.	GeH_4 + silent discharge or $Mg_2Ge + H^+$	(119,121) (65)	$Mg_2Ge + H^+$	(65)
SnH_4	$LiAlH_4 + SnCl_4$	(210)	$LiAlH_4 + SnCl_4$ or $H_2SnO_3 + BH_4^- + H^+$	(210) (34)
Sn_2H_6[a]	$H_2SnO_3 + BH_4^- + H^+$	(34)		
PbH_4[a]	"Mg_2Pb" $+ H^+$	(70)		
PH_3	$H_3PO_3 \xrightarrow{\Delta}$	(146)	$H_3PO_3 \xrightarrow{\Delta}$	(146)

Hydride	Large-Scale Synthesis		Small Scale (one-shot) Synthesis	
PD_3[b]	$LiAlD_4 + PCl_3$	(20)		
	or			
	$Ca_3P_2 + D^+$	(72)		
P_2H_4	$Ca_3P_2 + H^+$	(72)	$Ca_3P_2 + H^+$	(72)
P_3H_5[a]	$P_2H_4 \xrightarrow{\Delta}$	(~~102~~ 149)		
	or			
	$Mg_3P_2 + H^+$	(83)		
AsH_3	$H_3AsO_3 + BH_4^- + H^+$	(34)	$H_3AsO_3 + BH_4^- + H^+$	(34)
AsD_3[b]	$LiAlD_4 + AsCl_3$	(21)		
As_2H_4[a]	AsH_3 + silent discharge	(99,124)		
	or			
	arsenide + H^+	(74)		
As_3H_5[a]	$Mg_3As_2 + H^+$	(83)		
SbH_3	$H_3SbO_3 + BH_4^- + H^+$	(34)	$H_3SbO_3 + BH_4^- + H^+$	(34)
SbD_3[b]	$LiAlD_4 + SbCl_3$	(21)		
Sb_2H_4[a]	$H_3SbO_3 + BH_4^- + H^+$	(32)		
BiH_3[a]	$LiAlH_4 + BiCl_3$	(22)		
	or			
	"Mg_3Bi_2" + H^+	(70)		

[a]The syntheses of these ~~very~~ unstable hydrides are very inefficient, and ~~very~~ small yields are obtained even when large amounts of reactants are used. Consequently it is pointless to recommend "Small-Scale" syntheses for these hydrides.

[b]Generally, the deuteride can be prepared by using the corresponding deuterated reagents. In some cases (indicated in the table) it is more economical to use a different procedure.

Table III

Recommended Synthetic Methods for Ternary Hydrides

Hydride	Synthetic Method	References
SiH_3GeH_3	$KSiH_3 + GeH_3Cl$	44
	or	
	$SiH_4 + GeH_3$ + silent discharge	125
other		
$Si_xGe_yH_{2x+2y+2}$	$SiH_4 + GeH_4$ + silent discharge	126
	or	
	Mg-Ge-Si or Ca-Si-Ge alloy + H^+	79,81
SiH_3SnH_3	$LiAlH_4 + SiCl_3SnCl_3$	213a
SiH_3PH_2	$SiH_4 + PH_3$ + silent discharge	127,122
	or	
	$SiH_4 + PH_3 \xrightarrow{\Delta}$	138,139
$(SiH_3)_2PH$	$SiH_4 + SiH_3PH_2$ + silent discharge	128
$Si_2H_5PH_2$	$Si_2H_6 + PH_3$ + silent discharge	128
$(SiH_3)_3P$	$SiH_3X + KPH_2$	38,39,40
$(SiH_3)_2PSi_2H_5$	$SiH_3PH_2 + Si_2H_5PH_2 + BF_3$	162
$(Si_2H_5)_3P$	$Si_2H_5PH_2 + BF_5$	162
SiH_3AsH_2, Si_2AsH_7	$SiH_4 + AsH_3$ + silent discharge	127
$(SiH_3)_3As$	$SiH_3Br + KAsH_2$	39,41

Hydride	Synthetic Method	References
$(SiH_3)_3Sb$	$SiH_3Br + K_3Sb$	39,42
GeH_3SnH_3	$LiAlH_4 + GeCl_3SnCl_3$	213a
GeH_3PH_2	$GeH_4 + PH_3$ + silent discharge	127
	or	
	$CaGe/Ca_3P_2 + H^+$	82,83
Ge_2PH_7, Ge_3PH_9, and GeP_2H_6	$GeH_4 + PH_3$ + silent discharge	127
$(GeH_3)_3P$	$GeH_3Br + (SiH_3)_3P$	164
GeH_3AsH_2	$GeH_4 + AsH_3$ + silent discharge	127
	or	
	$CaGe/Ca_3As_2 + H^+$	82,83
AsH_2PH_2	$Mg_3P_2/Mg_3As_2 + H^+$	82,83

III. Recommended Procedures

In Tables II and III we have listed what we believe to be the best known methods for the preparation of the volatile hydrides. The methods listed are not always those with the best yield. Thus in some cases we have recommended methods which, although not as efficient as others, are reasonable compromises of efficiency, economy, and simplicity. Sometimes an experimenter needs only a small amount of a particular hydride, and is willing to use a relatively inefficient but simple preparative method if he can thereby avoid the use of unusual apparatus or reagents. In Table II, we have listed our recommendations for such "one-shot" syntheses. In the case of the very unstable hydrides, the higher silanes and germanes, and some of the ternary hydrides, we have of necessity listed methods which are extremely inefficient. These are areas for future synthetic research. Such compounds will never receive the extensive study they deserve until decent synthetic methods are developed.

Generally the volatile deuterides can be prepared by replacing the appropriate reagents with the corresponding deuterium compounds. In some cases, such procedure is very inefficient and expensive, and special synthetic procedures must be used. Such cases are indicated in Table II.

IV. Physical Properties

The hydrides are arranged in Table IV in the following order: binary Group IV hydrides, ternary Group IV hydrides, and binary Group V hydrides. Ternary Group IV-Group V hydrides are considered to be derivatives of Group V hydrides and are located accordingly.

The thermodynamic functions at 25°C are for compounds in their most stable state at that temperature. The various functions are expressed in the following units: $\Delta H_f°$, kcal. mole^{-1}; $\Delta F_f°$, kcal. mole^{-1}; S°, cal. deg.$^{-1}$ mole^{-1}; $C\hat{p}°$, cal. deg.$^{-1}$ mole^{-1}; ΔH° (fusion), kcal. mole^{-1}, and ΔS° (fusion), cal. deg.$^{-1}$ mole.$^{-1}$

When known, vapor pressures for the following "slush bath" temperatures are tabulated:

ice-water	0°
chlorobenzene	-45.2°
chloroform	-63.5°
Dry Ice	-78.5°
carbon disulfide	-111.6°

The reference numbers are italicized and in parentheses. Those in bold face type are references to spectral data in which actual spectra are presented.

Table IV

Physical Properties of the Hydrides of Groups IV and V

Compound	Thermodynamic functions at 25°C	Melting point, C° ΔH°(fusion) and ΔS°(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg slush bath)	Boiling point, °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
SiH_4	$\Delta H_f^\circ = 7.3$ (37)	-185 (214)	0.68 (-185) (214)	$-645.9/\tau + 6.881$ (215)	781 (CS_2) (215) (1)	111.2 (216)	2.9 (217)	18 (217)	(218)	(219)	(220)	(70) (221[a])
	$S^\circ = 48.7$ (217)	ΔH°(fusion)= 0.159 (217)										
	$C_p^\circ = 10.24$ (217)	ΔS°(fusion)= 1.80 (217)										
SiH_3D										(222)	(220)	
SiH_2D_2										(223)		
$SiHD_3$										(223)	(220)	
SiD_4		-186.4 (224[b]) (225)				-111.4 (216)				(223)		

here and hereafter, τ should be cap. T

error −111.2

Table IV (Continued)

2

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta H°$(fusion) and $\Delta S°$(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
Si_2H_6	$\Delta H_f°$=17.1 ± 0.3 (37)	-129.3[b] (224)	0.686 (-25) (214)	-1342/τ+12.918 -2.01 log τ (215)	26(CO_2) (123)	-14.2 (216)	5.2 (217)	20.1 (217)	(226)	(226)	(227)	(32)
Si_2D_6		-130.0[b] (224) (225)				-16.4 (216)			(226)	(226)		
Si_3H_8	ΔH_f(g)= 25.9 (228)	-114.8 (228)	0.725 (0) (229)	-1910/τ+16.319 -3.02 log τ (215)	94(H_2O) (59)	53.0 (59)	6.8 (217)	20.8 (217)	(230)	(118)	(120)	(231)
Si_3D_8		-116.8[b] (224)		-1281.7τ+13.7260 +9.6389 log τ -0.011267τ (225)								
n-Si_4H_{10}	$\Delta H_f°$(l)= 70.4[c] (211)	-88.2 (79)	0.79 (0)[c] (229)	-2594.5τ+20.186[c] (215)	10.0± 1.0 (H_2O) (120)	108.4[c] (est.) (57)	8.2[c] (215)	21.5[c] (215)	(230)	(120)	(120)	(120)
iso-Si_4H_{10}					ca.15 (H_2O) (120)				(230)	(120)	(120)	(120)

Table IV (Continued)

3

Compound	Thermodynamic functions at 25°C	Melting point, °C ΔH°(fusion) and ΔS°(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
Si_4D_{10}		-89.5[b,c] (224)		-6011.2/τ + 139.953 -51.3041 log τ + 0.029211 τ[c] (225)								
n-Si_5H_{12}		-138 (79)										
iso-Si_5H_{12}		-74.5 (79)										
GeH_4	ΔH_f°= 21.6 (37) ΔF_f°= 28±4 (238) S°= 46.56 (232) C_p°= 10.76 (239)	-165.9 (232) ΔH°(fusion)= 0.200 (232) ΔS°(fusion)= 1.86 (232)	1.523 (-142) (233)	-722.255/τ + 3.551 -1025 log τ -0.0063106 τ (234)	182 (CS_2) (1)	-88.51 (234)	3.608 (234)	18.19 (215)	(235)	(236)	(237)	(70)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta H°$(fusion) and $\Delta S°$(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor Pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
GeH_3D									(240)	(240)		
GeH_2D_2									(240)	(240)		
$GeHD_3$									(240)	(240)		
GeD_4		-166.2 (69)	1.684 (-160.5) (69)	$-818.4/\tau + 7.327$ (69)	186 (CS_2) (210)	-89.2 (69)	3.744 (69)	20.3 (69)	(240)	(240)		
Ge_2H_6	$\Delta H_f°(g) = 38.7 \pm 0.3$ (37)	-109 (65)	1.98 (-109) (65)	$-1556/\tau + 12.986 - 2.0 \log \tau$ (215)	236.5 (H_2O) (37)	29 (65)	6.0 (217)	19.8 (217)	(241)	(241)	(242) (243)	(32)
Ge_2D_6		-107.9 (69)	2.184 (-106.4) (69)	$-1417.0/\tau + 7.579$ (69)		28.4 (69)	6.483 (69)	21.2 (69)	(241)	(241)		

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C ΔH°(fusion) and ΔS°(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
Ge_3H_8	$\Delta H_f^\circ(g)$= 53.6 (228)	-101.8 (228)	2.20 (-105) (65)	-2153/τ + 16.286 -3.02 log τ (215)	13.9 (H_2O) (79)	110.5 (est.) (65)	7.7 (217)	20.0 (217)		(121)	(121)	(32)
Ge_3D_8		-100.3 (69)	2.618 (-99.9) (69)	-1721.5/τ + 7.367 (69)		110.5 (est.) (69)	7.876 (69)	20.5 (69)				
n-Ge_4H_10				-1714.6/τ + 6.692[c] (68)		176.9[c] (est.) (68)	7.842[c] (68)			(121)	(121)	(121)
iso-Ge_4H_10										(121)	(121)	(121)
Ge_5H_12				-1805.8/τ + 6.449[c] (68)		234[c] (est.) (68)	8.260[c] (68)			(121)		
$SiGeH_6$	$\Delta H_f^\circ(g)$= 27.8 (244) $\Delta H_f^\circ(g)$= 7.5[d] (245)	-119.7± 0.2 (125)		-1307.06/τ + 7.54701 (125)	7.0 (CO_2) (125)	7.0 (125)	6.00 (125)	21.3 (125)		(125)		(245)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta H°$(fusion) and $\Delta S°$(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
Si_2GeH_8		-113.4 (79)			39.6 (H_2O) (79)							
$SiGe_2H_8$		-108.5 (79)			19.3 (H_2O) (79)							
n-Si_3GeH_{10}		-87.1 (79)			4.7 (H_2O) (79)							
n-Si_4GeH_{12}		-71.5 (79)										
SnH_4	$\Delta H_f°$= 38.9 (37) $\Delta F_f°$= 99±4 (248) $S°$= 127.61 (246) $C_p°$= 11.73 (246)	-150 (239)		$-966/\tau$ + 7.257 (215)	17.5 (CS_2) (37) 198 (CO_2) (26)	-51.8 (239)	4.4 (217)	19.9 (217)		(246)	(247)	(70)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C ΔH°(fusion) and ΔS°(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: RAMAN	I.R.	NMR	MASS
$SnHD_3$										(249)		
SnD_4					17.4 (CS_2) (250)					(251)		
Sn_2H_6	ΔH_f°= 65.6[d] (32)									(33)	(32)	(32)
PbH_4	ΔH_f°= 59.7[d] (70)					ca.-13 (171)						(70)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta H°$(fusion) and $\Delta S°$(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: Raman	I.R.	NMR	Mass
PH_3	$\Delta H_f°$=1.3 ±0.4 (37)	-133.78 (212)	0.746 (-90) (229)	$-1027.30/\tau - 0.0178530\tau + 0.000029135\tau^2 + 9.73075$ (212)	171 (CS_2) (37)	-87.74 (252)	3.49 (252)	18.8 (217)	(253)	(254) (255)	(256) e	(257) (221) a
	S°=50.35 (212)	$\Delta H°$(fusion)= 0.270 (212)										
	$C_p°$=8.76 (258)	$\Delta S°$(fusion)= 1.94 (212)										
PH_2D										(259)	(260)	
PHD_2										(259)		
PD_3	S°=52.94 (258)								(253)	(254) (261)		(257)
	$C_p°$=10.00 (258)											
P_2H_4	$\Delta H_f°$=5.0 ±1.0 (37)	-99 (159)		-1498/τ + 7.330 (72)	73.0 (H_2O) (72)	63.5 (72)	6.889 (72)	20.46 (72)	(262)	(261)	(260)	(257)
P_2D_4									(262)	(261)		(257)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C ΔH°(fusion) and ΔS°(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slushpoint, bath)	Boiling °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: Raman	I.R.	NMR	Mass
SiH_3PH_2	$\Delta H_f°=1.9^d$ (263)	< -135 (138)			487 (H_2O) (138)	12.7 (138)				(264)	(243) (265)	(263)
SiH_3PD_2 (123)												
$(SiH_3)_2PH$					28±1 (H_2O) (128)					(128)	(122)	
$(SiH_3)_3P$				-1901.8/τ + 7.792 (38)	7.0 (H_2O) (39)	114 (est.) (38)	8.697 (38)		(47)	(47)	(47)	
$(SiD_3)_3P$										(47)		
$Si_2H_5PH_2$					31±1 (H_2O) (122)					(122)	(122)	(122)
$Si_2H_5P(SiH_3)_2$										(162)	(162)	(162)
$Si_2H_5)_3P$										(162)	(162)	(162)
GeH_3PH_2										(127)[f]	(265) (243)	
$(GeH_3)_3P$		-83.8 (164)			ca.1.0 (H_2O) (164)				(164)	(164)		

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta°H$(fusion) and $\Delta°S$(fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm}=	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: Raman	I.R.	NMR	Mass
AsH_3	$\Delta H_f°$=15.9 (266)	-116.93 (267)	1.622(-63) (267)	-1403.32/τ -9.45935 log τ +0.008037 τ +28.82835 (267)	35(CS_2) (53)	-62.48 (267)	3.988 (267)	18.93 (267)	(268)	(254) (269)	(270)	(70) (221)[a]
	$\Delta F_f°$=26.4 (266)	$\Delta H°$(fusion) = 0.2857 (267)										
	$S°$=53.18 (266)	$\Delta S°$(fusion)= 1.83 (267)										
	$C_p°$=9.207 (266)											
AsD_3	$C_p°$=10.55 (258)								(268)	(124) (269)		
	$S°$=53.22 (258)											
As_2H_4	$\Delta H_f°(g)$= 35.2[d] (32)				est.10 at 25° (124)					(124)		(32)
SiH_3AsH_2	$\Delta H_f°$=37[d] (271)									(127)[f]	(265) (243)	(271)

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C ΔH° (fusion) and ΔS° (fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm} =	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	ΔH° of vap'n at b.p.	ΔS° of vap'n at b.p.	Spectral Data: Raman	I.R.	NMR	Mass
$(SiH_3)_3As$			1.201 (20°) (39)	$-2142.6/\tau + 8.333$ (272)	7.7 (14.7°) (39)	120 (est.) (272)	9.798 (272)			(272)		
GeH_3AsH_2										f, (127)	(265) (243)	
SbH_3	$\Delta H_f° = 34.7$ (37)	-88 (273)	2.150 (75)	$1.48 \times 10^{-5} P_{mm}$ $-1446.34/\tau$ $+16.0522$ $-3.1200 \log \tau$ (266)	81($CHCl_3$) (30) 224 (C_6H_5Cl) (30)	-18.4 (30)	5.02 (30)	19.8 (30)		(274) (275)		(70)
	$\Delta F_f° = 44.82$ (266)											
	$S° = 55.65$ (266)											
	$C_p° = 9.887$ (266)											
SbD_3	$S° = 58.62$ (276)									(277)		
	$C_p° = 11.45$ (276)											

Table IV (Continued)

Compound	Thermodynamic functions at 25°C	Melting point, °C $\Delta H°$ (fusion) and $\Delta S°$ (fusion) when known	Density of Liquid (°C)	Vapor Pressure Equation for Liquid log P_{mm}=	Vapor pressure mm.Hg (slush bath)	Boiling point, °C	$\Delta H°$ of vap'n at b.p.	$\Delta S°$ of vap'n at b.p.	Spectral Data: Raman	I.R.	NMR	Mass
Sb_2H_4	$\Delta H_f°(g)$= 57.2[d] (32)											(32)
$(SiH_3)_3Sb$				-1607.3 + 6.041 (39)	1.81 (+15°) (39)	255 (est.) (39)	7.638 (39)			(39)		
BiH_3	$\Delta H_f°$=66.4[d] (70)			-1314.2/τ + 7.4146 (22)	4.62 (CO_2) (22)	16.8 (est.) (22)	6.011 (at -43°) (22)					(70)

[a]Negative ion mass spectrum

[b]These are triple-point melting points. However, since the vapor pressures are very low at the triple-point, there is a negligible difference between these and the normal melting points.

[c]Measurements apparently made on mixtures of isomers.

[d]Determined from mass spectrometric appearance potential data.

[e]Both ^1H and ^{31}P nuclear magnetic resonances are reported.

[f]Symmetrical deformation frequency of MH_3- group, only.

Acknowledgment. This work was supported by the auspices of the United States Atomic Energy Commission.

References

1. A. E. Finholt, A. C. Bond., Jr., K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).
2. H. I. Schlesinger et al., Final Report on Contract N173s-10421, 1945-1946, p. 8. (Mentioned in footnote 4 of reference 3).
3. T. Wartik and H. I. Schlesinger, J. Am. Chem. Soc., 75, 835 (1953).
4. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N.Y., 1960, pp. 91-103; F. Seel, "Atomic Structure and Chemical Bonding," John Wiley and Sons, New York, N.Y., 1963, pp. 83-84.
5. G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N.J., 1941.
6. N. L. Paddock, Nature, 167, 1070 (1951).
7. L. W. Trevoy and W. G. Brown, J. Am. Chem. Soc., 71, 1675 (1949).
8. J. S. Peake, W. H. Nebergall, and Y. T. Chen, J. Am. Chem. Soc., 74, 1526 (1952).
9. C. H. Lewis, M. B. Giusto and S. Johnson, AFCRC-TR-59-354, U.S. Dept. Com., Office Tech. Serv. PB Rept. 161,261; 1959.
10. L. G. L. Ward and A. G. MacDiarmid, Abstracts 137th Meeting Am. Chem. Soc., Cleveland, Ohio, p. 11M (1960); quoted in A. G. MacDiarmid, Advan. Inorg. Chem. Radiochem., 3, 207 (1961).
11. W. C. Schumb and D. W. Robinson, J. Am. Chem. Soc., 77, 5294 (1955).
12. G. Fritz, Z. Naturforsch., 10b, 423 (1955).
13. L. I. Zakharkin, V. V. Gavrilenko, I. M. Khorlina, and G. G. Zhigareva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1962, 1872; Chem. Abstr., 58, 10966c.

14. H. G. Weiss and H. D. Fisher, Inorg. Chem., 2, 880 (1963).

15. E. Ashley, Advan. Inorg. Chem. Radiochem., 8, 301 (1966).

16. S. Sujishi and J. N. Keith, J. Am. Chem. Soc., 80, 4138 (1958).

17. E. D. Macklen, J. Chem. Soc., 1984 (1959).

18. H. J. Emeléus and S. F. A. Kettle, J. Chem. Soc., 2444 (1958).

19. E. Wiberg and R. Bauer, Z. Naturf., 6b, 392 (1951).

20. E. Wiberg and G. Müller-Schiedmayer, Chem. Ber., 92, 2372 (1959).

21. E. Wiberg and K. Mödritzer, Z. Naturforsch., 12b, 123 (1957).

22. E. Amberger, Chem. Ber., 94, 1447 (1961).

23. E. Wiberg and K. Mödritzer, Z. Naturforsch., 11b, 747 (1956).

24. E. Wiberg and K. Mödritzer, Z. Naturforsch., 11b, 748 (1956).

25. A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobson, Inorg. Chem., 2, 504 (1963).

26. G. W. Schaeffer and M. Emilius, J. Am. Chem. Soc., 76, 1203 (1954).

27. T. S. Piper and M. K. Wilson, J. Inorg. Nucl. Chem., 4, 22 (1957).

28. E. D. Macklen, J. Chem. Soc., 1989 (1959).

29. J. E. Griffiths, Inorg. Chem., 2, 375 (1963).

30. L. Berka, T. Briggs, M. Millard and W. Jolly, J. Inorg. Nucl. Chem., 14, 190 (1960).

31. H. J. Emeléus and K. M. Mackay, J. Chem. Soc., 2676 (1961).

32. F. E. Saalfeld and H. J. Svec, Inorg. Chem., 2, 50 (1963).

33. W. L. Jolly, J. Am. Chem. Soc., 83, 335 (1961).

34. W. L. Jolly and J. E. Drake, Inorg. Syntheses, 7, 34 (1963).

35. W. L. Jolly, Angew. Chem., 72, 268 (1960).

36. T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, 2nd ed., 1958.

37. S. R. Gunn and L. G. Green, J. Phys. Chem., 65, 779 (1961).

38. E. Amberger and H. Boeters, Angew. Chem., 74, 32 (1962).

39. E. Amberger and H. Boeters, Chem. Ber., 97, 1999 (1964).

40. G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick and L. A. Woodward, Chem. Comm., 122 (1965).

41. E. Amberger and H. Boeters, Angew. Chem., 74, 293 (1962).

42. E. Amberger and H. Boeters, Z. Naturforsch, 18b, 157 (1963).

43. B. J. Aylett, H. J. Emeléus and A. G. Maddock, J. Inorg. Nucl. Chem., I, 187 (1955).

44. R. Varma and A. P. Cox, Angew. Chem., 76, 649 (1964).

45. R. C. Kennedy, L. P. Freeman, A. P. Fox and M. A. Ring, J. Inorg. Nucl. Chem., 28, 1373 (1966).

46. E. J. Bulten and J. G. Noltes, Tetrahedron Letters, 1967, 1443 (1967).

47. G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick and L. A. Woodward, Spectrochim. Acta, 22, 67 (1966).

48. M. A. Ring and D. M. Ritter, J. Am. Chem. Soc., 83, 802 (1961).

49. J. A. Morrison and M. A. Ring, Inorg. Chem., 6, 100 (1967).

50. C. A. Kraus and E. S. Carney, J. Am. Chem. Soc., 56, 765 (1934).

51. A. Joannis, Compt. Rend., 119, 557 (1894).

52. R. I. Wagner and A. B. Burg, J. Am. Chem. Soc., 75, 3869 (1953).

53. W. C. Johnson and A. Pechukas, J. Am. Chem. Soc., 59, 2065 (1937).

54. S. Cradock, C. H. Van Dyke and G. A. Gibbon, Paper presented before the Division of Inorganic Chemistry, 153rd Meeting of the American Chemical Society, April, 1967, Paper L158.

55. W. L. Jolly, D. S. Rustad, T. Birchall and D. J. Chazan, Inorg. Syntheses, 11, 000 (1968).

56. A. Besson, Compt. rend., 154, 116, 1603 (1912).

57. A. Stock and C. Somieski, Chem. Ber., 49, 111 (1916).

58. A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N.Y., 1933, p. 21.

59. A. Stock, P. Stiebeler and F. Zeidler, Chem. Ber., 56, 1695 (1923).

60. K. Borer and C. S. G. Phillips, Proc. Chem. Soc., 1959, 189.

61. H. J. Emeléus and A. G. Maddock, J. Chem. Soc., 1131 (1946).

62. W. C. Johnson and S. Isenberg, J. Am. Chem. Soc., 57, 1349 (1935).

63. W. C. Johnson and T. R. Hogness, J. Am. Chem. Soc., 56, 1252 (1934).

64. H. Clasen, Angew. Chem., 70, 179 (1958).

65. L. M. Dennis, R. B. Corey and R. W. Moore, J. Am. Chem. Soc., 46, 657 (1924).

66. C. A. Kraus and E. S. Carney, J. Am. Chem. Soc., 56, 765 (1934).

67. F. Fehér and J. Cremer, Z. Anorg. Allgem. Chem., 297, 14 (1958).

68. E. Amberger, Angew. Chem., 71, 372 (1959).

69. A. H. Zeltmann and G. C. Fitzgibbon, J. Am. Chem. Soc., 76, 2021 (1954).

70. F. E. Saalfeld and H. J. Svec, Inorg. Chem., 2, 46 (1963).

71. L. Moser and A. Brukl, Z. Anorg. Chem., 121, 73 (1922).

72. E. C. Evers and E. H. Street, Jr., J. Am. Chem. Soc., 78, 5726 (1956).

73. G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed., Academic Press, 1963.

74. R. Nast, Chem. Ber., 81, 271 (1948).

75. A. A. Durrant, T. G. Pearson and P. L. Robinson, J. Chem. Soc., 730 (1934).

76. R. Schwarz and F. Heinrich, Z. Anorg. Allgem. Chem., 221, 277 (1935).

77. P. Royen and R. Schwarz, Z. Anorg. Allgem. Chem., 211, 412 (1933); 215, 295 (1933).

78. P. Royen and C. Rocktäschel, Z. anorg. allgem. Chem., 346, 279 (1966).

79. P. L. Timms, C. C. Simpson and C. S. G. Phillips, J. Chem. Soc., 1467 (1964).

80. C. S. G. Phillips and P. L. Timms, Anal. Chem., 35, 505 (1963).

81. P. Royen and C. Rocktäschel, Angew. Chem. (Intl. Ed.), 3, 314 (1964).

82. P. Royen, C. Rocktäschel and W. Mosch, Angew. Chem. Intl. Ed., 3, 703 (1964).

83. P. Royen and C. Rocktäschel, Z. anorg. allgem. Chem., 346, 290 (1966).

84. S. Glasstone, "Textbook of Physical Chemistry," Van Nostrand Co., New York, N.Y., 1940, p. 1013.

85. E. Voegelen, Z. anorg. Chem., 30, 325 (1902).

86. F. Paneth and E. Schmidt-Hebbel, Chem. Ber., 55, 2615 (1922).

87. M. Green and P. H. Robinson, J. Electrochem. Soc., 106, 253 (1959).

88. F. Paneth, A. Johannsen and M. Matthies, Chem. Ber., 55, 769 (1922).

89. F. Paneth, Z. Elektrochem., 29, 97 (1923).

90. F. Paneth, "Radio-Elements as Indicators," McGraw-Hill Book Co., New York, N.Y., 1928, pp. 97-99.

91. F. Paneth and O. Nörring, Chem. Ber., 53, 1693 (1920).

92. T. Moeller, "Qualitative Analysis," McGraw-Hill Book Co., New York, N.Y., 1958, p. 301.

93. E. B. Dyuzheva and S. P. Bukhman, Tr. Inst. Khim. Nauk, Akad. Kaz. S.S.R., 12, 78 (1964); Chem. Abstr., 62, 7377g.

94. E. B. Muratova, S. P. Bukhman and M. V. Nosek, Izv. Akad. Nauk Kaz. S.S.R., Ser. Tekhn. i Khim. Nauk, 1963(2), 15; Chem. Abstr., 60, 15438a.

95. H. W. Salzberg and B. Goldschmidt, J. Electrochem. Soc., 107, 348 (1960).

96. M. V. Nosek, S. P. Bukhman and M. T. Kozlovskii, Trudy Inst. Khim. Nauk, Akad. Nauk Kazakh. S.S.R., 6, 131 (1960); Chem. Abstr., 55, 25435a.

97. S. P. Bukhman, M. V. Nosek and M. T. Kozlevskii, Izvest. Akad. Nauk Kazakh. S.S.R., Ser. Khim. No. 1, 69 (1960); Chem. Abstr., 55, 20581e.

98. N. Konopik and K. Szlaczka, Monatsh., 83, 290 (1952).

99. W. L. Jolly, L. B. Anderson and R. T. Beltrami, J. Am. Chem. Soc., 79, 2443 (1957).

100. N. Konopik and K. Sozaczka, Monatsh., 84, 1140 (1953).

101. A. Reisman, M. Berkenblit, E. C. Haas, and A. Gaines, Jr., J. Electrochem. Soc., 101, 387 (1954).

102. H. W. Salzberg and A. J. Andreatch, J. Electrochem. Soc., 101, 528 (1954).

103. A. I. Zebreva and M. T. Kozlovskii, Izvest. Akad. Nauk Kazakh. S.S.R., Ser. Khim., 1959, No. 1, 33; Chem. Abstr., 54, 23999i.

104. L. Tomlinson, J. Electrochem. Soc., 111, 592 (1964).

stet

105. ~~A. Reismann, M. Berkenblit, E. C. Haas and A. Gaines, J. Electrochem. Soc., 101, 387 (1954).~~

106. G. K. Teal and C. A. Kraus, J. Am. Chem. Soc., 72, 4706 (1950).

107. E. C. Evers and J. M. Finn, Jr., J. Phys. Chem., 57, 559 (1953).

108. Unpublished work of P. Kuznesof, 1967.

109. H. Gilman and C. W. Gerow, J. Am. Chem. Soc., 77, 4675 (1955).

110. H. Gilman and L. A. Gist, J. Org. Chem., 22, 689 (1957).

111. G. E. Coates, "Organometallic Compounds," 2nd ed., Wiley & Sons, New York, 1960, p. 195.

112. H. Gilman, W. H. Atwell and F. K. Cartledge, Adv. Organomet. Chem., 4, 1 (1966).

113. H. J. Emeléus, A. G. Maddock and C. Reid, J. Chem. Soc., 353 (1941).

114. A. Stock and K. Somieski, Chem. Ber., 54, 524 (1921).

115. E. R. Van Artsdalen and J. Gavis, J. Am. Chem. Soc., 74, 3196 (1952).

116. G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, New York, 1939.

117. W. L. Jolly, "Technique of Inorganic Chemistry," Interscience, New York, Vol. I, 1963, p. 179; W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall Inc., Englewood Cliffs, 1960.

118. E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 1, 432 (1962).

119. S. D. Gokhale, J. E. Drake and W. L. Jolly, J. Inorg. Nucl. Chem., 27, 1911 (1965).

120. S. D. Gokhale and W. L. Jolly, Inorg. Chem., 3, 946 (1964).

121. J. E. Drake and W. L. Jolly, J. Chem. Soc., 2807 (1962).

122. S. D. Gokhale and W. L. Jolly, Inorg. Chem., 3, 1141 (1964).

123. A. D. Norman and W. L. Jolly, unpublished data.

124. D. F. Shriver and W. L. Jolly, U.S. Atomic Energy Comm., UCRL-5148 (1958).

125. E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 2, 215 (1963).

126. T. D. Andrews and C. S. G. Phillips, J. Chem. Soc. (A), 46 (1966).

127. J. E. Drake and W. L. Jolly, Chem. and Ind., 1470 (1962).

128. S. D. Gokhale and W. L. Jolly, Inorg. Chem., 4, 596 (1965).

129. K. Stokland, Kgl. Norske Videnskab. Selskab. Skrifter, 3, 1 (1948).

130. K. Stokland, Trans. Faraday Soc., 44, 545 (1948).

131. G. Fritz, Z. Naturforsch., 76, 507 (1952).

132. D. G. White and E. G. Rochow, J. Am. Chem. Soc., 76, 3897 (1954).

133. H. J. Emeléus and C. Reid, J. Chem. Soc., 1021 (1939).

134. J. H. Purnell and R. Walsh, Proc. Roy. Soc. (London), 293, 543 (1966).

135. K. Tamaru, M. Baudart and H. Taylor, J. Phys. Chem., 59, 801 (1955).

136. P. J. Fensham, K. Tamaru, M. Baudart and H. Taylor, J. Phys. Chem., 59, 806 (1955).

137. H. J. Emeléus and H. H. G. Jellinek, Trans. Faraday Soc., 40, 93 (1944).

138. G. Fritz, Z. Anorg. Allgem. Chem., 280, 332 (1955).

139. G. Fritz, Z. Naturforsch., 8B, 776 (1953).

140. G. Fritz, Angew. Chem. (Int. Ed.), 5, 53 (1966).

141. E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, 1963, p. 67.

142. F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, 1962.

143. J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, 1958.

144. J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," VIII, Longmons, Green and Co., New York, 1928, p. 803.

145. D. T. Hurd, "Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, 1952, p. 127.

146. S. D. Gokhale and W. L. Jolly, Inorg. Syntheses, 9, 56 (1966).

147. D. R. Martin and R. E. Dial, J. Am. Chem. Soc., 72, 852 (1950).

148. T. P. Fehlner, J. Am. Chem. Soc., 88, 1819 (1966).

149. T. P. Fehlner, J. Am. Chem. Soc., 88, 2613 (1966).

150. M. J. Klein, B. C. Harrison and I. J. Solomon, J. Am. Chem. Soc., 80, 4149 (1958).

151. M. Baudler, H. Staendeke and H. Strobel, Naturwissenschaften, 52, 345 (1965).

152. M. Baudler, H. Staendeke, H. Strobel and J. Dobbers, Naturwissenschaften, 53, 106 (1966).

153. M. Baudler and L. Schmidt, Naturwissenschaften, 46, 577 (1959).

154. A. Stock, W. Bottcher and W. Langer, Chem. Ber., 42, 2839 (1909).

155. R. Schenk and E. Buck, Chem. Ber., 37, 915 (1904).

156. A. Stock, W. Bottcher and W. Langer, Chem. Ber., 42, 2848 (1909).

157. L. Hackspill, Compt. Rend., 156, 1466 (1913).

158. P. Royen, Z. Anorg. Allgem. Chem., 229, 112 (1936).

159. P. Royen and K. Hill, Z. Anorg. Allgem. Chem., 229, 97 (1936).

160. E. Amberger, Angew. Chem., 72, 494 (1960).

161. J. Datta, J. Indian Chem. Soc., 29, 101 (1952).

162. A. D. Norman and W. L. Jolly, Inorg. Chem., 0, 0000, 1967.

163. C. R. Russ and A. G. MacDiarmid, Angew. Chem. (Intl. Ed.), 5, 418 (1966).

164. S. Craddock, G. Davidson, E. A. W. Ebsworth and L. A. Woodward, Chem. Comm., 515 (1965).

165. H. J. Campbell-Ferguson and E. A. V. Ebsworth, J. Chem. Soc. (A), 1508 (1966).

166. A. D. Norman and W. L. Jolly, to be published.

167. M. A. Nay, G. N. C. Woodall, O. P. Strausz and H. E. Gunning, J. Am. Chem. Soc., 87, 179 (1965).

168. H. Niki and G. J. Mains, J. Phys. Chem., 68, 304 (1964).

169. Y. Rousseau and G. J. Mains, Abstracts of the 149th National Meeting of the American Chemical Society, Detroit, Michigan, April 1965, p. 85.

170. G. A. Gibbon, Y. Rousseau, C. H. Van Dyke and G. J. Mains, Inorg. Chem., 5, 114 (1966).

171. F. Paneth and E. Rabinowitsch, Chem. Ber., 58B, 1138 (1925).

172. R. De Pape, Ann. Chim., 8, 185 (1963).

173. E. R. Zabolotny and H. Gesser, J. Am. Chem. Soc., 81, 6091 (1959).

174. D. A. Armstrong and C. A. Winkler, J. Phys. Chem., 60, 1100 (1956).

175. A. Stock and C. Somieski, Chem. Ber., 56, 247 (1923).

176. A. Stock and F. Zeidler, Chem. Ber., 56, 986 (1923).

177. G. Schott and W. Herman, Z. Anorg. Allgem. Chem., 288, 1 (1956).

178. J. Messinger and C. Engels, Chem. Ber., 21, 326 (1888).

179. W. Sundermeyer and O. Glemser, Angew. Chem., 70, 625 (1958).

180. H. L. Jackson, F. D. Marsh and E. L. Muetterties, Inorg. Chem., 2, 43 (1963).

181. G. L. Wendt and R. S. Landauer, J. Am. Chem. Soc., 42, 930 (1920).

182. G. L. Wendt and R. S. Landauer, Phys. Rev., 15, 242 (1920).

183. G. L. Wendt and R. S. Landauer, J. Am. Chem. Soc., 44, 510 (1922).

184. R. W. Wood, Proc. Roy. Soc., 102A, 1 (1923).

185. K. F. Bonhoeffer, Z. Physik.Chem., 113, 199 (1924).

186. I. Langmuir, Gen. Elec. Rev., 29, 153 (1926).

187. T. G. Pearson, P. L. Robinson and E. M. Stoddort, Proc. Roy. Soc., 142A, 275 (1933).

188. I. Langmuir, Science, 62, 463 (1925).

189. G. Cairo and J. Frank, Z. Physik., 11, 162 (1922).

190. H. S. Taylor and A. L. Marshall, J. Phys. Chem., 29, 1140 (1925).

191. I. Langmuir, J. Am. Chem. Soc., 43, 1310 (1912).

192. K. F. Bonhoeffer, Z. Physik. Chem., 113, 199 (1924).

193. D. M. Wiles and C. A. Winkler, J. Phys. Chem., 61, 620 (1957).

194. H. Kroeplin and E. Vogel, Z. Anorg. Allgem. Chem., 229, 1 (1936).

195. K. H. Denbeigh, Trans. Faraday Soc., 35, 1432 (1939).

196. G. M. Schwab and F. Seuferling, Z. Electrochem., 34, 654 (1928).

197. A. Guntherschulze, Z. Physik., 36, 563 (1926).

198. S. Miyamoto, J. Chem. Soc. Japan, 53, 724, 788, 914, 933 (1932).

199. K. S. Bagdarzan and V. K. Semenchenko, J. Phys. Chem. (U.S.S.R.), 6, 1033 (1935).

200. B. Foresti and M. Mascaretti, Gazz. chim. ital., 60, 745 (1930).

201. G. M. Harris and A. W. Tickner, Can. J. Res., 26B, 343 (1948).

202. E. Hiedemann, Z. Physik. Chem., 153A, 210 (1931).

203. E. Hiedemann, Z. Physik. Chem., 164A, 20 (1933).

204. F. Paneth, M. Matties and E. Schmidt-Hebbel, Chem. Ber., 55, 775 (1922).

205. V. M. Vdovenko, J. Gen. Chem. (U.S.S.R.), 15, 581 (1945).

206. V. M. Vdovenko, Compt. Rend. Acad. Sci. (U.S.S.R.), 23, 801 (1939); C. A., 34, 3607 (1940).

207. F. Paneth, Chem. Ber., 53B, 1693 (1920).

208. E. Pietsch and F. Seuferline, Naturwiss., 19, 573 (1931).

209. B. R. Wells and M. W. Roberts, Proc. Chem. Soc., 173 (1964).

209a. P. L. Timms and C. S. G. Phillips, Inorg. Chem., 3, 606 (1964).

210. A. D. Norman, J. Webster and W. L. Jolly, Inorg. Syntheses, 11, 000 (1968).

211. F. Feher, G. Jansen and H. Rohmer, Z. Anorg. Allgem. Chem., 329, 31 (1964).

212. C. C. Stephenson and W. F. Giauque, J. Chem. Phys., 5, 149 (1937).

213. A. G. MacDiarmid (private communication) reports that GeH_4 can be made from GeO_2 and $LiAlH_4$ by a process analogous to that described in reference 16.

213a. E. Wiberg, E. Amberger and H. Cambensi, Z. anorg. allgem. Chem., 351, 164 (196

214. A. Stock, Z. Electrochem., 32, 341 (1926).

215. K. K. Kelly, Bureau of Mines Bulletin, 383, Washington (1935).

216. K. Stokland, Kgl. Norske Videnskab. Sebskabs. Forh., 12, 122 (1939); C. A. 35, 23808, 1941.

217. National Bur. Standards (U.S.), Cir. 500. "Selected Values of Thermodynamic Properties," 1952.

218. H. Murata and K. Kawai, J. Chem. Phys., 23, 2451 (1955).

219. C. H. Tindahl, J. W. Straley and H. N. Nielsen, Phys. Rev., 62, 151 (1942).

220. E. A. V. Ebsworth and J. J. Turner, J. Chem. Phys., 36, 2628 (1962).

221. E. Ebinghaus, K. Kraus, W. Mueller-Duysing and H. Neuert, Z. Naturforsch., 19a, 732 (1964).

223. J. H. Meal and M. K. Wilson, J. Chem. Phys., 24, 384 (1956).

224. K. Stokland, Kgl. Norske Videnskab. Sebskabs. Forh., 19, 33 (1946); C. A., 41, 7182d (1947).

225. G. T. Armstrong, N. B. S. Report 2306, "A Compilation of Vapor Pressure Data of Deuterium Compounds," 1953.

226. G. W. Bethke and M. K. Wilson, J. Chem. Phys., 26, 1107 (1957).

227. C. H. Van Dyke and A. G. MacDiarmid, Inorg. Chem., 3, 1071 (1964).

228. S. R. Gunn and L. G. Green, J. Phys. Chem., 68, 946 (1964).

222. S. R. Polo and M. K. Wilson, J. Chem. Phys., 22, 1559 (1954)

229. International Critical Tables, Vol. I., 1st ed., McGraw-Hill, 1926, p. 106 ff.

230. F. Feher and H. Fischer, Naturwissenschaften, 51, 461 (1964).

231. J. D. Pupezin and K. F. Zmbov, Bull. Inst. Nucl. Sci. (Belgrade), 8, 89 (1958); C. A., 52, 17980i (1958).

232. K. Clusius and G. Faber, Z. Physik. Chem., 51B, 352 (1942).

233. R. B. Corey, A. W. Laubengayer and L. M. Dennis, J. Am. Chem. Soc., 47, 112 (1925).

234. G. G. Devyatykh and I. A. Prolov, Zh. Neorgan. Khim., 8, 265 (1963); C. A., 59, 2179h (1963).

235. K. Schaefer and J. M. Gonzalez-Barredo, Z. Physik. Chem., 193, 334 (1944).

236. J. W. Straley, C. H. Tindal and H. H. Nielsen, Phys. Rev., 62, 161 (1942).

237. H. Dreeskamp, Z. Naturforsch., 19a, 139 (1964).

238. M. M. Faktor, J. Phys. Chem., 66, 1003 (1962).

239. W. L. Jolly, U.S. Atomic Energy Commission Report, UCRL No. 9630, 1961.

240. L. P. Lindeman and M. K. Wilson, Z. Physik. Chem., 9, 29 (1956).

241. V. A. Crawford, K. H. Rhee and M. K. Wilson, J. Chem. Phys., 37, 2377 (1962).

242. E. A. V. Ebsworth, S. G. Frankiss and A. G. Robiette, J. Mol. Spectroscopy, 12, 299 (1964).

243. J. E. Drake and W. L. Jolly, University of California, Lawrence Radiation Laboratory Report UCRL-10422, August, 1962.

244. S. R. Gunn and J. H. Kindsvater, J. Phys. Chem., 70, 1750 (1966).

245. F. E. Saalfeld and H. J. Svec, J. Phys. Chem., 70, 1753 (1966).

246. L. May and C. R. Dillard, J. Chem. Phys., 34, 694 (1961).

247. N. Flitcroft and H. D. Kaesz, J. Am. Chem. Soc., 85, 1377 (1963).

248. N. De Zoulov and E. Deltombe, Proc. 7th Intern. Comm. Electrochem. Thermodynam. and Kinet., 240 (1957).

249. G. R. Wilkinson and M. K. Wilson, J. Chem. Phys., 25, 784 (1956).

250. W. L. Jolly and J. R. Webster, unpublished data.

251. P. E. Potter, L. Pratt and G. Wilkinson, J. Chem. Soc., 524 (1964).

252. K. Clusius and A. Frank, Z. Physik. Chem., 34B, 405 (1936).

253. M. De Hemptinne and J. M. Delfosse, Ann. soc. sci. Bruxelles, 56B, 373 (1936); C. A., 31, 2512 (1937).

254. E. Lee and C. K. Wu, Trans. Faraday Soc., 35, 1366 (1939).

255. P. A. Tierney, D. W. Lewis and D. Berg, J. Inorg. Nucl. Chem., 24, 1165 (1962).

256. H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys., 21, 279 (1953).

257. Y. Wada and R. W. Kiser, Inorg. Chem., 3, 174 (1964).

258. S. Sundaram, F. Suszek and F. F. Clevland, J. Chem. Phys., 32, 251 (1960).

259. R. E. Weston, Jr. and M. H. Sirvetz, J. Chem. Phys., 20, 1820 (1952).

260. R. M. Lynden-Bell, Trans. Faraday Soc., 57, 888 (1961).

261. E. R. Nixon, J. Phys. Chem., 60, 1054 (1956).

262. M. Baudler and L. Schmidt, Naturwissenschaften, 44, 488 (1957).

263. F. E. Saalfeld and H. J. Svec, Inorg. Chem., 3, 1442 (1964).

264. H. R. Linton and E. R. Nixon, Spectrochim. Acta, 15, 146 (1959).

265. J. E. Drake and W. L. Jolly, J. Chem. Phys., 38, 1033 (1963).

266. S. R. Gunn, W. L. Jolly and L. G. Green, J. Phys. Chem., 64, 1334 (1960).

267. R. H. Sherman and W. F. Giauque, J. Am. Chem. Soc., 77, 2154 (1955).

268. J. M. Delfosse, Nature, 137, 868 (1936).

269. K. Tamaru, J. Phys. Chem., 59, 777 (1955).

270. H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys., 19, 1259 (1951).

271. F. E. Saalfeld and M. V. McDowell, Inorg. Chem., 6, 96 (1967).

272. E. Amberger and H. Boeters, Angew. Chem. (Int. Ed.) 1, 268 (1962).

273. A. Stock and W. Doht, Chem. Ber., 35, 2270 (1902).

274. American Petroleum Institute Research Project 44, "Infrared Spectral Data," Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1959.

275. D. C. Smith, J. Chem. Phys., 19, 384 (1951).

276. S. Sundaram, Can. J. Physics, 39, 370 (1961).

277. W. H. Haynie and H. H. Nielsen, J. Chem. Phys., 21, 1839 (1953).

278. D. Hagenmuller and R. de Pape, Compt. rend., 251, 2032 (1960)

279. B. Siegel, J. Chem. Education, 38, 496 (1961).

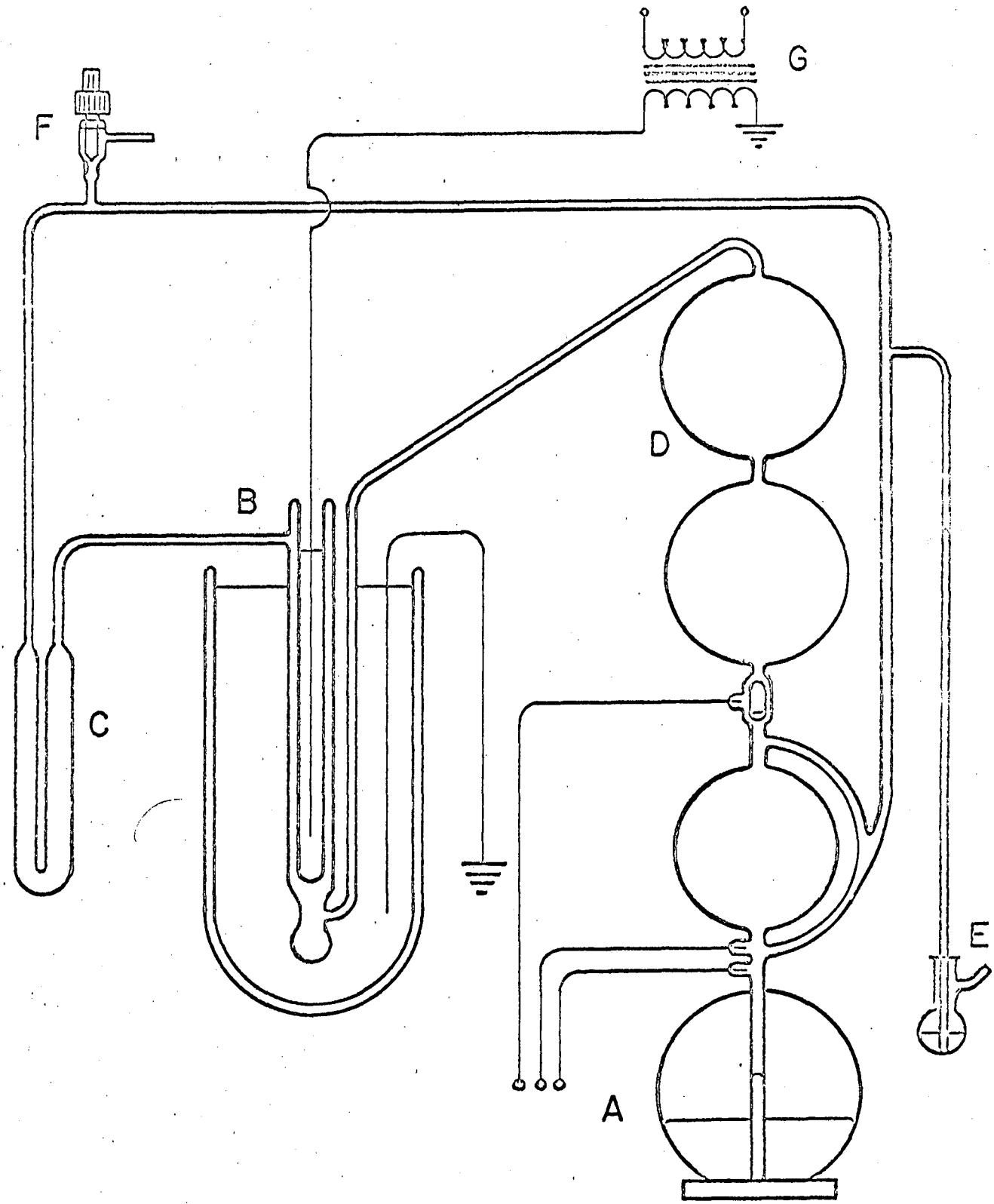


Fig. 1
Ozonizer Apparatus

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