GERMANIUM AND ITS INORGANIC COMPOUNDS

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I. Introduction

The first recorded reference to the existence of the element that is now called germanium is probably that of the English chemist J. A. R. Newlands, who observed (140) that silicon and tin formed the extremities of a triad, the middle member of which "is at present wanting." Following Newlands, Mendeleef not only recognized the possible existence of this element but predicted many of its properties.

In the fall of 1885, Albin Weisbach, professor of mineralogy at the Freiberg School of Mines, obtained from a vein of ore at the Himmelsfürst mine near Freiberg a new mineral which he named argyrodite. Weisbach asked Clemens Winkler, professor of chemistry at the Freiberg School of Mines, to make a quantitative analysis in order to establish the composition of the mineral (25). Winkler succeeded in isolating the sulfide of germanium by discovering that it is quite insoluble in concentrated acids.

Compared with the vast amount of information available about the chemistry of the more abundant elements, our knowledge of the chemistry of germanium is extremely meager. To date *Chemical Abstracts* has abstracted less than fifteen hundred articles on germanium. Many of these papers deal with organic compounds and have recently been reviewed (92). Because much of our knowledge of germanium is elementary, considerable material of a qualitative and descriptive nature has been included in this review, in order that the reader may more readily evaluate the discrepancies and contradictions that occur in the literature.

II. Nomenclature of Inorganic Germanium Compounds

In the early history of the element, germanium compounds were named as individual compounds and not as members of a particular class. In this review the recommendations of Scott (181) for the naming of inorganic compounds will be followed with a few minor exceptions, such as the use of commonly accepted names in place of or interchangeably with the recommended ones.

III. Elemental Germanium

A. OCCURRENCE

The mineral argyrodite, $4AgS \cdot GeS_2$, from which germanium was first obained (208), contains from 5 to 7 per cent of germanium, but this mineral is comparatively rare and is not an important source. Another sulfide mineral, germanite, $7CuS \cdot FeS \cdot GeS_2$, found in southwest Africa, contains about 6 per cent of germanium (44), but its value as a source of commercial quantities of germanium is still in doubt.

Most of the germanium produced in the United States comes from the smelting of germanium-rich zinc ores mined in the Tri-State district of Missouri, Kansas, and Oklahoma (143, 201). The zinc sulfide mineral in these ores contains from 0.01 to 0.1 per cent of germanium, and the germanium is obtained as a byproduct of zinc smelting. Recently, commercially important quantities of a germanium sulfide mineral, renierite, yielding from 6.4 to 7.8 per cent of germanium, have been discovered in the Prince Leopold copper mine at Kipushi in the Belgian Congo (202). Coal ashes and flue dusts are another potential source (124, 125).

B. PHYSICAL PROPERTIES

Elementary germanium is a silvery-white metal having much the outward appearance of bright solder when fused. This appearance is deceptive, however, since germanium is very hard and has a decided tendency to fracture when drilled or cut. When germanium is fractured, the break is shiny and hard, similar to that of metallic silicon. Like bismuth and gallium, the metal expands on freezing.

TABLE 1

The physical constants of germanium

Atomic number	34	Specific heat, cal./g.	0.074
Atomic weight	72.60	Hardness, Moh's scale	6.0–6.5
Density, g./ml., 20°C	5.36	Electrical resistivity, ohms/cm., 20°C	0.089
Atomic volume, ml./mole	13.2	Ionization potentials:	
Diameter of M^{+4} ion in crystals, cm.	5.3×10^{-9}	First electron	8.09
Melting point, °C	958.5	Second electron	15.86
Boiling point, °C	2700 (?)	Crystal form	Face-centered cubic

Germanium metal is not appreciably affected by water, 50 per cent sodium hydroxide, concentrated hydrochloric acid, or dilute hydrochloric or sulfuric acid. It is tarnished by 10 per cent sodium hydroxide and by concentrated nitric acid. Slight corrosion is observed with sulfuric acid and with hydrogen fluoride. It is dissolved by 3 per cent hydrogen peroxide. The metal is volatile at low pressure at 760°C. (138). It will absorb 0.186 ml. of hydrogen per gram of metal when melted and cooled in that gas (138).

The common physical properties of germanium are given in table 1.

Hopkins (81) places germanium below hydrogen in the activity series, since it will displace silver from its solution but will not displace copper, mercury, tin, antimony, or bismuth. Einecke (50) places germanium between zinc and tin in the electromotive series. Land, on the basis of electromotive force measurements (115), places germanium between copper and silver.

C. ELECTRICAL PROPERTIES

The electrical property of germanium that is receiving the greatest attention at present is its semiconductance. Germanium diodes and triodes are already replacing the conventional vacuum tube in many installations. Shockley has published a semipopular discussion of germanium triodes (183) as well as a detailed technical exposition (184).

Germanium may be easily deposited as a film on glass, quartz, or dense ceramic materials by the decomposition of monogermane at temperatures above

370°C. Practical use is made of this property in the construction of film resistors (31, 90). Resistances measured over a 2.5-cm. length of germanium film deposited inside 7-mm. tubing range from about 100 ohms to several megohms, depending upon the conditions of deposition. Such resistors have low temperature coefficients, varying from 0.001 to 0.003 ohm/°C. By depositing the germanium film over silver, resistors with lower resistance values but with temperature coefficients of less than 0.0001 ohm/°C. are obtained.

Germanium powder compacts show some microphone properties in that the resistance varies considerably with the external pressure. Complete return to the initial resistance does not result, however, and its possible application for microphone uses would seem to be limited by this factor.

The electrodeposition of germanium from aqueous baths is apparently limited to thin flashes of the metal, because of the low overvoltage of hydrogen on germanium (56). Copper, silver, tin, cobalt, and nickel have been codeposited with germanium from aqueous solutions. The intermetallic compound, Cu_3Ge, deposits from alkaline solution.

IV. Inorganic Compounds of Germanium

A. HALOGEN COMPOUNDS

1. The simple germanium(IV) halides

Preparation of germanium(IV) chloride: Germanium(IV) chloride is usually prepared by the action of chlorine upon metallic germanium or by the action of hydrogen chloride upon germanium(IV) oxide (9, 10, 32, 24, 49, 55, 62, 78, 79, 121, 148, 149, 156, 188, 191). The preparation of germanium(IV) chloride from germanium(IV) oxide is described in detail in Volume II of *Inorganic Syntheses* (55).

Physical properties of germanium(IV) chloride: Germanium(IV) chloride is a colorless mobile liquid with a specific gravity, $d_{25°}^{25°}$, of 1.874; it boils at 83.1°C. and freezes at −49.5°C. It fumes in the air and is hydrolyzed by water. Germanium(IV) chloride is practically insoluble in concentrated hydrochloric acid and is not attacked by concentrated sulfuric acid; this behavior is in sharp contrast to the behavior of lead(IV) chloride, which reacts with explosive violence when heated (64).

Germanium(IV) chloride is soluble in absolute ethanol, carbon disulfide, benzene, chloroform, and ethyl ether. It is completely miscible with sulfur dioxide (13) and partially miscible with liquid phosphine (77). The molecular refractivity is 31.465; the atomic refractivity of germanium, calculated from this value, is 7.597 (121). The molecular volume is 84.3 at 0°A. (12), and the dielectric constant is 2.65 at 30°C. (123). The indices of refraction and the vapor pressures of germanium(IV) chloride at various temperatures are tabulated in reference 121.

The chemical properties of germanium(IV) chloride: Germanium(IV) chloride enters into Grignard, Wurtz–Fittig, and similar reactions very readily. It undergoes disproportionation with other halides. Most of the other reactions that have been investigated are concerned with its behavior in ammonia and in certain organic compounds.

Dry gaseous ammonia reacts with germanium(IV) chloride to yield a light fluffy white powder of the composition $GeCl_4 \cdot 6NH_3$; this powder is a mixture of one molecule of germanium imide, $Ge(NH)_2$, and four molecules of ammonium chloride (156, 198). A similar reaction occurs with an excess of ethylamine, which yields a mixture of "germanium diethyl diimide," $Ge[N(C_2H_2)_5]_2$, and ethylamine hydrochloride in a 1:4 ratio. The tetrachlorides of silicon and germanium differ from the tetrachlorides of tin and lead in that the latter two form true ammines, whereas silicon and germanium do not form ammines (199).

Aniline reacts with germanium(IV) chloride to give a solid of the composition $GeCl_4 \cdot 4C_6H_5NH_2$, regardless of whether the chloride or the base is present in excess (199). This solid may be separated into aniline hydrochloride and an ether-soluble portion thought to be the hydrochloride of the diimide, $Ge(NC_6H_5 \cdot HCl)_2$.

Germanium(IV) chloride reacts with eight molecular proportions of piperidine:

$$GeCl_4 + 8C_5H_{10}NH \rightarrow Ge(NC_5H_{10})_4 + 4C_5H_{10}NH \cdot HCl$$

The resulting germanium compound is stable. This stability is readily explained by the fact that the nitrogen atoms are an integral part of the cylic piperidine radicals and are combined with germanium only externally, so that the formation of an unsaturated compound would involve rupture of the stable piperidine ring. Should similar saturated compounds be formed by the interaction of the chloride with bases such as primary amines, internal condensation could readily occur. It is presumed that this course is the one actually followed, and in the case of aniline the complete reactions would be:

$$GeCl_4 + 8C_6H_5NH_2 \rightarrow Ge(NHC_6H_5)_4 + 4C_6H_5NH_2 \cdot HCl$$

$$Ge(NHC_6H_5)_4 \rightarrow Ge(NC_6H_5)_2 + 2C_6H_5NH_2$$

$$Ge(NC_6H_5)_2 + 2C_6H_5NH_2 \cdot HCl \rightarrow Ge(NC_6H_5 \cdot HCl)_2 + 2C_6H_5NH_2$$

The difference in behavior between silicon and germanium becomes more pronounced when the interactions of their chlorides with secondary amines is considered. It has been reported (128) that the compound $(C_2H_5)_2NSiCl_3$ is obtained by the reaction of silicon(IV) chloride with diethylamine. The reaction in the case of germanium is quite different (199) and yields a solid product of variable composition, the exact nature of which was not determined.

Preparation of germanium(IV) bromide: Germanium(IV) bromide is prepared by passing bromine vapor over metallic germanium (34, 209) or by the action of hydrobromic acid on germanium(IV) oxide (79, 117). The latter method is more efficient and results in a 90 per cent yield.

Physical properties of germanium(IV) bromide: Germanium(IV) bromide melts at 26.1°C. In the liquid state it is a colorless mobile liquid which fumes in contact with air. Its specific gravity, $d_{29°}^{29°}$, is 3.1315, and its refractive index at 25°C. is 1.6269 (34). Its vapor pressure ranges from 3.6 mm. at 18.35°C. to

649.8 mm. at 180.39°C. (17). The substance shows the property of supercooling to a marked degree and may be chilled to -18°C. before solidifying. It is soluble in ethanol, carbon tetrachloride, benzene, and ether without decomposition. Slow decomposition with liberation of bromine takes place in acetone.

Chemical properties of germanium(IV) bromide: Germanium(IV) bromide hydrolyzes rapidly in water with the evolution of heat, depositing germanium(IV) oxide. In aqueous potassium hydroxide the hydrolysis is much more vigorous, the oxide formed dissolving in the alkaline solution. Addition of carbon dioxide precipitates germanium(IV) oxide (34).

When germanium(IV) bromide and concentrated sulfuric acid are brought into contact the bromide sinks to the bottom and no visible changes occur at room temperature even for several days (34). This behavior is somewhat similar to that of the tetrachlorides of tin and lead, although the latter two substances decompose in a much shorter length of time.

A vigorous reaction occurs between germanium(IV) bromide and concentrated nitric acid (34). The nitric acid is reduced and copious quantities of nitric oxide are evolved. The products of the reaction have not been identified.

Preparation of germanium(IV) iodide: Germanium(IV) iodide is obtained in 85 per cent yield by refluxing germanium(IV) oxide with 57 per cent hydriodic acid (117). It is also formed by heating the metal in iodine vapor (35).

Chemical properties of germanium(IV) iodide: Germanium(IV) iodide is stable in air (35). It hydrolyzes slowly in water, depositing germanium(IV) oxide. It does not react with sulfuric acid. Concentrated hydrochloric acid dissolves the iodide slowly at room temperature.

Germanium(IV) iodide dissociates into germanium(II) iodide and iodine when heated (35). Heating germanium(IV) iodide with germanium metal gives small yields of germanium(II) iodide (18). Partial reduction occurs when germanium(IV) iodide is heated with hydrogen or acetylene, while zinc in 25 per cent sulfuric acid yields germanium(II) oxide and small quantities of monogermane (7).

Preparation of germanium(IV) fluoride: Clemens Winkler attempted to prepare germanium(IV) fluoride but did not succeed in isolating it. No further work was published on the compound until 1921, when a detailed study of the halogen compounds of germanium was begun at Cornell University (34).

Dennis and Laubengayer (42) prepared germanium(IV) fluoride in 87 per cent yield by heating barium hexafluogermanate(IV), $BaGeF_6$, in quartz containers. The germanium(IV) fluoride was purified by distillation. Earlier attempts to prepare the tetrafluoride by this method, using apparatus made of copper, yielded only small quantities of the germanium(IV) fluoride, owing to the fact that germanate was reduced by the copper to germanium(II) fluoride, which was obtained as an oily liquid in warm parts of the delivery tube and as a white solid at room temperature.

Physical properties of germanium(IV) fluoride: At room temperatures germanium(IV) fluoride is a colorless gas fuming strongly in air. It has a pungent garlic-like odor. When it is cooled rapidly in liquid air, a flocky white mass of minute crystals is obtained. Slower cooling gives large, well-formed, prismatic and diamond-shaped cyrstals.

Under ordinary conditions the fluoride does not form a liquid phase but sublimes directly when warmed. Under a pressure of 3032 mm. of its own vapor, germanium(IV) fluoride melts at -15°C. Measurements of its vapor density (42, 57, 58) indicate the molecular formula GeF_4. The specific magnetic susceptibility, as computed by the Angus method, is -0.33 ± 0.01, and an observed value of -49 ± 2 has been reported for the molecular susceptibility (75, 107).

Chemical properties of germanium(IV) fluorides: When germanium(IV) fluoride is bubbled through water, the gas is rapidly absorbed with the evolution of considerable heat. An acid solution results, and if the passage of the gas is continued there is separation of gelatinous hydrated germanium(IV) oxide. Addition of potassium hydroxide to the clear solution precipitates potassium hexafluogermanate(IV), indicating the presence of fluogermanic acid (42).

$$3GeF_4 + 2H_2O \rightarrow GeO_2 + 2H_2GeF_6$$

Germanium(IV) fluoride does not appreciably attack dry glass at ordinary temperatures, but etching results if a trace of moisture is present. If the glass is finely divided, as in glass wool, the attack is quite rapid. There is no action upon quartz below 700°C. No dissociation was observed when the gas was heated to 1000°C. in a quartz tube under a pressure of 100 mm.

Germanium(IV) fluoride has a very irritating effect upon the nasal passages, and inhalation of small amounts causes extreme hoarseness.

2. The simple germanium(II) halides

Germanium(II) chloride: Germanium(II) chloride is prepared by passing germanium(IV) chloride vapor over heated germanium (43). Attempts to prepare the compound by the removal of hydrogen chloride from trichlorogermane or by the reduction of germanium(IV) chloride have not been successful (18, 38, 43, 208). When heated, germanium(II) chloride begins to dissociate at 75°C.; at 450°C. dissociation into germanium and germanium(IV) chloride is complete.

Chemical properties of germanium(II) chloride: Dry oxygen slowly converts germanium(II) chloride into germanium(IV) oxide and germanium(IV) chloride:

$$2GeCl_2 + O_2 \rightarrow GeO_2 + GeCl_4$$

Germanium(II) chloride is hydrolyzed by water. When moist oxygen is passed over the compound some oxidation probably takes place in accordance with the preceding reaction, but the moisture acts much more vigorously on the substance than does the oxygen (38). The first stage is doubtless the following reaction:

$$GeCl_2 + 2H_2O \rightarrow Ge(OH)_2 + 2HCl$$

The hydrogen chloride then instantly combines with unchanged germanium(II) chloride to form trichlorogermane, which is carried out by the current of oxygen.

Ammonium hydroxide converts germanium(II) chloride into an orange-colored substance, the composition of which has not been determined (38). Concentrated hydrochloric acid changes it into a white solid, which soon dissolves in the acid with the probable formation of trichlorogermane. Chlorine acts rapidly upon germanium(II) chloride, converting it to germanium(IV) chloride. Bromine forms a colorless liquid consisting almost entirely of a mixture of germanium(IV) chloride and germanium(IV) bromide with not more than a trace of the mixed halide, $GeBr_2Cl_2$. Hydrogen sulfide acts at once upon germanium(II) chloride at room temperature, yielding germanium(II) sulfide (38).

The addition of cesium chloride to a solution of germanium(II) chloride strongly acidified with hydrochloric acid gives a sparsely soluble, white, microcrystalline precipitate of trichlorogermylcesium, $CsGeCl_3$ (193). The rubidium analog, $RbGeCl_3$, is obtained with rubidium chloride, but similar compounds are not obtained with lithium chloride, sodium chloride, or potassium chloride. At 100°C., in an atmosphere of dry hydrogen chloride, the cesium salt liberates germanium(II) chloride. At higher temperatures germanium(II) chloride is not liberated in the presence of dry hydrogen chloride but trichlorogermane is formed instead.

Germanium(II) chloride forms two types of salts with alkaloids such as quinine and pilocarpine (193). Germanium(II) chloride solutions, in common with germanium(II) bromide, reduce gold and silver salts, potassium permanganate, and indigocarmine (7).

Germanium(II) bromide: Germanium(II) bromide is obtained as one of the products resulting from preparation of tribromogermane by the action of hydrogen bromide on heated powdered germanium (18). The compound is a colorless crystalline solid. Rapid crystallization yields the crystals as small glistening plates, while gradual crystallization results in the formation of needles.

Germanium(II) bromide is not appreciably soluble in benzene, toluene, or other hydrocarbons unless germanium(IV) bromide is also present. It dissolves in alcohol and acetone to give colorless solutions of strong reducing power.

The color of the solution of germanium(II) bromide in germanium(IV) bromide is always yellow, whereas in the solid state both are colorless. Brewer and Dennis relate the color to the unsaturated nature of the dihalide and compare it with the analogous carbon compounds (18).

Chemical properties of germanium(II) bromide: When germanium(II) bromide is heated a black residue results simultaneously with the appearance of drops of an oily liquid which subsequently volatilize. The final decomposition is probably represented by the following equation (18):

$$2GeBr_2 \rightarrow Ge + GeBr_4$$

Solutions of germanium(II) bromide are strong reducing agents. Water converts the compound to the yellow, hydrated germanium(II) hydroxide, but an excess of water dissolves the product to give a solution showing the characteristics of the germanium(II) ion.

Germanium(II) bromide absorbs bromine, developing some heat and forming germanium(IV) bromide, but the reaction is not vigorous. It unites with hydrogen bromide to form tribromogermane (18).

Germanium(II) iodide: This compound is prepared from germanium(IV) iodide by reduction with hypophosphorous acid (5):

$$GeI_4 + H_2O + H_3PO_2 \rightarrow GeI_2 + 2HI + H_3PO_3$$

Other methods include treatment of germanium(II) chloride with potassium iodide and the solution of germanium(II) oxide in concentrated hydriodic acid (18, 40, 194).

Germanium(II) iodide is a yellow solid, insoluble in hydrocarbons but slightly soluble in chloroform and carbon tetrachloride. It can be recrystallized from concentrated hydriodic acid. Solutions of the compound in water and in dilute acids have reducing properties associated with the germanium(II) ion.

Chemical properties of germanium(II) iodide: When germanium(II) iodide is exposed to air it is slowly hydrolyzed with the formation of germanium(IV) oxide. When heated in air it does not melt, but at 210°C. it is rapidly oxidized to a mixture of germanium(IV) oxide and germanium(IV) iodide. At higher temperatures decomposition occurs with the formation of germanium(IV) iodide and free germanium. The compound is quite stable when preserved in a sealed tube (18, 151).

Germanium(II) fluoride: The preparation of germanium(II) fluoride has not been definitely established, but heating the vapors of germanium(IV) fluoride with metallic germanium yields a white sublimate believed to be the difluoride (7, 42).

Comparison of the Group(IV) dihalides: A comparison of the germanium(II) halides with the analogous halides of tin and lead shows that the thermal stability of the germanium(II) halides is in conformity with the position of this element in the Periodic Table (16). At elevated temperatures the germanium dihalides dissociate much more readily than do the tin(II) and lead(II) halides, the decomposition proceeding according to the final reaction:

$$2GeX_2 \rightarrow Ge + GeX_4$$

In general, there is an increase in thermal stability and a decrease in reactivity with an increase in the atomic number of either the Group IV element or the halogen. Thus germanium(II) chloride reacts with chlorine with almost uncontrollable speed, whereas tin(II) chloride unites readily but quietly at room temperature and lead(II) chloride takes up two additional atoms of chlorine only under special conditions. In contrast to the dihalides, the tetrahalides show decreasing thermal stability with an increase in the atomic number of the Group IV element.

The reactivity of the Group IV dihalides towards oxygen is again less with the increase in atomic number of the Group IV element. Lead(II) chloride, for example, is stable in air and is only slowly decomposed when heated. Tin(II) chloride is fairly stable in air and yields tin(IV) chloride and an oxychloride when heated to its boiling point. Germanium(II) chloride is rapidly attacked by oxygen at room temperature. Germanium(II) bromide and germanium(II) iodide are less readily affected by oxygen, the latter being converted to germanium(IV) oxide and germanium(IV) iodide when heated in air to 210°C.

As a direct corollary of the behavior towards oxygen, the reducing power decreases with the increase in the atomic number of the Group IV element, a solution of germanium(II) chloride having powerful reducing action, whereas lead(II) is almost lacking in reducing action.

In general the germanium(II) halides are but slightly soluble in hydrocarbons, but they react with liquids which contain an actual or potential hydroxyl group (16). This action is presumably solvolytic in nature, yet, whereas the action of a small quantity of water on germanium(II) bromide produces a voluminous precipitate, no such precipitate is formed with dry ethanol.

Germanium(II) iodide reacts slowly with cold water but is soluble in large quantities of water. Alcohol dissolves it readily, but the complete lack of color in the alcoholic solution indicates that possibly dissociation, but more probably alcoholysis, has taken place. Since recrystallization cannot be effected from the colorless solutions, either aqueous or alcoholic, these solutions cannot be regarded as strictly analogous to the colorless solution of lead(II) iodide in hot water.

Tin(II) halides are soluble in water. There is evidence of hydrolysis but the salts can be recrystallized from aqueous solution in a hydrated condition. In contrast to this fact, the lead(II) halides are remarkable for their extremely low solubility in cold water and their steep solubility curves, hydrolysis being negligible.

With regard to non-polar solvents, tin(II) chloride is soluble to a small extent in benzene and other non-hydroxylic solvents which are quite without action upon lead salts.

Solubility relationships, therefore, bear out the more definitely polar character of germanium(II) iodide (16). That is to say, the diiodide forms the link with the metallic, or salt-like, halides, whereas the dichloride and the dibromide are more closely allied to the halides of the non-metals and metalloids. As might be expected from certain theories of solution involving similarity of constitution between solvent and solute, the most effective solvents for germanium(II) chloride and germanium(II) bromide appear to be the corresponding tetrahalides.

The solution formed by the colorless germanium(II) bromide in germanium(IV) bromide is yellow in color and it is possible that the colorless solid is a polymer, whereas the yellow solution contains unassociated dibromide. A polymerization of this sort is seen in the case of the tin(II) chloride which, near its boiling point, has a vapor density that indicates the presence of molecules of the polymer Sn_2Cl_4.

Germanium(II) salts are quantitatively precipitated from slightly acid solutions by hydrogen sulfide as deep orange-red germanium(II) sulfide (7).

3. Trihalogermanes

The trihalo derivatives of monogermane possess properties that are unique in comparison with the properties of similar compounds of the other Group IV elements. Present knowledge of these compounds indicates a close relationship to the germanium(II) halides.

Preparation of trihalogermanes: Treating germanium(II) chloride with hydrogen chloride results in a highly exothermic reaction yielding trichlorogermane (43):

$$GeCl_2 + HCl \rightarrow HGeCl_3$$

The germanium(II) chloride is prepared by passing germanium(IV) chloride over heated germanium. Tribromogermane is prepared by a similar reaction (18).

Trichlorogermane is also formed by the action of hydrogen chloride upon heated germanium or germanium sulfide, but the product is a mixture of trichlorogermane and germanium(IV) chloride. These two compounds cannot be separated by fractionation (43, 208).

Physical and chemical properties of the trihalogermanes: Trichlorogermane is a colorless mobile liquid having a density of 1.93 g./ml. (43). When heated, it begins to decompose at 140°C. and is rapidly decomposed at 175°C. During thermal decomposition, germanium(II) chloride and hydrogen chloride are apparently first formed, the germanium(II) chloride then slowly dissociating as the temperature increases, yielding metallic germanium and germanium(IV) chloride.

Trichlorogermane becomes turbid in the presence of air. The exact reaction is not known but two possibilities have been considered:

$$2HGeCl_2 + O_2 \rightarrow 2GeOCl_2 + 2HCl \qquad (209)$$

$$4HGeCl_3 + O_2 \rightarrow 2GeCl_4 + 2GeCl_2 + 2H_2O \qquad (43)$$

The amount of trichlorogermane in a mixture of this compound with germanium(IV) chloride may be determined by titration with iodine, which does not react with germanium(IV) chloride but acts on trichlorogermane according to the following equation:

$$HGeCl_3 + I_2 \rightarrow GeICl_3 + HI$$

The actual titration is performed by breaking a sealed bulb containing the sample under a solution containing an excess of iodine and some hydrochloric acid and titrating the excess iodine with sodium thiosulfate solution (43).

The reactions of trichlorogermane are essentially those of germanium(II) chloride and hydrogen chloride (16). When trichlorogermane is brominated, hydrogen bromide is not evolved as might be expected from the reaction:

$$HGeCl_3 + Br_2 \rightarrow GeBrCl_3 + HBr$$

In every reaction where substitution by two similar groups takes place, hydrogen chloride is evolved. The product formed by the substitution is the same as that which would result from the addition of such groups to germanium(II) chloride. Trichlorogermane is polar to a marked degree, in contrast to the carbon analog, chloroform, which is essentially non-polar.

Electrolysis of a hydrochloric acid solution of trichlorogermane under specified conditions produces germanium(II) hydroxide at the anode and no germanium at the cathode (174). The explanation is suggested that the ion $GeCl_3^-$ is formed at the anode and hydrolyzed by the dilute hydrochloric acid.

Treatment of trichlorogermane with silver oxide produces germanium oxychloride, $GeOCl_2$:

$$2HGeCl_3 + 3Ag_2O \rightarrow 2GeOCl_2 + 4Ag + 2AgCl + H_2O$$

Germanium oxychloride is a clear colorless oily liquid, insoluble in all inorganic and organic solvents and rapidly hydrolyzed by water. Heating the compound decomposes it into germanium(II) oxide (174).

4. Mixed halides of germanium(IV)

As early as 1929 Raeder (157) pointed out that when two different halides of phosphorus, arsenic, antimony, titanium, tin, and probably germanium are mixed, the different halogen atoms are readily interchangeable and enter into reciprocal interchanges. The equilibria are easily disturbed, and mixed halides are formed that cannot be isolated in solid or gaseous form.

In contrast, the tetrahalides of carbon and silicon have very little reactivity, are reluctant to enter into reciprocal interchanges, and form mixed halides only by special methods of preparation. When formed, the mixed halides of these two elements may be isolated as stable compounds.

In 1892 Swarts (190) discovered that partial replacement of halogen in an aliphatic halide by fluoride could be accomplished through the use of antimony trifluoride in the presence of a catalyst. Forty years later Booth and Morris (14) applied this technique to the fluorination of germanium(IV) chloride by antimony(III) fluoride, using antimony(V) chloride as a catalyst, and obtained the three mixed germanium(IV) chlorofluorides, $GeClF_3$, $GeCl_2F_2$, and $GeCl_3F$.

All of the mixed chlorofluorides of germanium are unstable and rearrange even at the temperature of solid carbon dioxide to form the tetrachloride and the tetrafluoride. When these compounds are heated in contact with metallic copper, rapid and sometimes explosive decomposition takes place with the formation of germanium(II) chloride and germanium(II) fluoride (14).

The chlorobromides of germanium also tend towards random distribution. When compared with similar compounds of the other elements of Group IV it has been observed (60) that, whereas the halides of carbon require a catalyst such as aluminum chloride, the mixed halides of silicon, germanium, and tin all react with successively greater speed at distillation temperatures. Chloro-isocyanate compounds of germanium, such as $GeCl_3NCO$, undergo similar rearrangements.

Iodotrichlorogermane has been mentioned as resulting from the titration of trichlorogermane with iodine (43). The proposed reaction,

$$HGeCl_3 + I_2 \rightarrow GeICl_3 + HI$$

is in direct contradiction to the results observed when trichlorogermane is brominated (16), in which case hydrogen chloride is evolved instead of the expected hydrogen bromide.

5. The hexahalogermanates(IV)

The first recorded preparation of a hexahalogermanate is that of potassium hexafluogermanate(IV) by Krüss and Nilson (114), who precipitated the compound by adding potassium fluoride to a solution of germanium(IV) oxide in hydrofluoric acid. Cesium hexafluogermanate(IV), Cs_2GeF_6, is obtained as a crystalline precipitate by dissolving germanium dioxide in hydrofluoric acid and adding a solution of cesium fluoride. Rubidium hexafluogermanate(IV) is prepared in similar fashion (185, 186).

Barium hexafluogermanate(IV) results as a granular precipitate when germanium dioxide is dissolved in 48 per cent hydrofluoric acid and the calculated amount of barium chloride is added in the form of a saturated solution. When heated in a quartz tube the compound begins to decompose at 500°C., yielding barium fluoride and germanium tetrafluoride. Evolution of germanium tetrafluoride becomes copious at 600°C. and very rapid at 700°C. Heating barium hexafluogermanate in a copper tube does not give the expected tetrafluoride, presumably owing to its reduction to copper(II) fluoride and germanium(II) fluoride by the copper (42).

When germanium tetrafluoride is bubbled through water the gas is rapidly absorbed, considerable heat is evolved, and a clear solution with a strong acid reaction results. When potassium hydroxide is added to the clear solution, potassium hexafluogermanate precipitates, a fact which has been interpreted (42) to indicate the formation of hexafluogermanic acid:

$$3GeF_4 + 2H_2O \rightarrow GeO_2 + 2H_2GeF_6$$

A series of compounds of hexafluogermanic acid with nitrogen bases have been made (47) and are listed in table 5 of Section VI.

B. THE OXIDES AND HYDROXIDES OF GERMANIUM

1. *Germanium(IV) oxide*

Germanium dioxide, prepared by the hydrolysis of the germanium tetrahalides or the alkali germanates, forms an exceedingly fine-grained precipitate, the individual particles of which do not reveal any definite structure under the microscope. However, examination by powder x-ray diffraction methods shows that the material is microcrystalline. If the dioxide is formed under conditions more favorable for crystal growth, grains of appreciable size may be obtained. Germanium dioxide obtained by crystallization from its aqueous solution is in the form of trigonal crystals closely resembling trigonal-trapezohedral low-quartz (65, 211). The fundamental lattice is simple hexagonal.

Crystalline germanium dioxide is also obtained by the devitrification of the glass formed when fused germanium dioxide solidifies. The crystals prepared in this manner gives the same x-ray diffraction patterns as the crystals produced by the hydrolysis of the tetrachloride or by crystallization from aqueous solutions and are, therefore, the same crystalline modification (132). This form of germanium is somewhat soluble in water; hence it has been termed "soluble" germanium dioxide in many of the earlier papers.

Ignition at about 380°C. of the residue left from the evaporation of an aqueous solution of germanium dioxide produces a second crystalline modification, sometimes designated as "insoluble" germanium dioxide (135). Conversion to the insoluble form by this procedure is never complete; the yield of the insoluble form depends upon the conditions of evaporation and upon the time and temperature of ignition of the residue. Temperatures above and below 380°C. decrease the yield and the yield increases with the time of ignition, although at a decreasing rate approaching a limiting maximum of about 15 per cent.

The insoluble form is extraordinarily inert towards substances which act readily on the oxide in the freshly precipitated condition. Besides being virtually insoluble in water, it does not react with hydrochloric or hydrofluoric acid. It gives a powder x-ray diffraction pattern completely different from that of the soluble modification. Quantitative conversion of the soluble hexagonal modification of germanium dioxide into the insoluble rutile type results from the addition of saturated ammonium fluoride solution to dioxide that has been ignited to 380°C. and then reheating of the mixture again to 380°C. for 8 hr. Lowering the heating temperature below 380°C. and omitting the slow evaporation of the aqueous solution prevents the conversion to the rutile type.

TABLE 2

Properties of germanium dioxide

PROPERTY	INSOLUBLE CRYSTALLINE FORM	SOLUBLE CRYSTALLINE FORM	GLASS
Crystal system	Tetragonal	Hexagonal	Amorphous
Crystal type	Rutile	Low-quartz	
Density, g./ml., 25°C	6.239	4.228	3.637
Density, g./ml., x-ray	6.26	4.28	
Index of refraction, ω	1.99	1.695	
Index of refraction, ϵ	2.05–2.10	1.735	1.607
Inversion point	1033 ± 10°C.	1033 ± 10°C.	
Melting point	1086 ± 5°C.	1116 ± 4°C.	
Solubility, g./100 g. water	Insoluble (25°C.)	0.453 (25°C.)	0.5184 (30°C.)
Action of hydrofluoric acid	None	Reacts, giving H_2GeF_6	Reacts, giving H_2FeF_6
Action of hydrochloric acid	None	Reacts, giving $GeCl_4$	Reacts, giving $GeCl_4$
Action of 5 *N* sodium hydroxide at 100°C	Dissolves very slowly	Dissolves rapidly	Dissolves rapidly

A very soluble, transparent, and "glassy" form results on quickly cooling melted germanium dioxide obtained from any source (132, 175). This latter form is amorphous and a true glass. It does not have a definite melting point but softens far below the melting point of the other form of the oxide and is completely soluble in water. It spontaneously devitrifies into an opaque white glass resembling porcelain.

The "insoluble" form is chiefly distinguished by its extraordinary inertness towards alkaliës and acids, and especially by its inertness towards hydrofluoric acid, which dissolves the other modifications of the oxide with a hissing noise and the evolution of much heat, a fact noted by Krüss and Nilson (114) as early as 1887. After fusion all of the commonly known properties of the "soluble" form are regained.

Müller (133) reports the solubility of the "insoluble" form as 0.00045 g./100 g. of water at 25°C. and 0.00117 g./100 g. at 100°C. The specific gravities, $d_{24°}^{24°}$, are given as 6.0039 for the "insoluble" form, 3.5205 for the "soluble evaporated" form, 3.3037 for the soluble "glassy" form, and 3.6128 for the soluble "hydrolyzed" form. These values vary from those reported by Laubengayer and Morton (119) in table 2.

The solubility of the hydrolyzed form of germanium dioxide is repressed by hydrochloric acid from a solubility of 0.4470 g./100 ml. of pure water to a minimum of 0.073 g./100 ml. at an acid concentration of 5.3 *N* (153). At higher concentrations of hydrochloric acid the solubility increases rapidly. With sulfuric acid the solubility diminishes continuously as the concentration is increased to 16 *N*, a fact which is interpreted to mean that germanium sulfate is incapable of existence, at any rate in solutions containing much water.

The solubility of germanium dioxide in sodium hydroxide solutions increases with increasing concentration of sodium hydroxide, but the condition in which the germanium dioxide exists in alkali solutions is uncertain (153). The solutions are colloidal and may contain salts of condensed germanic acids. Addition of alkali to a solution of germanium dioxide in 2 *M* potassium chloride results in the formation, at pH 8–10.2, of a white microcrystalline precipitate corresponding to the composition $K_2Ge_5O_{11}$ (196). A close resemblance between the systems K_2O–GeO_2 and K_2O–SiO_2 has been noted (152).

Treatment of tetraethoxygermane in alcohol with calculated amounts of water gives a firm gel readily freed from alcohol (116). Methods involving aqueous solutions are apparently unsuitable for the production of germanium dioxide gels free from other compounds. Hydrolysis of the tetrachloride, tetrabromide, or tetraiodide by water and by aqueous solutions of the corresponding hydrogen halides always yields crystalline germanium dioxide. The same form is obtained when aqueous solutions of sodium germanate are treated with hydrochloric acid. A gelatinous precipitate is formed when carbon dioxide is bubbled through dilute solutions of sodium germanate, but this gel is difficult to obtain free from sodium ions.

Germanium dioxide gel has an adsorptive power for the vapors of benzene, ethyl ether, and carbon tetrachloride comparable to that of silica gel. The gel adsorbs water vapor, but upon the removal of the adsorbed water the adsorptive power of the gel for benzene is decreased. The colloidal particles in germanium dioxide sol are negatively charged (175).

Germanium dioxide undergoes appreciable reaction with carbon tetrachloride at 500°C. (33):

$$GeO_2 + CCl_4 \rightarrow GeCl_4 + CO_2$$

and

$$GeO_2 + 2CCl_4 \rightarrow GeCl_4 + 2COCl_2$$

The formation of $GeOCl_2$ was not observed in the above case. Treatment with bromine trifluoride results in the quantitative evolution of oxygen (51):

$$3GeO_2 + 4BrF_4 \rightarrow 3GeF_4 + 3O_2 + 2Br_2$$

Solid–solid reactions of lithium hydride with germanium dioxide at 610°C. reduce the dioxide to the monoxide and some free germanium. Treatment of ignited germanium dioxide with thionyl chloride in a bomb under pressure at 300°C. results in partial formation of $GeCl_4$ (74).

Germanium dioxide is reduced to the monoxide by heating an intimate mixture of equivalent quantities of germanium and germanium dioxide at low pressure (138), but the reaction appears to be incomplete. The reaction begins vigorously at about 800°C. with volatilization of germanium(II) oxide.

The Ge–GeO_2 electrode has been found unsatisfactory for the determination of hydrogen-ion concentration (141, 142). When used for potentiometric titrations the electrode functions fairly well except for the titration of weak bases and salts by hydrochloric acid, where it is generally unsatisfactory.

The heat of formation of germanium dioxide at 20°C. and constant pressure as determined by the combustion of the metal (11) is 128.1 kcal. ± 0.5 per cent. The heat of formation of germanium tetrachloride was calculated to be 125 kcal. The heats of solution of germanium dioxide at 12°, 22°, 32°, and 42°C. are, respectively, 1310, 2380, 3380, and 3400 cal. (175).

Germanium light flint, crown, barium crown, and boro-crown glasses have been made by substituting equimolecular amounts of germanium dioxide for silicon dioxide in the corresponding silicate glasses (41). Germanium glasses have a higher refractivity and dispersion, approximately the same transmission in the visible and infrared regions, and lower transmission in the ultraviolet than do comparable silicate glasses. The partial dispersion ratios of germanium and silicate glasses are about the same. Germanium glasses have a greater density, a higher coefficient of expansion, about the same hardness, and lower softening temperatures. Such glasses devitrify somewhat more readily and their durability and resistance to weathering is slightly lower than that of comparable silicate glasses. Partial replacement of silicon dioxide by germanium dioxide (110) results in lower chemical stability, lower viscosity, shorter melting time, and greater ease of purification.

2. Germanium(II) oxide

The first serious study of germanium(II) oxide was made by Dennis and Hulse (37). These investigators prepared it by dissolving germanium dioxide in a slight excess of 5 *N* potassium hydroxide, adding hydrochloric acid until the solution was 5 *N* with respect to hydrogen chloride, and reducing the dioxide by treatment with 30 per cent hypophosphorous acid at 95°C. for 2 hr. The wet monoxide is readily oxidized by air, and the precipitation and subsequent washing must be done in an inert atmosphere. Germanic salts are reduced by zinc in 25 per cent sulfuric acid to a voluminous flocculent precipitate of germanium(II) oxide (7).

Freshly precipitated germanium(II) oxide varies in color from yellow to red, depending upon the conditions of precipitation. It is readily soluble in the halogen acids. Dilute sulfuric acid changes it to a dark brown color, probably owing to partial dehydration, and causes slow decomposition. It is only slightly soluble in alkalies but forms red colloidal solutions. When the oxide is dried at reduced pressure water is steadily removed and no evidence of the presence of any definite hydrates is found. As the temperature of drying is raised, the color changes from red to brown to black with a decrease in solubility.

Hydrous germanium(II) oxide is completely dehydrated when heated in nitrogen to 650°C., yielding jet-black crystals. Anhydrous germanium(II) oxide is not acted upon by moisture or atmospheric oxygen at room temperature. It is attacked slightly, if at all, by hydrochloric or sulfuric acid or by alkalies. It is slowly oxidized by fuming nitric acid, potassium permanganate, or chlorine water and readily oxidized by ammoniacal hydrogen peroxide. Oxidation in dry air begins at 550°C.

When heated in nitrogen in a platinum or nickel boat to a temperature above 550°C. germanium(II) oxide yields germanium dioxide and metallic germanium, the latter forming an alloy with the metal of the boat. When heated in boats of siliceous materials the monoxide reacts above 800°C. to form yellow glazes.

Germanium(II) oxide is rapidly attacked by hydrogen chloride at about 175°C., with the formation of trichlorogermane and water. Chlorine attacks the compound at 250°C., forming germanium dioxide and germanium tetrachloride. Bromine has similar action. Dennis and Hulse (37) reported that no evidence for the formation of the oxychloride, $GeOCl_2$, could be found.

3. Germanium(II) hydroxide

Germanium(II) hydroxide is formed by the reduction of germanium dioxide in hydrochloric acid solution by hypophosphorous acid (7, 37, 208). The compound is readily oxidized by air. When it is heated at reduced pressure, water is continuously removed with no evidence of hydrate formation (37). Pugh (153) states that germanium(II) hydroxide resembles arsenic(III) oxide, that it is a true amphoteric hydroxide, acting as a base and forming a series of salts with the halogen acids and acting as an acid and forming germanates with alkalies. Pugh's observation is contradicted by the findings of Everest and Terrey (53). These investigators could find no evidence of reaction between germanium(II) hydroxide and sodium hydroxide and concluded that the acidic properties ascribed to this compound by earlier investigators were attributable to the presence of quadrivalent germanium. No tendency towards the formation of colloidal solutions is evident if quadrivalent germanium is absent. The earlier view advanced by Hantzsch (72) that germanium(II) hydroxide exists in equilibrium with germanoic acid has been apparently disproved.

C. THE SULFIDES OF GERMANIUM

1. Germanium(IV) sulfide

Germanium disulfide is insoluble in strongly acid solutions. It was this property which led to the discovery of the element by Winkler (204). Winkler believed that the element that he was seeking should precipitate as the sulfide from slightly acid solution. When he could not bring about precipitation under these conditions he became discouraged and, in a moment of frustration, poured in a large quantity of hydrochloric acid. A heavy flaky white precipitate immediately appeared and was subsequently identified as germanium disulfide. This method of preparing germanium disulfide, by precipitation from strongly acid solution by hydrogen sulfide, is still used with only minor variations from the original procedure.

Germanium(IV) sulfide is formed when germanium dioxide is heated in sulfur vapor. The resulting disulfide vaporizes readily at 850°C. and is obtained as pearly-white iridescent scales in the cooler parts of the apparatus and as fused transparent amber-colored glass in the hotter regions (154).

Properties of germanium(IV) sulfide: Crystalline germanium disulfide has a specific gravity, $d_{14^\circ}^{14^\circ}$, of 2.942. It melts at about 800°C. to a dark liquid, which solidifies to an amber-colored glass with a density of 5.81. The compound is wetted by water only with difficulty and is resistant to attack by concentrated acids. It is readily soluble in hot caustic alkalies and in ammonium hydroxide. Repeated treatment with nitric acid or with hydrogen peroxide oxidizes the disulfide to germanium(IV) oxide (91, 136).

2. Germanium(II) sulfide

Germanium(II) sulfide may be prepared by heating a mixture of germanium(IV) sulfide and metallic germanium, by heating germanium(IV) sulfide in a current of hydrogen (39, 208), or by precipitation by hydrogen sulfide from germanium(II) chloride solution (37).

Properties of germanium(II) sulfide: Germanium(II) sulfide crystallizes in black, glistening, opaque crystals resembling iodine. The crystals are of different habits, most of them being in the form of thin plates or in needles, but occasionally large fern-like growths appear. The compound has a specific gravity, $d_{14^\circ}^{14^\circ}$, of 4.012 and has a hardness of about 2 on the Moh scale (155). It melts at about 530°C. to a black liquid and volatilizes rapidly above 650°C. The crystalline mass is difficultly soluble and is attacked very slowly by acids and alkalies even at boiling temperature. When finely powdered, the material dissolves rapidly in hot dilute caustic alkalies and in moderately concentrated hydrochloric acid with the liberation of hydrogen sulfide by the latter. Acids reprecipitate it from caustic alkali solutions as an amorphous reddish-brown precipitate.

Germanium(II) sulfide is difficultly soluble in ammonium hydroxide and in ammonium sulfide but is more soluble in ammonium polysulfide. Acids precipitate the white germanium disulfide from the latter solution. Dilute nitric acid dissolves it slowly when hot, and concentrated nitric acid attacks it vigorously, precipitating sulfur and germanium dioxide. Samples may be prepared for analysis without separation of sulfur by dissolving in ammoniacal hydrogen peroxide. There is some reduction of germanium(II) sulfide to germanium by hydrogen at high temperatures. It reacts with chlorine and bromine in the cold with the evolution of considerable quantities of heat.

Precipitated germanium(II) sulfide is a dark red amorphous substance with a density of 3.31 at 20°C. (37). It is readily soluble in dilute hydrochloric acid but is only slowly attacked by sulfuric, phosphoric, or organic acids. It is readily oxidized by hot dilute nitric acid and by aqueous solutions of hydrogen peroxide, potassium permanganate, chlorine, or bromine.

The red sulfide is readily soluble in solutions of alkali hydroxides or sulfides, forming deep red solutions from which red viscous liquids separate upon the addition of alcohol. The sulfide is slowly oxidized in air at 350°C. and rapidly at higher temperatures, forming germanium dioxide and sulfur dioxide. When it is heated in hydrogen chloride to about 150°C., trichlorogermane and hydrogen sulfide are formed. Chlorine attacks germanium(II) sulfide at room temperature, forming germanium tetrachloride and chlorides of sulfur. When red amorphous germanium(II) sulfide is held at 450°C. in an atmosphere of nitrogen it changes in a few hours to the black crystalline variety.

D. NITROGEN COMPOUNDS OF GERMANIUM

1. Germanium(IV) imide

Germanium(IV) imide is formed when germanium tetrachloride or germanium tetraiodide reacts with liquid ammonia (97, 177).

$$GeCl_4 + 6NH_3 \rightarrow Ge(NH)_2 + 4NH_4Cl$$

Germanium(IV) imide, $Ge(NH)_2$, is a white amorphous powder which rapidly changes in air to germanium dioxide with the evolution of ammonia.

When heated in an atmosphere of nitrogen germanium(IV) imide first yields ammonia and a white compound, Ge_2N_3H, called germanam (177). Germanam is stable up to 300°C. but decomposes at slightly higher temperatures to the nitride, Ge_3N_4, and ammonia. The nitride in turn decomposes at still higher temperatures into metallic germanium and nitrogen. This series of reactions is analogous to those undergone by silicon under somewhat similar conditions.

$$Si(NH_2)_4 \xrightarrow{0^\circ C.} Si(NH)_2 \xrightarrow{900^\circ C.} \underset{\text{Silicam}}{Si_2N_3H} \xrightarrow{1200^\circ C.} Si_3N_4 \xrightarrow{?} Si + N_2$$

$$\underset{\text{(unstable)}}{Ge(NH_2)_4} \longrightarrow Ge(NH)_2 \xrightarrow{150^\circ C.} \underset{\text{Germanam}}{Ge_2N_3H} \xrightarrow{350^\circ C.} Ge_3N_4 \xrightarrow{1000^\circ C.} Ge + N_2$$

2. Germanium(II) imide

Germanium diiodide is quantitatively ammonolyzed in liquid ammonia to germanium(II) imide and ammonium iodide (95).

$$GeI_2 + 3NH_3 \rightarrow GeNH + 2NH_4I$$

The germanium(II) imide may be separated from the ammonium iodide by means of liquid ammonia. The imide is insoluble, whereas ammonium iodide is very soluble in this solvent.

Germanium(II) imide is a canary-yellow solid. It reacts vigorously with dry oxygen, liberating sufficient heat to cause the material to glow brightly. When the imide is exposed to air a violent reaction takes place, releasing considerable heat and yielding germanium dioxide and a black residue. "presumably germanous nitride," which is inert to nitric acid. Small amounts of water, or dilute alkali, destroy the imide:

$$\mathrm{GeNH + 2H_2O \rightarrow Ge(OH)_2 + NH_3}$$

3. Germanium compounds containing organic bases

With aniline, germanium tetrachloride forms the compound, $Ge(NC_6H_5)_2 \cdot 2HCl$ (199). Ethylamine reacts to give $Ge(NC_2H_5)_2$. Diethylaniline is reported to be without action on germanium tetrachloride, in accord with the observation (97) that tertiary amines do not react with germanium tetraiodide by aminolysis but instead form aminates with 5 moles of amine combined with 1 mole of germanium tetraiodide.

Treatment of germanium tetrachloride with diethylimine, $(C_2H_5)_2NH$, first gives a product of the composition $GeCl_4 \cdot 6(C_2H_5)_2NH$, which readily rearranges to a substance in which the Ge:Cl:N ratios are 1:4:5 (199). This product can then be separated further into a mixture of $(C_2H_5)_2NH \cdot HCl$, $(C_2H_5)_3N \cdot NCl$, and $Ge(NC_2H_5)_2 \cdot HCl$. Germanium tetrachloride reacts with 8 moles of piperidine to give $Ge(C_5H_{10}N)_4$. The above results indicate that germanium tetrachloride resembles silicon tetrachloride more closely in its behavior towards organic bases than the other chlorides of Group IV. Germanium tetraiodide reacts with organic bases to give analogous compounds (97).

It should be noted that the results reported by Johnson and Sidwell (97) are at variance with those reported earlier by Karantasis and Capatos (102), who concluded that a simple addition compound is formed by ammonia and by amines rather than the imide. The conclusion of Karantasis and Capatos that simple addition compounds are formed is apparently correct only for the tertiary amines.

4. Germanium(IV) nitride

Germanium(IV) nitride is prepared by the action of ammonia on the metal at 650–700°C. or on germanium dioxide at 700–750°C. (70, 93, 129).

$$\mathrm{3Ge + 4NH_3 \rightarrow Ge_3N_4 + 6H_2}$$

The compound is described as having a bright gray color with a reddish tinge. It is stable towards air, water at 100°C., and boiling sodium hydroxide solution, and is only slowly attacked by strong acids. Germanium(IV) nitride is reduced by hydrogen at 600–700°C. to metallic germanium and ammonia. With pure oxygen oxidation occurs at 800–900°C. The compound decomposes at 600–1000°C. into its elements and a brown volatile substance, possibly germanium(II) nitride, Ge_3N_2 (93).

Germanium(IV) nitride has a density of 5.35. The heat of formation is -15.6 ± 1.7 kcal./mole, the heat of combustion is -369.0 ± 0.7 kcal./mole, and the magnetic susceptibility is -3.3×10^{-7} (70). The crystal form is rhombohedral and is isomorphous with that of phenacite, Be_2SiO_4 (99, 100).

Dissociation data for germanium(IV) nitride between the temperatures of 610°C. and 664°C. are given in table 3, in which K is the equilibrium constant for the reaction $Ge_3N_4 \rightleftharpoons 3Ge + 2N_2$.

The nitride is somewhat unstable thermally, but it does not appear to dissociate appreciably at ordinary temperatures. The heat effects calculated from the equations,

$$3Ge + 4NH_3 \rightarrow Ge_3N_4 + 6H_2$$

and

$$2N_2 + 6H_2 \rightleftharpoons 4NH_3$$

gave the value $-103{,}000$ cal. for ΔH for Ge_3N_4. Plotting the logarithm of K against $1/T$ gave $\Delta H = -102{,}000$ cal.

Attempts to prepare germanium(IV) nitride from the elements at atmospheric pressure always ended in failure. The results of Morey and Johnson show that it is impossible to prepare the nitride by direct union of the elements at any pressures experimentally attainable. The behavior of silicon nitride is quite different. The pressure of nitrogen in equilibrium with silicon and silicon nitride is only a few millimeters of mercury at 1327°C. (76), and the heat effect accompanying the dissociation of silicon nitride is positive in contrast to the negative value found for germanium(IV) nitride.

TABLE 3

Dissociation data for germanium(IV) nitride

TEMPERATURE	K	FREE ENERGY, ΔF
°C.		calories
610	19.63×10^{-16}	−69,900
614	12.10×10^{-16}	−69,300
638	2.224×10^{-16}	−68,150
654	1.250×10^{-16}	−68,300
664	0.6501×10^{-16}	−67,800

5. *Miscellaneous nitrogen compounds*

Attempts to obtain "germanium urea," $GeO(NH_2)_2$, by heating germanium oxychloride with ammonia yielded a hitherto unknown modification of germanium monoxide instead of the expected compound (174).

A compound with the formula $Ge(OCN)_4$ has been prepared (120) by treating germanium tetrachloride with powdered silver isocyanate. The product is a colorless liquid which hydrolyzes rapidly to germanium dioxide. Thermal decomposition occurs slowly above 140°C. The boiling point, extrapolated, is given as 196°C., the melting point as −8°C., the heat of vaporization as 12.6 kcal./mole, and the density as 1.7694. It was not determined whether the compound was the cyanate, the isocyanate, or a mixture of the two. Later, Forbes and Anderson (59) reported a boiling point of 204°C. for germanium isocyanate, $Ge(NCO)_4$. The compound supercools to −65°C. but melts quite sharply at −8°C. A solid residue, believed to be the cyanate, $Ge(OCN)_4$, was also obtained. The formation of $GeCl_3NCO$ has been reported (61) as resulting from the disproportionation taking place when a mixture of germanium tetrachloride and germanium tetraisocyanate is heated at 500°C.

A number of organogermanium isocyanates, isothiocyanates, and nitriles have been reported (2, 3, 4, 61).

E. GERMANIDES AND ALLOYS

The chemistry of binary compounds of germanium with metals is not well developed, and many of the compounds reported have not been isolated. Binary systems and alloys, as well as pure compounds, are accordingly included here.

Heating equiatomic proportions of powdered germanium with small pieces of sodium to 1000°C. in a small steel crucible provided with an air-tight steel cover gave a homogeneous alloy of the composition NaGe (46). The alloy is a hard dense pyrophoric substance, which is slowly acted upon by moist air. When this alloy is added to cold water or to dilute or concentrated hydrochloric acid a brown powder is formed. If this brown powder is collected on a filter and dried in air, it decomposes with a puff but without detonation. When water is removed from it by washing with alcohol and then with ether it explodes with a slight detonation as soon as the ether has run through the funnel. Analysis of the brown powder gave the composition $(GeH)_x$.

Sodium germanide prepared by heating finely powdered germanium metal with about 50 per cent excess of sodium metal in an iron bomb at 650–700°C. for 2 days and then distilling off the excess sodium yielded a loose product containing small, well-developed, needle-shaped crystals with a metallic luster. Potassium germanide prepared in the same way did not form definite crystals. In the preparation of rubidium germanide the rubidium distilled at 200°C., leaving bronze-colored crystals. Cesium distilled from cesium germanide at 150°C., leaving deep black crystals.

The binary compounds of germanium with sodium, potassium, rubidium, and cesium are stable only under dry inert gases. In the air they decompose into the hydroxide and a brown amorphous substance having the formula $(GeH)_x$. When the alkali germanides are brought into contact with water they decompose rapidly, often with slight flaming. The decomposition proceeds more slowly in the case of germanium compounds than with the analogous silicon compounds. Differences in sensitivity and rapidity of decomposition are not as great between the different germanides as in a comparable silicon series.

Decomposition temperatures are reported (80) as 480°C. for sodium germanide, 400–420°C. for potassium germanide, and 390–410°C. for rubidium and cesium germanides. The corresponding silicon compounds show a similar lowering of the decomposition temperatures with increasing atomic number of the alkali metal, but the temperature is about 60° lower in each case. The decomposition products in the case of sodium germanide were sodium and germanium, but the heavier alkali metals gave new compounds tentatively reported as KGe_4, $RbGe_4$, and $CsGe_4$.

Intermetallic compounds of the more positive metals have been divided into four general groups (85): (*1*) substances containing the alkali, alkaline earth, and rare-earth metals; (*2*) compounds containing the transition elements from the titanium to the nickel groups; (*3*) compounds containing elements intermediate between metals and metalloids; and (*4*) compounds containing metalloids.

Germanium is classified with the metalloids. The factors that govern the formation of an intermetallic compound of a metal of the first class listed above with the metalloids of the fourth class are: (*1*) the tendency of the metal to ionize when it comes in contact with the metalloid, (*2*) the number of positive charges acquired as a result, and (*3*) the dimensions of the ions formed. With respect to the metalloid the governing factors include: (*1*) the electron affinity, (*2*) the tendency to form a partial negative lattice, (*3*) the number of electrons which the partial lattice can acquire, and (*4*) the dimensions of the atoms of the metalloid that forms the lattice.

The silver–germanium system has been investigated at 600–1000°C. (20). The alloy forms a simple eutectiferous series. The eutectic temperature is 650°C., and the eutectic composition is 26 atomic per cent germanium. Germanium and silver form no stable compounds at the temperatures studied. The solid phases in equilibrium with the melt are pure germanium and a solid solution of germanium in silver. The latter phase when saturated contains between 6 and 7 per cent of germanium at 650°C. Electrical conductances were found to be low, and from this it was concluded that in these particular alloys the germanium predominates in the continuous phase. In a comparison of its properties with those of silver–silicon and silver–tin alloys, the silver–germanium alloy occupied the expected intermediate position.

Among the germanides of the Group II elements, calcium germanide, CaGe, has been obtained as a dark grey crystalline powder by the direct union of the elements in an evacuated quartz tube at red heat (162). It was also obtained as a product from the reaction between calcium hydride and powdered germanium.

From a thermal analysis of the magnesium–germanium system it was found (109) that the compound Mg_2Ge had a melting point of 1115°C. The eutectic mixture of magnesium and Mg_2Ge contains 1.2–1.3 per cent of germanium and melts at 635°C. The eutectic mixture of germanium and Mg_2Ge melts at 690°C. All Mg_2X phases have very narrow composition ranges; this is explained on the basis of an intolerance of the antifluorite lattice for incompletely occupied lattice points. Raynor (158) found a eutectic for the magnesium–germanium system at 634.7°C., containing 1.15 per cent germanium. The solid solubility of germanium in magnesium is very slight, being about 0.003 atomic per cent at 600°C. and negligible at 430°C.

The reactivity of magnesium alloys of the Group IV elements with water (30) increases in the order $Mg_2Si < Mg_2Ge < Mg_2Sn < Mg_2Pb$, parallel to the increasing metallic character and the decreasing ionic character of the bond. The Group IV elements of these intermetallic compounds play the role of electron-transferring agents from magnesium to the hydrogen ions from the water.

Among the Group III elements, Kroll (112, 113) studied the aluminum–germanium system and constructed a phase diagram for mixtures containing up to 60 per cent of germanium. The two metals apparently form a simple eutectiferous series of alloys, in which the solid phases are the individual components. The addition of germanium brings about marked improvement in the engineering properties of aluminum.

Gallium, indium, and thallium when alloyed with germanium yield phase diagrams with curves of the eutectic type, with eutectic compositions and temperatures very near the lower-melting component (108).

Some workers (108) state that of the Group IV elements, germanium and silicon are completely miscible but germanium and lead form a eutectic system. Briggs and Benedict (19), however, believe that germanium and lead are consolute as liquids and form no solid solutions. When the liquid mixture cools, the germanium separates completely before any of the lead leaves the solution. The usual type of eutectic point is therefore absent. The position of germanium with respect to silicon and tin is that expected from the relationship in the Periodic Table. Lead and silicon exhibit complete immiscibility, whereas lead and tin are completely miscible in the liquid state and partially miscible in the solid state. Germanium shows closer relationship to tin, in that it also is completely miscible with lead in the liquid state instead of being partially miscible, as might be expected from its intermediate position between silicon and tin. There is close similarity between the germanium–lead system and the silicon–tin system.

In Group V, phosphorus, when heated in an evacuated sealed tube above 555°C. with germanium in the ratio 4:1, reacted incompletely, yielding a solid product having a germanium–phosphorus ratio of approximately 1:1 (212). The presence of the compound GeP was indicated by the pattern obtained by x-ray analysis. Tensiometric measurements confirmed the conclusion that the solid product was a two-phase system of germanium and germanium phosphide, GeP. The following heats of formation were estimated:

$$4\text{Ge (solid)} + \text{P}_4 \text{ (gas)} \rightarrow 4\text{GeP (solid)} + 37 \text{ kcal.}$$

$$\text{Ge (solid)} + \text{P (white)} \rightarrow \text{GeP (solid)} + 6 \text{ kcal.}$$

The germanium–arsenic system exhibits weak maxima at 732°C. and 737°C., corresponding to the compounds $GeAs_2$ and GeAs (189). These compounds were reported as being very resistant to atmospheric oxidation. Germanium and antimony form a eutectic mixture melting at 592°C. and containing 13.5 atomic per cent of germanium. The solubility of germanium in antimony is given as 2.2 atomic per cent at 540°C. and the solubility of antimony in germanium as 2.5 atomic per cent at the same temperature. Germanium and bismuth form a eutectic mixture melting at 271°C. and containing almost 100 per cent bismuth. At 250°C. the solubility of germanium in bismuth is not more than 1.5 atomic per cent and that of bismuth in germanium not more than 2 per cent.

F. THE INORGANIC ACIDS OF GERMANIUM

1. *The simple inorganic acids*

There are many discrepancies in the work reported on the simple germanium acids. Roth and Schwartz (160) measured the conductivity of aqueous solutions of germanium dioxide and reported a value of 1.2×10^{-7} for the primary ionization constant of metagermanic acid:

$$H_2GeO_3 \rightleftharpoons H^+ + HGeO_3^-$$

Pugh (154) calculated the primary ionization constant of this acid from the hydrolysis of sodium acid metagermanate, $NaHGeO_3$, and also from the pH value at the equivalence point. The value of K_1 from hydrolysis studies is given as 2.1×10^{-9} and the value from electrometric titration studies as 3.2×10^{-9}. Pugh expresses the opinion that the high value obtained by Roth and Schwartz was due to the high conductivity of the water used. Pugh reports a value of 1.9×10^{-13} for the secondary ionization constant.

Schwarz and Huf (175), using conductivity measurements in aqueous solutions of germanium dioxide, obtained a value of 4.9×10^{-8} for K_1 for metagermanic acid. Gulezian and Müller (68) determined the primary ionization constant of metagermanic acid obtained from the different modifications of germanium dioxide. From conductance measurements they reported that the value for the primary ionization constant lies between 1.0×10^{-9} and 3.0×10^{-9}. These values are in close agreement with those obtained by Pugh (154). Gulezian and Müller (69) also determined the primary ionization constant by titration with sodium hydroxide, using both the conductimetric and the colorimetric determination of the equivalence point. The average value of 1.5×10^{-9} agrees well with that found by the same authors by the conductance method and also with the value reported by Pugh (154).

McGowan (126) expressed the ionization constants in the form of free energies. Using the relation, $\Delta G_0 = -RT \ln K$, he reported the value of 11.7 for orthogermanic acid, H_4GeO_4, and 17.3 for the ion, $H_3GeO_4^-$.

Carpéni and Tchakirian (29) titrated solutions of germanium dioxide in pure water, and in 2 *M* potassium chloride, with potassium hydroxide. The change in the shape of the titration curve, as the initial concentration of germanium dioxide was varied, was interpreted as indicating the existence of an equilibrium, varying with the dilution, between pentagermanic acid, $H_2Ge_5O_{11}$, and metagermanic acid, H_2GeO_3.

Metagermanic acid forms complex acids with polyhydroxy alcohols such as glycerol and mannitol, and these acids are much stronger than the original metagermanic acid (150). Quinalizarin is suggested as a reagent for detecting metagermanic acid. Tchakirian (192) states that in the presence of mannitol, germanium dioxide acts as a monoprotic acid and may be titrated with sodium hydroxide. If calcium chloride or strontium chloride is added to the mannitol solution of germanium dioxide, it then reacts as a diprotic acid.

Carpéni (27) identified pentagermanic acid, $H_2Ge_5O_{11}$, in solution. For metagermanic acid at 12°C. he reported a value of 9.1 for pK_1 and of 12.7 for pK_2. For the pentagermanic acid pK_1 is given as 6.2 and pK_2 as 7.8. Carpéni expressed the opinion that the digermanic acid did not exist.

2. The heteropoly acids of germanium

Schwarz and Giese (171) prepared the heteropoly acids $H_8[Ge(Mo_2O_7)_6] \cdot 28H_2O$ and $H_8[Ge(W_2O_7)_6] \cdot 28H_2O$. The tungsten acid yields two stereoisomeric potassium salts but only one acid appears to exist. Both acids crystallize in well-defined octahedra. The tungsten acid is white and the molybdenum acid is greenish yellow. Both acids are readily soluble in water, and the crystals disintegrate in air with extreme rapidity. Grosscup (67) states that there is considerable variation in the water content of these acids and suggests that the maximum for the water of crystallization is apparently 26. Titration with sodium hydroxide (67) proceeds in accordance with the equation:

$$GeO_2 \cdot 12MoO_3 \cdot xH_2O + 24NaOH \rightarrow GeO_2 + 12Na_2MoO_4 + xH_2O$$

Apparently progressive decomposition, with the formation of compounds of lower MoO_3 content, takes place during the titration.

The molybdenum acid gives the same color reaction with alkaline tin(II) chloride as does the molybdosilico acid. Tungsten and germanium may be separated by distilling the complex acid from 70 per cent sulfuric acid in a current of hydrogen chloride. The molybdenum and germanium may be separated by heating to 500°C. and then vaporizing the molybdenum as molybdic anhydride, MoO_3, in a current of oxygen at 1000°C., the germanium remaining behind as germanium dioxide.

Brukl and Hahn (23) obtained a number of hydrated acids and salts from the heteropoly acid $H_8Ge(W_2O_7)_6 \cdot 28H_2O$. Above 36°C. two phases are present, with the solid phase having the formula $H_8Ge(W_2O_7)_6 \cdot 22H_2O$. Above 50°C. the solid phase was reported to be $H_8Ge(W_2O_7)_6 \cdot 15H_2O$, whereas equilibrium over sulfuric acid or potassium hydroxide yields the tetrahydrate.

Tschakirian and Souchay (197) studied the decomposition of the Ge-12-tungstates by alkali and found that they formed the Ge-11-tungstates, a reaction analogous to that of the Si-12-tungstates.

$$(GeO_4 \cdot 12WO_3)^{4-} + 4.5NaOH \rightleftharpoons (GeO_6 \cdot 11WO_3)^{8-} + \tfrac{1}{6}(H_3W_6O_{21})^{3-} + 2H_2O$$

The Ge-11-tungstates in turn decompose at a sufficiently high pH value into germanates and tungstates.

$$(GeO_6 \cdot 11WO_3)^{8-} + 16OH^- \rightleftharpoons GeO_3^{--} + 11WO_4^{--} + 8H_2O$$

The transformations of the Ge-12-tungstates and the Ge-11-tungstates are functions of the pH. The transformation of the Ge-12-tungstates to the Ge-11-tungstates starts at pH 3.2 and is practically complete at pH 4.2. Above pH 7.3 the Ge-11-tungstates decompose into germanates and tungstates. A zone of reversible equilibria occurs between pH values 7 to 8. Complex tungstic ions and germanium dioxide combine rapidly at any pH to form Ge-11-tungstic ions. Ions of the Ge-12-tungstates, however, form only at pH values less than 4 and then very slowly. The complex salts are decomposed by hydrogen peroxide with the formation of a peroxytungstate. Souchay and Tchakirian (187) found that the complex molydic compounds were, in general, less stable than the corresponding tungstic complexes. Ge-11-molybdate exists within the limited pH range of 3.5 to 4.2. Above 4.2 the compound begins to decompose into germanate and molybdate and this reaction is complete at pH 5.4. The Ge-11-tungstates do not show the polarographic deviation at a potential of 0.4 v. which is characteristic of the Ge-12-compounds.

G. THE GERMANATES

1. The orthogermanates

Magnesium orthogermanate, Mg_2GeO_4, is quantitatively precipitated by the action of magnesia mixture upon solutions of germanium dioxide in the presence of free ammonia (131). The compound is a white amorphous substance without any apparent crystals even under microscopic examination. It is infusible at high temperatures and is non-volatile at white heat. It is very soluble in solutions of mineral acids when freshly precipitated but is only slowly soluble in the same acids after ignition. If the excess of ammonia is boiled off, the precipitate. will go into solution in the nearly neutral ammonium salt solution but it reprecipitates immediately upon the addition of more ammonia.

Lithium orthogermanate was obtained by fusing two equivalents of lithium carbonate with one equivalent of germanium dioxide (152). In this respect germanium dioxide resembles silicon dioxide, in that the corresponding silicates have been similarly obtained. The only other orthogermanates which have been reported are sodium orthogermanate (152), beryllium orthogermanate (168), zinc orthogermanate (168), and lead orthogermanate (169).

2. The metagermanates

In common with other weakly acidic oxides, germanium dioxide displaces carbon dioxide from sodium carbonate at its melting point (152). When equivalent proportions of germanium dioxide and sodium carbonate are fused together, sodium metagermanate, Na_2GeO_3, is obtained as a white crystalline substance which is very hygroscopic and which absorbs carbon dioxide from the atmosphere. Sodium metagermanate is very soluble but the solution is strongly alkaline; the compound hydrolyzes rapidly and hydrated germanium dioxide precipitates. When this solution is evaporated in a carbon dioxide-free atmosphere it thickens to the consistency of water glass without crystallizing. This viscous solution is highly supersaturated; on seeding it solidifies completely with the evolution of much heat. The heptahydrate, $Na_2GeO_3 \cdot 7H_2O$, crystallizes readily on evaporation at room temperature. A hexahydrate has also been reported (173).

Freshly prepared sodium germanate heptahydrate dissolves completely in water, giving a strongly alkaline solution, but the partly dehydrated or carbonated hydrate does not dissolve completely. The solubility, in grams of anhydrous Na_2GeO_3 per 100 ml. of water, is 14 at 0°C. and 25.9 at 25°C. The aqueous vapor pressure of the crystals is 4 mm. at 20°C.

Metagermanic acid, H_2GeO_3, is a weak acid. Consequently, good results are obtained on the direct titration of the sodium salt with sulfuric acid and a suitable indicator such as methyl orange.

The systems Na_2GeO_3–GeO_2 and K_2GeO_3–GeO_2 have been investigated and the existence of the following compounds has been reported: Na_2GeO_3, m.p.

1083°C.; $Na_2Ge_2O_5$, m.p. 799°C.; $Na_2Ge_4O_9$, m.p. 1052°C.; K_2GeO_3, m.p. 842°C.; $K_2Ge_2O_5$, m.p. 797°C.; $K_2Ge_4O_9$, m.p. 1038°C. (173, 176).

Potassium metagermanate, K_2GeO_3, unlike sodium metagermanate, cannot be prepared by fusing potassium carbonate with germanium dioxide (152). In this respect germanium also resembles silicon, since it has been shown that in the $K_2O–SiO_2$ system the only stable silicates are the metasilicate and the disilicate and that when potassium carbonate is fused with silicon dioxide the following equilibrium is established:

$$K_2Si_2O_5 + K_2CO_3 \rightleftharpoons 2K_2SiO_3 + CO_2$$

A similar equilibrium is suggested for the $K_2O–GeO_2$ system (152). Carpéni (27) reports that K_2GeO_3 is 50 per cent hydrolyzed even in solutions as dilute as 0.04 *M*.

Lithium metagermanate, Li_2GeO_3, is readily obtained by fusing equimolar proportions of germanium dioxide and lithium carbonate (152). A hydrated lithium metagermanate with the composition $Li_2GeO_3 \cdot \frac{1}{3}H_2O$ has been described (152). This result is questioned by Schwarz and Heinrich (173), who found lithium metagermanate incapable of forming a hydrate.

Anhydrous silver metagermanate, Ag_2GeO_3, is precipitated when solutions of silver nitrate and sodium metagermanate are mixed (152). It is a light brown powder which is practically insoluble in water but is soluble in acids and in aqueous ammonia. It is sensitive to light, turning almost jet-black on exposure to sunlight. When heated it melts to a dark liquid and decomposes with the evolution of oxygen. The loss in weight at red heat is 4.7 per cent, the residue consisting of metallic silver and germanium dioxide.

Müller and Gulezian (137) found that the neutralization of dilute germanic acid by calcium hydroxide produced a colloidal calcium metagermanate of unusually high dispersion. Firmly set gels were obtained with the total anhydrous constituents as low as 0.065 per cent of the gel mass. Calcium metagermanate hydrogels ranging from 99.90 to 99.94 per cent water content are permanent dispersoids if protected from dry air and from carbon dioxide and have been kept for over a year without syneresis.

The water present in dispersed calcium metagermanate appears to be simply trapped water, nearly all of which may be removed by pressure or by suction filtration. The solid structure or filterable mass is practically pure calcium metagermanate. All of the germanium is present in the insoluble or filterable structure if the proportion of calcium hydroxide reaches or exceeds the amount present in the molecular ratio $2CaO \cdot GeO_2$.

The water of the calcium metagermanate hydrogel may be replaced by a number of other liquids such as methanol, ethanol, or acetone. These non-aqueous liquids may, in turn, be replaced by ethyl ether or benzene, to yield a series of non-aqueous dispersoids which are permanent if protected from evaporation.

Strontium metagermanate yields a dispersoid similar to the calcium salt, but the minimum concentration of the strontium salt required for a stable gel is higher than in the case of the calcium metagermanate (137). Schwarz and Heinrich (173) obtained strontium metagermanate in crystalline form from aqueous solution. Apparently the compound does not form a hydrate.

When aqueous solutions of sodium metagermanate and barium chloride are mixed, a white granular precipitate of variable composition is formed (152). The composition depends upon the concentrations of the solutions and on the extent of the washing. Prolonged washing decreases the barium content, apparently owing to progressive hydrolysis of the normal germanate, $BaGeO_3$. The trihydrate, $BaGeO_3 \cdot 3H_2O$, is obtained when the precipitation is carried out in an excess of barium oxide or sodium hydroxide. The tetra- and pentahydrates have been reported (173). Barium metagermanate is a white powder, insoluble in alcohol and ether, readily soluble in dilute acids, and slowly decomposed by water. The compound differs markedly in its behavior from the calcium and strontium metagermanates (137). It is distinctly crystalline, forming shining aggregates, and has a solubility of 0.07536 g. per 100 g. of water at 25°C.

When solutions of sodium metagermanate and lead acetate are mixed, lead metagermanate is formed as a bulky white gelatinous precipitate which becomes granular on heating (152). It is a white powder practically insoluble in water, alcohol, or ether but soluble in dilute mineral acids. At red heat it melts to a red oily liquid; on cooling again it solidifies to a pale yellow solid. It does not decompose on fusion.

Only one germanite has been described. Royen and Schwarz (164) reported the formation of sodium germanite, Na_2GeO_2, by the reaction of sodium hydroxide on the hydride, $(GeH_2)_x$.

$$GeH_2 + 2NaOH \rightarrow Na_2GeO_2 + 2H_2$$

Schwarz and Giese (170) obtained the salts $K_6Ge_2S_7 \cdot 9H_2O$ and $Na_6Ge_2S_7 \cdot 9H_2O$ by adding freshly precipitated germanium sulfide to a concentrated aqueous solution of the appropriate alkali sulfide and pouring the mixture into acetone. An oil is precipitated which becomes crystalline when preserved over phosphoric anhydride in an atmosphere of hydrogen sulfide. These salts decompose rapidly when exposed to air. Addition of silver nitrate to a solution of germanium sulfide in sodium sulfide yields a salt having the composition $GeS_2 \cdot 4Ag_2S$.

The addition of 30 per cent hydrogen peroxide to a concentrated solution of potassium metagermanate, K_2GeO_3, at 0°C. causes the slow precipitation of potassium digermanate, $K_2Ge_2O_7 \cdot 4H_2O$. The sodium digermanate, $Na_2Ge_2O_7 \cdot 4H_2O$, is similarly prepared. The addition of considerable alcohol to the filtrate from the sodium compound precipitates a second salt, $Na_2GeO_5 \cdot 4H_2O$. The alkali digermanates decompose slowly at room temperature.

Attempts to obtain the corresponding lead compounds by this procedure were not successful (170). The tendency of germanium to form salts of this nature appears to be more pronounced than that of other members of its main group; in this respect it resembles more closely the elements of its companion subgroup.

The addition of alkali to a solution of germanium dioxide in 2 *M* potassium chloride causes the formation of a white microcrystalline precipitate with the composition $K_2Ge_5O_{11}$ at the pH range 8–10.2 (196). The solubility of the compound is at a minimum at pH 9.2.

When treated with aluminum chloride in neutral solution, sodium metagermanate precipitates the compound $Al_2O_3 \cdot 2GeO_2 \cdot nH_2O$, which, when dried at 100°C., yields $Al_2O_3 \cdot 2GeO_2 \cdot 3H_2O$ (180). Treatment with alkali gives compounds of a permutite-like character showing zeolithic linkage of water.

V. Physiological Properties of Germanium Compounds

Considerable interest has been shown from time to time in the pharmacological activity of germanium compounds, but all chemotherapeutic tests thus far made have given either negative or inconclusive results (82, 134, 179). A large number of organo derivatives of germanium have proven ineffective against trypanosomes and spirochetes and in experimental rat sarcoma. Early investigators agree that germanium compounds are only slightly toxic although some, like Keeser (106), have reported that such compounds may cause a transient rise in the number of red blood cells and in the hemoglobin content of rabbit blood. Burschkies likewise concluded (26) that organogermanium compounds have apparently no chemotherapeutic significance.

Schwarz and Scholz (179) noted the fact that in industrialized regions where much coal is burned, tuberculosis is not particularly prevalent in spite of generally unfavorable living conditions. They believed that considerable germanium dioxide was emitted with coal smoke and attempted to verify experimentally the possible beneficial effects of small amounts of the dioxide. Aqueous solutions of germanium dioxide were administered both orally and intravenously. Oral administration of 10 mg. of the dioxide every other day was completely harmless and resulted in an improvement of the hemoglobin content and an increase in the number of red blood cells; these effects, contrary to the results reported by Keeser (106), were not merely transient. Combined oral and intravenous administration was well tolerated by all of the patients and resulted in the same improvement in the blood picture. The number of white blood cells and their composition remained unchanged, but in some patients there was a marked qualitative change in the leucocyte picture, characterized by 20–22 per cent of rod nuclei and a considerable decrease of the lymphocytes and monocytes.

The results indicate that germanium dioxide taken orally is harmless, although intravenous administration may be harmful and should not be used. Keeser (106) has reported that supersaturated colloidal solutions of germanium dioxide cause immediate collapse and cardiac arrest when given intravenously. The effect of germanium dioxide on the oxygen uptake of rat tissue has been discussed in a lengthy article by Read (159).

Harrold, Meek, and McCord (73) also concluded that germanium dioxide is a stimulant of red blood cell formation. There is apparently no prospect of a harmful extent of polycythemia, since a critical level of accumulation of germanium is apparently established, beyond which germanium is either not absorbed or otherwise does not exert its customary action within the body.

In spite of the inconclusive results thus far reported, the possibility of finding a germanium compound for a specific chemotherapeutic purpose should not be disregarded.

VI. Tabulated Summary of Inorganic Germanium Compounds

Tables 4 to 12, inclusive, summarize the literature references regarding the inorganic compounds of germanium.

TABLE 4

Inorganic halogen compounds of germanium

COMPOUND	REFERENCES
GeF_4	(14, 34, 42, 57, 58, 75, 107)
$GeCl_4$	(1, 9, 10, 12, 13, 14, 18, 32, 33, 34, 43, 49, 55, 60, 61, 62, 72, 77, 78, 79, 121, 123, 144, 145, 148, 149, 156, 166, 171, 188, 191, 199, 208)
$GeCl_4 \cdot 6NH_3$	(156, 177, 198)
$GeCl_4 \cdot 16NH_3$	(156)
$GeBr_4$	(9, 17, 18, 34, 72, 77, 79, 117, 160, 209)
GeI_4	(9, 18, 35, 36, 55, 72, 77, 89, 97, 101, 103, 117, 208)
$GeCl_3F$	(14)
$GeBrCl_3$	(14, 60)
$GeICl_3$	(43)
$HGeCl_3$	(16, 18, 38, 43, 118, 174, 193, 195, 208, 209, 211)
$HGeBr_3$	(18)
$HGeI_3$	(18)
$CsGeCl_3$	(105, 193, 195)
$RbGeCl_3$	(193)
$CsGeI_3$	(105)
$GeCl_2F_2$	(14)
$GeBr_2Cl_2$	(38)
$GeClF_3$	(14)
$GeCl_3NCO$	(61)
GeF_2	(7, 42)
$GeCl_2$	(7, 16, 18, 37, 38, 43, 164, 193, 194, 208, 209)
$GeBr_2$	(7, 16, 18, 104)
GeI_2	(5, 7, 16, 18, 35, 40, 52, 55, 95, 151, 164, 194)
$GeOCl_2$	(7, 33, 37, 110 176, 211)
Ge_2OCl_6	(178)
$Ge(ClO_4)_4$	(145)
$CsBr \cdot GeBr_2$	(104)
$CsBr \cdot 2GeBr_2$	(104)
$3N(CH_3)_4Br \cdot 2GeBr_2$	(104)
$2As(CH_3)_4Br \cdot 3GeBr_2$	(104)
$As(CH_3)_3(C_2H_5)Br \cdot GeBr_2$	(104)
$N(CH_3)_4GeI_3$	(105)
$3(C_{17}H_{21}NO_4 \cdot HI) \cdot 2GeI_2$	(105)
$GeI_4 \cdot 4C_8H_{10}N_4O_2$	(103)
$GeI_4 \cdot 4C_6H_{12}N_4$	(103)
$GeI_2 \cdot CH_3NH_2$	(52)

TABLE 5

Hexahalogermanates

COMPOUND	REFERENCES	COMPOUND	REFERENCES
H_2GeF_6	(42, 47, 210)	$(NH_2OH)_2 \cdot H_2GeF_6$	(47)
K_2GeF_6	(42, 114, 189, 210)	$(N_2H_2)_2 \cdot H_2GeF_6$	(47)
Rb_2GeF_6	(185, 186)	$(C_6H_5NH_2)_2 \cdot H_2GeF_6$	(47)
Cs_2GeF_6	(168, 185, 186)	$(C_6H_5NHCH_3)_2 \cdot H_2GeF_6$	(47)
$(NH_4)_2GeF_6$	(47)	$[C_6H_5N(CH_3)_2]_2 \cdot H_2GeF_6$	(47)
$BaGeF_6$	(42, 130)		

TABLE 6

Oxides and hydroxides of germanium

COMPOUND	REFERENCES	COMPOUND	REFERENCES
GeO	(7, 37, 53, 174, 208)	$Ge(OH)_2$	(7, 37, 43, 53, 71, 105, 153, 174, 195, 208, 209)
GeO_2	(7, 11, 32, 33, 41, 48, 51, 55, 65, 66, 68, 69, 74, 91, 110, 116, 119, 132, 133, 135, 136, 138, 141, 142, 146, 152, 153, 155, 172, 175, 196, 211)	$Ge(OH)_4$	(28, 177)

TABLE 7

Sulfides of germanium

COMPOUND	REFERENCES	COMPOUND	REFERENCES
GeS	(7, 37, 39, 42, 53, 54, 55, 94, 155, 208)	$GeS_2 \cdot 4AgS$	(45, 170, 208)
GeS_2	(5, 6, 39, 54, 55, 63, 91, 98, 136, 155, 170, 208)	$GeS_2 \cdot 3NaS_2 \cdot 9H_2O$	(170)

TABLE 8

Nitrogen compounds of germanium

COMPOUND	REFERENCES	COMPOUND	REFERENCES
GeNH	(55, 95, 96)	$GeO(NH_2)_2$	(174)
$Ge(NH)_2$	(55, 97, 177, 198)	$Ge(NCO)_4$	(2, 59, 120)
$Ge(NH_2)_4$	(77, 177, 198)	$GeCl_3NCO$	(61)
Ge_3N_2	(93, 95, 96)	$Ge(NC_2H_5)_2$	(97, 199)
Ge_3N_4	(70, 93, 99, 100, 129, 176, 177)	$Ge(NC_2H_5)_2 \cdot HCl$	(199)
		$Ge(NC_6H_5)_2 \cdot 2HCl$	(199)
Ge_2N_3H	(177)	$Ge(C_5H_{10}N)_4$	(199)

TABLE 9

Germanides and alloys

COMPOUND	REFERENCES	COMPOUND	REFERENCES
NaGe	(46, 80, 111)	GeP	(212)
KGe	(80)	GeAs	(189)
RbGe	(80)	$GeAs_2$	(189)
CsGe	(80)	$Mn_{3.25}Ge$	(213)
KGe_4	(80)	Mn_5Ge_3	(213)
$RbGe_4$	(80)	Mn_3Ge_2	(213)
$CsGe_4$	(80)	Mn_5Ge_2	(213)
Mg_2Ge	(15, 30, 109, 164)	PdGe	(147)
CaGe	(162, 163, 164)	IrGe	(147)
GaGe	(108)	Ir_3Ge_7	(147)
InGe	(108)	PtGe	(147)
ThGe	(108)	Ge–Ag*	(20)
Fe_2Ge	(122, 203)	Ge–Mg*	(83, 158)
$FeGe_2$	(203)	Ge–Pb*	(19, 108)
Co_2Ge	(122, 203)	Ge–As*	(189)
$CoGe_2$	(167)	Ge–Sb*	(165, 189)
NiGe	(147)	Ge–Bi*	(165, 189)
Ni_2Ge	(122, 165)	Ge–Cu*	(83, 84)
Ni_3Ge	(147)	Ge–Ag*	(83, 84)
Cu_3Ge	(56)	Ge–Fe*	(165)
Ag_4Ge	(139)	Ge–Ni*	(165)

* The dash between the symbols indicates a system of the two metals.

TABLE 10

Germanic acids, germanates, and thiogermanates

COMPOUND	REFERENCES	COMPOUND	REFERENCES
Na_2GeO_2	(164)	$Na_6Ge_2S_7 \cdot 9H_2O$	(170)
H_2GeO_3	(27, 29, 139, 150, 154, 160, 175)	$K_6Ge_2S_7 \cdot 9H_2O$	(170)
		$Ag_6Ge_2S_7$	(170)
$NaHGeO_3$	(69, 71, 154)	H_4GeO_4	(28, 126)
Na_2GeO_3	(152, 154, 173, 176, 180)	Li_4GeO_4	(152)
		Na_4GeO_4	(152)
K_2GeO_3	(152, 173, 176, 206)	Mg_2GeO_4	(66, 131)
Li_2GeO_3	(152, 173)	Zn_2GeO_4	(66, 168)
$BaGeO_3$	(137, 152, 173)	Be_2GeO_4	(168)
$PbGeO_3$	(152)	Pb_2GeO_4	(169)
Ag_2GeO_3	(152)	$Na_2GeO_5 \cdot 4H_2O$	(170)
$CaGeO_3$	(137)	$Na_2Ge_2O_5$	(173)
$SrGeO_3$	(137, 173)	$K_2Ge_2O_5$	(152, 173)
$Na_2GeO_3 \cdot 6H_2O$	(173)	$Na_2Ge_2O_7 \cdot 4H_2O$	(170)
$Na_2GeO_3 \cdot 7H_2O$	(152, 173)	$K_2Ge_2O_7 \cdot 4H_2O$	(170)
$BaGeO_3 \cdot 4H_2O$	(173)	$Al_2Ge_2O_7$	(180)
$BaGeO_3 \cdot 5H_2O$	(173)	$Na_2Ge_4O_9$	(173)
Na_8GeS_6	(170)	$K_2Ge_4O_9$	(173)
$H_2Ge_2S_5$	(206)	$H_2Ge_5O_{11}$	(27, 28, 29, 175)
$K_2Ge_2S_5$	(206, 207)	$K_2Ge_5O_{11}$	(196)

TABLE 11

Heteropoly acids and salts of germanium

COMPOUND (FORMULA GIVEN IN REFERENCE)	REFERENCES
$H_8[Ge(Mo_2O_7)_6]aq$	(67, 171, 197)
$(CN_3H_5)_4H_8[Ge(Mo_2O_7)_6]$	(67)
$(CN_3H_5)_8H_8[Ge(Mo_2O_7)_6]$	(171)
$GeO_2 \cdot 12MoO_3 \cdot 32H_2O$	(24)
$H_4GeW_{12}O_{40} \cdot 5H_2O$	(86)
$H_8[Ge(W_2O_7)_6] \cdot 28H_2O$	(22, 23, 171)
$Na_4H_4[Ge(W_2O_7)_6] \cdot 19H_2O$	(22)
$Ag_4H_4[Ge(W_2O_7)_6] \cdot 7H_2O$	(22)
$Ag_4H_4[Ge(W_2O_7)_6] \cdot 10H_2O$	(22)
$Ba_2H_4[Ge(W_2O_7)_6] \cdot 14H_2O$	(22)
$(CN_3H_5)H_8[Ge(W_2O_7)_6]$	(171)
$Cs_3HGeW_{12}H_{40} \cdot 5H_2O$	(86)
$Hg_8Ge(W_2O_7)_6 \cdot 5H_2O$	(23)
$Na_7[Ge(W_2O_7)_5 \cdot OH]$	(197)
$K_7Ge(W_2O_7)_5 \cdot 12H_2O$	(23)
$7(CN_3H_5) \cdot GeO_2 \cdot 10WO_3 \cdot 13H_2O$	(23)
$7Ag_2O \cdot 2GeO_2 \cdot 20WO_3 \cdot 6H_2O$	(23)
$3K_2O \cdot 8NH_3 \cdot 2GeO_2 \cdot 20WO_3 \cdot 17H_2O$	(23)
$H_4[GeMo_{10}V_2O_{39}] \cdot nH_2O$	(87)
$H_8[Ge(Mo_2O_7)(V_2O_6)] \cdot 28H_2O$	(87)
$Rb_3H[GeMo_{10}V_2O_{39}] \cdot 1.5H_2O$	(87)
$Cs_3H[GeMo_{10}V_2O_{39}] \cdot 1.5H_2O$	(87)
$(CN_3H_5)_4[GeMo_{10}V_2O_{39}] \cdot 1.5H_2O$	(87)
$(C_5H_5N)_4[GeMo_{10}V_2O_{39}] \cdot 1.5H_2O$	(87)

TABLE 12

Miscellaneous germanium compounds

COMPOUND	REFERENCES	COMPOUND	REFERENCES
$(GeH)_x$	(46)	$Ge(C_{17}H_{33}COO)_4$	(200)
$(GeH_2)_x$	(162, 165, 166)	$BaTiGe_3O_9$	(66)
$Ge(SO_4)_2$	(28, 153)	$[Ge(OH)_6]^{--}$	(21)
$Ge(SO_4)_2 \cdot GeO$	(178)	$Ge(H_2PO_2)_2 \cdot GeCl_2$	(52)
$Ge(CH_3COO)_4$	(166)	$Ge(H_2PO_2)_2 \cdot GeBr_2$	(52)

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