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COMPLEX COMPOUNDS OF GERMANIUM AND ITS STATE IN SOLUTION

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In connection with the increasing interest taken in germanium in the last two decades, many of its complex compounds have been described, particularly in the literature on analytical chemistry, but the available information is extremely limited. In many cases, only the fact of complex formation has been established, and even the composition of the complexes has not been determined. There are very few quantitative data on the stability and other properties of germanium complexes. The incomplete nature of the experimental material makes it difficult to use for the solution of various theoretical and practical problems in technology, analytical chemistry, geochemistry, etc.

No reviews have been published on the chemistry of germanium complexes. Grinberg's monograph [1] characterises the ability of germanium to form complexes, in relation to its position in the Periodic System. Reviews of the chemistry of germanium [2,3] and textbooks of general chemistry give only fragmentary information.

In the present review we have tried to summarise data on the present state of the chemistry of germanium complexes. Since complex formation is closely related to the state of an element in solution and since this question has been insufficiently studied for the case of germanium, we shall examine this problem at the same time.

The chemistry of germanium complexes has certain characteristic features. In accordance with its position in the Periodic System, germanium, which is an analogue of silicon and tin, shows in its complex compounds the dual nature characteristic of an element intermediate between metal and non-metal. As in the case of silicon, complexes with oxygen-containing ligands are more characteristic of germanium, but in the formation of these complexes in aqueous medium, germanium in many cases behaves as a cation, like tin. Like silicon, germanium readily forms heteropoly-acids with molybdenum and tungsten. On the other hand, germanium, like tin, belongs to the hydrogen sulphide analytical group, and forms thio-complexes, although these are less stable than those of tin. Complexes with nitrogen-containing ligands, in the form of addition compounds of the tetrahalides, are known both for germanium and for silicon and tin, but only germanium and tin, unlike silicon, form complexonates.

The characteristic coordination number of quadrivalent germanium is 6, and that of bivalent germanium 4.

State of Germanium in Aqueous Solution

Bivalent germanium is formed by the reduction of GeO_2 with hypophosphorus acid in hydrochloric-acid solution [4,5]. According to Pugh [6], the acidic properties of bivalent germanium hydroxide are similar to those of tervalent arsenic hydroxide. According to the data of Everest and Terrey [7], however, bivalent germanium hydroxide exhibits no acidic properties. These authors concluded that the acidic properties attributed to $Ge(OH)_2$ were due to the presence of quadrivalent germanium. The suggestion of Hantzsch and Carlsohn [8] that equilibrium exists between bivalent germanium hydroxide and germanic acid is not now taken into consideration.

As a result of the ease of hydrolysis and the tendency to form complexes, Ge^{2+} cations do not exist in aqueous solution, although they have been found in crystalline germanium diiodide [9].

Aqueous solutions of GeO_2 contain the ions of metagermanic acid H_2GeO_3 and pentagermanic acid $H_2Ge_5O_{11}$. The ratio between them is determined by the pH of the solution and the total germanium concentration [10,11]. At a GeO_2

concentration less than 0.01 M, only the ions of metagermanic acid are present; the ions of pentagermanic acid are present in more concentrated solutions [12,13] at definite pH values. Everest and Salmon [14,15] showed by the ion-exchange method that in the pH range 6.9–9.4 the only germanium ion is the singly charged ion of pentagermanic acid $HGe_5O_{11}^-$. Above and below these pH values, depolymerisation of the pentagermanate ions takes place with the formation of metagermanic acid. It has been suggested [16,17] that germanium forms not pentagermanate ions but complex heptagermanate ions $HGe_7O_{16}^{3-}$ and $H_2Ge_7O_{16}^{2-}$. Brintzinger [18] showed that in strongly alkaline solutions (2.5 M KOH) quadrivalent germanium is present in the form of $[Ge(OH)_6]^{2-}$ ions. On the basis of all these data, Dhar [19] established the following ranges of existence of various ions of germanic acids in solution —

$$HGeO_3^- \rightleftarrows HGe_5O_{11}^- \rightleftarrows HGeO_3^- \rightleftarrows [Ge(OH)_6]^{2-},$$
$$pH\ 6 \leftrightarrow pH\ 9.4 \leftrightarrow pH\ 11 \leftrightarrow pH > 13.$$

It has not been possible to isolate germanic acids in the solid state from solution. The isolation of pentagermanic acid, reported by Carpeni and Tchakirian [10,20], was not confirmed by later work [21].

The following values are accepted [22] for the ionisation constants of metagermanic acid: $K_1 = 2.6 \times 10^{-9}$ and $K_2 = 1.9 \times 10^{-13}$ at 20°, in accordance with Pugh's measurements [23]. Later, other workers obtained for the first ionisation constant of metagermanic acid values close to that given above: Gulezian and Müller [24] between 1.0×10^{-9} and 3.0×10^{-9} at 25°, Carpeni [25] 0.79×10^{-9} at 12°, and Lourijsen-Teyssèdre [12] 0.89×10^{-9}. The thermodynamic value of the first ionisation constant of H_2GeO_3 according to Antikainen [26] is 1.86×10^{-9} at 25°. The values of K_1 for metagermanic acid, obtained by Roth and Schwarz [27] (1.2×10^{-7} at 18°) and by Schwarz and Huf [28] (0.5×10^{-7} at 20°) are too high, owing to the inadequate purity of the germanium dioxide used. The value obtained by Carpeni [25] for the second ionisation constant of metagermanic acid (2×10^{-13} at 12°) agrees with the value given by Pugh.

Antikainen [26] established that temperature has an unexpectedly marked influence on the ionisation of metagermanic acid. Thus with increase in temperature from 10° to 45°, the first ionisation constant of H_2GeO_3 increases by a factor of almost 20. This marked effect of temperature is not observed with weak acids [29]. Increase in temperature apparently leads to the polymerisation of metagermanic acid and the formation of a certain quantity of the stronger polygermanic acids.

Antikainen [30] also observed the formation of polygermanic acids in the preparation of concentrated (0.23 M) solutions of germanium dioxide by means of a cation-exchange resin. According to him, these solutions contain singly charged di- and tri-nuclear oxoanions of germanium. The polynuclear peroxo-complex of germanium $[Ge_n(H_2O_2)_4]^-$, where $n = 2–3$, is formed by the action of hydrogen peroxide on 0.01–0.02 M solutions of metagermanic acid [31]. The equilibrium constant for the formation of the mononuclear peroxo-complex is $K = [Ge(H_2O_2)_2^-]/[HGeO_3^-][H_2O_2]^2 = 48$. The stability of certain polyoxoanions has been examined by Yatsimirskii [32].

Tchakirian suggested that metagermanic acid, like boric, phosphoric, and arsenious acids, reacts under certain conditions with the sulphates, chlorides, or nitrates of alkali and alkaline earth metals to form complex acids [33].

Hardly any work has been done on quadrivalent germanium cations. De Carvalho and Lederer [34] merely point out the possibility that cationic forms of germanium may exist in acidic solutions. On the basis of a comparison of the solubilities of germanium dioxide and arsenic sesquioxide, Pugh [35] suggested that the basic dissociation constant of GeO_2 should be less than that of As_2O_3, which is close to 10^{-14}. Everest and Salmon [14], on the basis of experiments with cation-exchange resins, concluded that no germanium cations are present in solution in the pH range 7–1. The statement [36] that the Ge^{4+} cation is formed at pH 3.36–3.31, according to the equilibrium $GeO_3^{2-} + 6H^+ \rightleftharpoons Ge^{4+} + 3H_2O$, is without foundation and has been criticised [37,38]. Ge^{4+} cations probably appear as one of the equilibrium forms only in strongly acid solutions.

The existence of germanium cations in weakly acidic solutions is confirmed by observation and by everyday analytical practice. Germanium lies in the same group of the Periodic System as tin, titanium, zirconium, and hafnium, for which MO^{2+}, $M(OH)_2^{2+}$, and M^{4+} ions are known. Like tin and zirconium, germanium reacts with phenylarsonic acid and its derivatives [39]. In its reactions with sulphides and *o*-hydroxyquinones, the behaviour of germanium is analogous to that of tin. The existence of the germanyl ion $Ge(OH)_2^{2+}$ or GeO^{2+} is confirmed by the formation of germanyl cyanoferrate(II) $[Ge(OH)_2]_2[Fe(CN)_6]$ or $(GeO)_2[Fe(CN)_6].2H_2O$ when potassium cyanoferrate(II) is added to an acidic solution of sodium germanate [40].

Migration experiments have made it possible to detect germanium cations in weakly acidic solutions and to establish the approximate ranges of their existence [41]. The germanium dioxide concentration chosen for these experiments excluded the possibility of formation of colloidal particles of GeO_2. The results show that germanium cations are produced at pH ~ 7 and exist together with anions of germanic acids. The relative quantity of germanium cations increases with decrease in pH. These data have been subsequently confirmed by experiments on the sorption of germanium by cation-exchange resins (KU-1, KU-2, and Wofatit No. 4) and anion-exchange resins (AV-16, AV-17, AV-27) on columns [42] and under static conditions [43].

State of Germanium in Inorganic Acid Solutions

Everest [44] suggests that bivalent germanium exists in acidic solutions only in the form of complex compounds. Hydrohalic acids contain acido-complexes $HGeX_3$, whose salts $MGeX_3$ (where M is an alkali metal and X chlorine, bromine, or iodine) have been isolated [45,46]. The complex phosphate $Ge_3(PO_4)_2.2GeHPO_4$ [44] and complex halogenohypophosphites of germanium $Ge(H_2PO_2)_2.GeCl_2$, $Ge(H_2PO_2)_2.GeBr_2$, and $3Ge(H_2PO_2)_2.GeI_2$ [44,46] have been prepared.

The state of quadrivalent germanium in solutions of inorganic acids has been studied considerably more fully. In hydrofluoric acid, quadrivalent germanium readily forms six-coordinated complexes. Tananaev and Avduevskaya [47] established in the GeO_2–HF–H_2O system the existence of complex acids having the compositions $H_2[GeOF_4].2H_2O$ and $H_2[GeF_6].2H_2O$, which were isolated in the solid state. These acids are stronger than hydrofluoric acid; hydrogen hexafluorogermanate H_2GeF_6, which is formed at higher HF concentrations, is the strongest acid. No complexes of higher fluorine content are formed. Fluorogermanate complexes are more stable than fluorosilicate complexes. Thus alkali-metal hexafluorogermanates dissolve in

100% HF without decomposition[48], unlike the hexafluorosilicates, which decompose under these conditions with the liberation of silicon tetrafluoride[49]. Comparison of the relationship between the stability of the fluoro-complexes and the position of the element in the Periodic System[50] shows that the stability in general increases with decrease in the radius of the central ion, but this relationship is complicated by the competing influence of the bond between the complex-forming ion and oxygen. The competing influence of the bond with oxygen is clearly shown for the fluoro-complexes of the Ge–Si pair.

Cryoscopic studies[52] in 0.01–0.2 M solutions of K, Rb, and Cs hexafluorogermanates show that a molecule of the salt forms three ions. The solubilities of K_2GeF_6, Rb_2GeF_6, and Cs_2GeF_6 in water at 25° are 0.0221 M, 0.0167 M, and 0.0471 M respectively.

Hexafluorogermanates are decomposed completely by alkalis. The hydrolysis of hexafluorogermanates in water is autocatalytic and takes place by a solvolytic dissociation mechanism[51]:

$$GeF_6^{2-} + H_2O \rightleftarrows Ge(OH)F_5^{2-} + HF.$$

This reaction is followed by rapid hydrolysis of the $Ge(OH)F_5^{2-}$ ion to GeO_2.

According to the data of Benoit and Place[53], the hexafluorogermanate complex is not formed in acid solutions. Depending on the HF concentration, mononuclear hydroxofluorogermanate complexes $Ge(OH)_jF_i$ are formed, where the maximum value of i is 5. The overall stability constants of the complexes $Ge(OH)_jF_5^{(j+1)-}$ and $Ge(OH)_jF_4^{j-}$, determined in 0.5 M $HClO_4$, are $\beta_5' = (8.8 \pm 0.2) \times 10^8$ and $\beta_4' = (2.0 \pm 0.3) \times 10^7$ respectively. The fluoro-complexes of germanium, like the tin complexes, are not decomposed by hydrogen sulphide, and this is used in analysis to separate germanium from arsenic[54]. The sorption of hydrogen fluorogermanate on an anion-exchange resin is also used for this separation[55].

The fluorination of metallic germanium by the action of ClF_3 in liquid hydrogen fluoride leads to the formation of hydrogen hexafluorogermanate, which can then be isolated as the silver salt[56]. As in the case of aqueous solution, the fluorogermanate complex in liquid hydrogen fluoride is more stable than the fluorosilicate complex, and is readily formed.

The ease of formation of the fluoro-complexes also extends to the fluoro-organometallic compounds of germanium and the fluorogermanes. Thus the addition of KF to trifluoromethyltrifluorogermane CF_3GeF_3 in aqueous solution gives a sparingly soluble precipitate of $K_2[CF_3GeF_5]$. Clark and Willis[57] studied this reaction and suggest that in aqueous solution CF_3GeF_3 forms ionised molecules of the type $CF_3Ge(OH)_2F_3^{2-}$ and $CF_3Ge(OH)_3F_2^{2-}$ as a result of hydrolysis. The hydrolysis is readily reversible, and the addition of KF to the solutions precipitates $K_2[CF_3GeF_5]$. Monofluorogermane GeH_3F reacts with ammonia at -78° to give[58] the addition product $GeH_3F.2NH_3$, which decomposes at 25° to NH_3 and $[GeH_3.NH_3]F$. The latter compound decomposes only at 180°.

The hexachlorogermanate complex is formed much less readily than the hexafluorogermanate complex. The hexachlorogermanates of caesium[59–61] and rubidium[60,61] are formed under special conditions. After unsuccessful attempts[62] tetramethylammonium hexachlorogermanate $[N(CH_3)_4]_2GeCl_6$ was also prepared[60]. Attempts to isolate free hydrogen hexachlorogermanate H_2GeCl_6 were unsuccessful[59,61,63]. Nevertheless, the maximum on the solubility curve for germanium dioxide in hydrochloric acid[64] and the mechanism of the extraction of germanium from hydrochloric-acid solutions[65,66] are attributed to the existence of this acid as one of the equilibrium forms. It is claimed that the decrease in the solubility of GeO_2 after the maximum[64], and the decrease in the partition coefficient for germanium[65,66], are due to the decomposition of H_2GeCl_6 and the separation of $GeCl_4$ as a separate phase with increase in the concentration of hydrochloric acid.

A study of solutions of germanium dioxide and tetrachloride in hydrochloric acid using ion exchange led Everest and Harrison[61] to the conclusion that in 6–9 M HCl an equilibrium exists between metagermanic acid or germanium dioxide and the chlorogermanate anions $GeCl_5^-$ or $GeCl_6^{2-}$. Intermediate acido-complexes of the type $[Ge(OH)_xCl_{5-x}]^-$ and $[Ge(OH)_xCl_{6-x}]^{2-}$, where x = 3 or 4, take part in the equilibrium. It is suggested that the singly charged acido-complex is more likely to be formed. The intermediate acido-complex is the chief form of germanium compound in 6.5–9 M HCl. At HCl concentrations lower than 6.5 M, hydrolysis of the intermediate complex takes place with the precipitation of germanium dioxide. Increase in the hydrochloric acid concentration above 9 M leads to chlorination of the intermediate acido-complex with the separation of germanium tetrachloride as a separate phase. The quantity of $GeCl_6^{2-}$ ions taking part in the equilibrium could not be determined by the ion-exchange method. By measuring the ultraviolet absorption of hydrochloric-acid solutions of germanium tetrachloride, Angerstein and Davidson[67] found that photometrically measurable quantities of $GeCl_6^{2-}$ ions appear in 6–7 M HCl and reach a concentration of 80% in 12 M HCl; with increase in the HCl concentration above 12 M, the concentration of hexachlorogermanate ions increases, but does not reach 100%. This last fact agrees with the data of Benoit and Clerc[68], who consider, moreover, that formation of the $GeCl_6^{2-}$ ion in anhydrous HCl is unlikely. In this, germanium differs from tin, since the $SnCl_6^{2-}$ ion is formed under these conditions[62].

Using the ion-exchange method, Nelson and Kraus[69] obtained results which indicated that the formation of anionic complexes of germanium is negligible at HCl concentrations in the range 0.1–4 M. This was confirmed by later work in the same laboratory[70]. With increase in the HCl concentration, the degree of complex formation increases, giving no maximum up to the highest HCl concentrations and passing through the range of formation of the uncharged $GeCl_4$ species without the separation of germanium tetrachloride as a separate phase. The lack of agreement in this respect with other data[61,64–66,67–69] is most probably due to differences in the germanium concentrations in the solutions. Thus in the experiments of Nelson and Kraus[69] at low germanium concentrations, $GeCl_4$ could not separate as an individual phase because of its dissolution, so that all the germanium remained in solution; increase in the HCl concentration produced hexachlorogermanate ions, which were more strongly absorbed by the resin. The solubility of $GeCl_4$ in hydrochloric acid has been discussed by Knyazev[71].

Brauer and Müller[64] assume that hydrobromic acid solutions contain uncharged complex species of the type $Ge(OH)_{4-x}Br_x$, where x may have values of 1–3, depending on the acid concentration. The existence of a small quantity of species of this type in hydriodic acid is also possible.

The solubility curve for germanium dioxide in sulphuric acid shows a slight maximum at an H_2SO_4 concentration of 15 N, but this is not explained by Brauer and Müller. The formation of a more soluble sulphato-complex of germanium may be assumed in this case. In general, however, the tendency of germanium to form complexes with sulphate ions is slight. This can be seen from the fact that the solubility curve for GeO_2 in sulphuric acid differs little from the corresponding curves for perchloric and nitric acids, in which germanium is thought to form no anionic complexes. Other workers also observed no formation of complexes by germanium in nitric-acid solutions [72,73].

On the basis of the results of a study of ion exchange in germanium dioxide solutions containing sulphate and phosphate ions, Everest and Salmon [15] suggest the existence of complex ions $[GeO_2(SO_4)]^{2-}$ and $[HGeO_2(PO_4)]^{2-}$ in the pH range 7–9. In a study of the reaction of soluble germanium dioxide with orthophosphoric acid, Everest [44] established that in 35–50% H_3PO_4 a compound is formed corresponding to the formula $Ge(HPO_4)_2$; this compound is readily hydrolysed and dissolves in concentrated H_3PO_4. Avduevskaya and Tananaev [74] consider that the dissolution of germanium dioxide in concentrated orthophosphoric acid is due chiefly to complex formation. They therefore regard the new phase with composition $GeO_2.P_2O_5.2H_2O$, which they isolated, as hydrogen diphosphatogermanate, having the formula $H[Ge(OH)(HPO_4)_2]$ or $H_2[GeO(HPO_4)_2]$.

Germanium Heteropoly-Acids

On the basis of the work of Pfeiffer [77], who supplemented the theories of Miolati and Rosenheim, the first workers to study germanium heteropoly-acids [68,75,76] ascribed to these compounds the formulae $H_8[Ge(Mo_2O_7)_6]$ and $H_8[Ge(W_2O_7)_6]$. Subsequent work on the preparation, structure, and properties [80,83–92] of germanium heteropoly-acids was related to their extensive use in analysis [93]. The compounds prepared included molybdovanadogermanic [78–83] and tungstovanadogermanic [83–92] heteropoly-acids, in which isomorphous replacement of molybdenum or tungsten in the heteropoly-anion by vanadium takes place. This is confirmed by electron-diffraction studies of molybdovanadogermanic heteropoly-acids [88].

Heteropoly-acids of germanium, like those of other elements, are formed in acid medium. The optimum acidity for molybdogermanic acid is 0.2–0.5 N H_2SO_4. Once formed, the germanium complexes are stable in more acidic solution; thus molybdogermanic acid does not decompose [94] even in 3.3 N H_2SO_4. The ternary heteropoly-complexes of germanium are less stable than the binary complexes. The acidity of stable solutions of molybdovanadogermanic acid [95] corresponds to 0.20–0.28 N.

Germanium heteropoly-acids also decompose with increase in the pH of the solution.

Tchakirian and Souchay [86] found that at pH 3.2 dodecatungstogermanates begin to undergo conversion to undecatungstogermanates. The conversion is almost complete at pH 4.2. At pH > 7.3, undecatungstogermanates decompose completely to germanates and tungstates. The molybdenum heteropoly-complexes are less stable than the corresponding tungsten compounds. The undecamolybdogermanate anion exists in the pH range 3.5–4.2; at pH > 4.2, this compound begins to decompose to germanate and molybdate [96], the reaction being complete at pH 5.4. Unlike molybdosilicic acid, molybdogermanic acid [97] resembles molybdophosphoric acid [98] in its ready decomposition by hydroxy-carboxylic acids, e.g. citric acid.

Spectrophotometric and electron-diffraction study of the blue products of the reduction of germanium heteropoly-acids showed that the heteropolyanions and the blue compounds formed from them have the same structure [87,88]. In the blue anion, part (approximately one-quarter) of the molybdenum or tungsten is present in the quinquevalent state but occupies the same position in the complex as in the original heteropoly-acid. The blue colour is produced as a result of the intensification of the polarisation effect, due to the presence, in the molecule of the compound, of ions of the element with different valencies. In contrast to the previously accepted view [99,100] that the molybdenum or tungsten coordinated in heteropoly-acids exhibits an increased oxidising power, it was shown [87,88] that the redox potentials of the Mo^{VI}/Mo^{V} and W^{VI}/W^{V} systems in heteropoly-compounds are not higher but lower than the potentials of uncomplexed molybdenum and tungsten, and that the increased redox potential is shown by the whole complex heteropolyanion. The introduction of vanadium into the heteropolyanion considerably raises the redox potential of the latter [87].

A large amount of practical information, which has been obtained and used chiefly in analytical chemistry [76,78,85,90,101,112], shows that the germanic heteropoly-acids form no more than tetra-substituted salts with simple and complex inorganic and organic bases. This contradicts the views of Miolati, Rosenheim, and Pfeiffer, according to whom germanium heteropoly-acids should be octabasic. The low basicity of molybdenum and tungsten heteropoly-acids was explained successfully by Keggin and his followers [85,113–115] on the basis of X-ray structural measurements. Physicochemical studies established that dodecatungstophosphoric acid is tribasic [116] and that dodecatungstogermanic [91] and dodecatungstosilicic [117] heteropoly-acids are tetrabasic. On the other hand, there are experimental data confirming the high basicity of certain other heteropoly-acids and these data cannot be explained by Keggin's treatment. Thus it has been shown that dodecamolybdoceric [118–120], dodecamolybdothoric [121], and dodecamolybdostannic [122] heteropoly-acids are octabasic.

Babko and Shkaravskii [123] explain the contradiction between the views of Miolati, Rosenheim, and Pfeiffer on the one hand and Keggin on the other in terms of the ratios of the radii of oxygen and the central ions in the heteropoly-complex. With small central ions (radius 0.30–0.56 Å) — Bi^{III}, Si^{IV}, Ge^{IV}, P^{V}, and As^{V} — the compounds should show a coordination number of 4 with tetrahedral configuration of the oxygen environment and a corresponding basicity for the heteropoly-acids of 8 - n, where n is the valency of the central ion. With large central ions having a radius of 0.56–0.99 Å — Sn^{IV}, Ce^{IV}, and Th^{IV} — the octahedron is the more stable, and the basicity of the corresponding heteropoly-acids should be 12 - n. Not all of the facts, however, fit into this scheme: dodecamolybdozirconic [124,126] and dodecamolybdotitanic [125,126] heteropoly-acids are tetrabasic, although the radii of the Ti^{4+} and Zr^{4+} ions are greater than 0.56 Å (0.64 Å and 0.87 Å respectively).

The experimental data and theoretical considerations indicate nevertheless that germanium heteropoly-acids are tetrabasic.

Addition Compounds Formed by Germanium Tetrahalides

The complex-forming properties of germanium tetrahalides are due to the ability of the central atom to fill the *d* level of its outer electronic shell by using the free electron pairs of attached ligands. In the addition products formed by germanium tetrahalides, these ligands are chiefly ammonia [127] and nitrogen-containing bases — hydrazine, piperidine, pyrrolidine [127], ethylenediamine [127,128], 2,2′-bipyridyl [129], 1,10-phenanthroline [130], pyridine [128-130], trimethylamine, *NNN′N′*-tetramethylethylenediamine [131], triethylamine [132,133], and *o*-hydroxyquinoline [128,134]. These addition products are usually readily hydrolysed by water. On the other hand, amines of high molecular weight, e.g. an *N*-dodecyltrialkylmethylamine [135], form stable addition complexes with germanium tetrachloride, and these can be extracted from hydrochloric-acid solutions with non-aqueous solvents.

Addition products are particularly numerous with germanium tetrafluoride, which forms complexes $GeF_4.2L$ and $GeF_4.L$ (here and subsequently L represents a ligand) with compounds containing nitrogen, phosphorus, oxygen, or sulphur [127]. Besides the complexes with the nitrogen-containing compounds listed above, complexes have been prepared with phosphine and trimethylphosphine, with acetone, ethylene oxide, methanol, tetrahydrofuran, and dioxan, with hydrogen sulphide, dimethyl sulphide, methanethiol, and tetrahydrothiophen. These complexes are relatively unstable. It is suggested that the 1:2 complexes have an octahedral structure with *cis*- and *trans*-arrangement of the ligands, and that the 1:1 complexes are polymeric fluorine-bridged structures [127].

Udovenko and Fialkov measured the viscosity [136] and dielectric constant [137] of systems formed by germanium tetrachloride with ethers and esters, and established that in these systems $GeCl_4$, unlike the tetrachlorides of titanium and tin, does not form addition compounds. The lower complex-forming power of germanium tetrachloride compared with $SnCl_4$ and $TiCl_4$ was attributed [136] to the smaller ionic radius of germanium compared with the ionic radii of tin and titanium, and the consequent greater screening of the germanium ion by chloride ions. The greater screening of the germanium ion by chloride ions, compared with the screening by fluoride ions, may also explain the fact that the complex-forming power of $GeCl_4$ is less than that of GeF_4.

Complex Compounds of Germanium with Polyhydroxy-Compounds.

The addition of a polyhydric alcohol or a monosaccharide to a neutral aqueous solution of germanium dioxide leads to a decrease in the pH of the solution as a result of the formation of complex acids which are stronger than simple germanic acids. Tchakirian [33,138], who was the first to describe this phenomenon, assumed that in the case of mannitol a dinuclear complex with a germanium:ligand ratio of 1:1 and the properties of a dibasic acid is formed. Saito [139] found by high-frequency titration and pH and polarographic measurements that in the complex fructosatogermanic acid the germanium:ligand ratio is 1:4, but this was not confirmed by other authors. In addition, a 1:1 complex which is reduced at a mercury electrode is also formed. Contradictory data on the composition of the complexes of germanium with ethylene glycol, glycerol, and mannitol were obtained by Everest and Harrison [140,141] by an ion-exchange method. Antikainen [142,143] established by a differential potentiometric method that germanium forms 1:2 complexes with mannitol, glucose, galactose, mannose, and fructose, and also 1:1 complexes with glycerol and glycols. Antikainen's data were confirmed by pH measurements [144]. It was established that in the presence of excess of glycerol, mannitol, glucose, galactose, and fructose, complex monobasic acids with a germanium:ligand ratio of 1:2 are formed; the thermodynamic ionisation constants of these acids at 25° are 5.05×10^{-6}, 1.21×10^{-5}, 8.35×10^{-6}, 2.39×10^{-5}, and 1.04×10^{-4} respectively. Mannitol [33,138,145-148], fructose [149], and invert sugar [150], consisting of fructose and glucose, are used in analytical chemistry for the alkalimetric determination of germanium.

According to Antikainen [143,151], the ability of polyhydroxy-compounds to form complexes increases in the sequence — ethylene glycol, propylene glycol, butylene glycol, 3-methoxypropane-1,2-diol, glycerol, D-galactose, D-glucose, D-mannose, D-mannitol, and D-fructose. This agrees with the results obtained by other authors [140,152,153]. Antikainen and his coworkers [142,143,151,154,155] determined the formation consists of a large number of complexes of germanium with polyhydroxy-compounds, in order to characterise their relative stability. In the calculations these workers used the apparent ionisation constants of metagermanic acid in the presence of the polyhydroxy-compound and neglected the changes in the activity coefficients of the ions present in the solution with change in the concentration of the polyol, assuming that the latter concentration and the ionic strength of the solution had no influence on the formation constants of the complexes. In fact, however, it has been shown [153] that both the concentration of polyhydroxy-compound and the ionic strength have a marked influence on the formation of polyol complexes of germanium. The thermodynamic constants for dissociation of the diglycerolato-, diglucosato-, digalactosato-, dimannitolato-, and difructosato-germanate complexes, according to the equation $GeL_2^- + m H_2O \rightleftharpoons HGeO_3^- + 2L$, determined with allowance for this influence, have the values 7.85×10^{-2}, 3.54×10^{-2}, 7.64×10^{-3}, 4.04×10^{-4}, and 4.24×10^{-5} respectively at 25°.

Some of the factors influencing the formation of complexes by germanium with polyhydroxy-compounds have been studied [139,151,154,155]. Increase in the number of carbon atoms and hydroxy-groups in the ligand leads to the formation of more stable complexes. Ketoses give more stable complexes than do aldoses. Complexes having the ratio 1:2 are characteristic of polyhydroxy-compounds containing a large number of hydroxy-groups, and the spatial arrangement of the latter is also important. The formation of lactol forms in solution by saccharides decreases their tendency to form complexes. Mutarotation, which changes the spatial arrangement of the hydroxy-groups and depends on the pH of the solution, also influences the formation of complexes. When the saccharide ligand is present in the lactol form, the influence of the number of carbon atoms and hydroxy-groups in less marked than that for an open chain.

Complexes of Germanium with Carboxylic Acids.

Complexes of germanium with tartaric [156-161], tartronic [159], quinic, 1-hydroxycyclopentanecarboxylic [160], malic [157,158,160], mucic [160,161], phenyllactic, bromomandelic, benzilic, 2-hydroxyoctanoic [162], lactic [161,162], gluconic [160,161,163], mandelic [158-160,162,164,165], and oxalic [33,166-168] acids have been described. Acids such as tropic, diglycollic, glyceric,

ascorbic, and γ-hydroxybutyric acids do not form complexes with germanium [160].

Data on the composition of the complexes of germanium with carboxylic acids are often contradictory. Thus the values of the germanium : ligand ratio given by different authors are 1 : 1 and 1 : 2 for tartaric acid, 1 : 1, 1 : 2, and 1 : 3 for lactic acid, 1 : 1 and 1 : 2 for mucic acid, and 1 : 2 and 1 : 3 for mandelic acid. These discrepancies are due to the fact that the compounds formed and the ranges of their existence in solution have been inadequately studied. The tartrato- and oxalato-complexes of germanium have been studied in more detail, because of their use in analysis [169-172].

Everest and Harrison [161] established by an ion-exchange method that a 1 : 1 tartrato-complex of germanium is formed in the pH range 0.78–9; the complex is decomposed completely at pH > 11. With increase in the germanium concentration in a large excess of tartaric acid, a complex having a germanium : ligand ratio of 2 : 3 is formed; an excess of germanium leads to the formation of a 5 : 4 polynuclear complex. Everest and Harrison did not establish the existence of the 1 : 2 tartrato-complex, but the isolation [169] of barium tartratogermanate $Ba_2GeC_8H_8O_{14}.2H_2O$ indicates its existence.

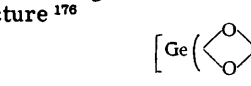
The oxalato-complex of germanium is a dibasic acid; salts of this acid with the organic bases quinine, strychnine, and benzoquinoline have been isolated [33,172-174]. The hexahydrate $H_2[Ge(C_2O_4)_3].6H_2O$ has been obtained in crystalline form [168]. Study of the infrared spectra of solutions of germanium dioxide in oxalic acid confirms that the compound formed is complex [175]. It was found by an ion-exchange method [167] that oxalato-complexes of germanium are not formed in alkaline medium; at pH < 3, complex ions $[Ge(C_2O_4)_3]^{2-}$ are sorbed, together with a small quantity of $[HGe(C_2O_4)_3]^-$ and $[HGeO(C_2O_4)_2]^-$ ions; in the pH range 3–6, and also when the solution contains insufficient oxalate ions, the complexes $[GeO(C_2O_4)_2]^{2-}$ and $[GeO_2(C_2O_4)]^{2-}$ are formed. Solubility studies and measurement of the pH and electrical conductivity [168] in the GeO_2–$H_2C_2O_4$–H_2O system also established the existence, in addition to hydrogen trioxalatogermanate, of an intermediate complex acid having a Ge : ligand ratio of 1 : 2; the ammonium and potassium salts of this acid were isolated.

The stability of the complexes of germanium with carboxylic acid has been little studied. According to Vartapetian [158] the stability increases in the order — lactic, malic, mandelic, and tartaric acids.

Complexes of Germanium with Dihydric Phenols

Germanium dioxide reacts in aqueous solution with simple *o*-dihydroxy-derivatives (catechol, pyrogallol, benzene-1,2,4-triol, naphthalene-2,3-diol, etc.) to form two types of compound — sparingly soluble neutral complexes $GeL_2.2H_2O$, the so-called germanium–diphenols [176], and the soluble complexes H_2GeL_3, termed phenolgermanic acids [177-179] or hydrogen trisdiphenolatogermanates.

Bisarenediolatogermanium complexes are formed in concentrated solutions of germanium dioxide and the dihydric phenol, and are insoluble in organic solvents. The dicatecholatogermanium complex has been assigned the structure [176]



and this has been confirmed by chemical and thermogravimetric analysis [176], by determination of the infrared spectra [180], and by X-ray diffraction studies [181]. The composition $GeL_2.2.5H_2O$ ascribed to this complex [180] does not agree with the above structure.

Bisarenediolatogermanium complexes do not exist in solution but dissociate according to the scheme [176]

$$3\,GeL_2 \cdot 2\,H_2O \rightleftarrows 2\,GeL_3^{2-} + 4\,H^+ + GeO_2.$$

Polarographic, spectrophotometric, and pH measurements have in fact established [182-186] that the only complexes present in germanium dioxide solutions containing dihydric phenols are the corresponding hydrogen trisarenediolatogermanates, which are very strong acids. The thermodynamic second ionisation constants [186] for hydrogen tricatecholatogermanate and tripyrogallolatogermanate at 25° are $(1.85 \pm 0.06) \times 10^{-2}$ and $(2.21 \pm 0.07) \times 10^{-2}$ respectively.

Hydrogen trisarenediolatogermanates are more stable than bisarenediolatogermanium complexes. The formal constants for the formation of the tricatecholato- [185,187], tripyrogallolato- [187], and trithyroninato-complexes [187] were determined without allowance for the ionisation of germanic acid and the corresponding complex acids, and the values do not characterise their true stability. The thermodynamic constants for dissociation of the tricatecholato- and tripyrogallolato-complexes at 25° according to the scheme [188]

$$HGeL_3^- + 3H_2O \rightleftarrows HGeO_3^- + 3H_2L$$

are $(2.16 \pm 0.12) \times 10^{-9}$ and $(0.88 \pm 0.09) \times 10^{-9}$ respectively.

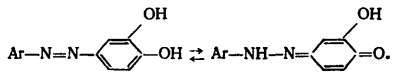
Numerous disubstituted salts of hydrogen trisarenediolatogermanates have been prepared with ammonia, organic bases (pyridine, quinoline, and triphenylmethane dyes), and the complex phenanthrolineiron(II) cation [179]. The formation of phenanthrolinecadmium tricatecholatogermanate $[Cd\,phen_2][Ge(O_2C_6H_4)_3]$ is used for the gravimetric determination of germanium [189], and that of 2,3′-bipyridylium tricatecholatogermanate for the extraction-photometric determination of germanium [190]. The formation of hydrogen tricatecholatogermanate itself is also used in analysis for the volumetric [176,191-193], polarographic [194,195], and amperometric [196] determination of germanium.

Noteworthy complexes are formed by germanium with tannin and humic acids, whose structures are characterised by the presence of one or more aromatic nuclei with two or more phenolic hydroxy-groups. Tannin is of importance in the technology [197] and the analytical chemistry [93,103,198,199] of germanium. In the geochemistry of germanium, the accumulation of the element in coals has been attributed to humic acids. It is suggested that the accumulation is due to the sorption of germanium by humic acids from circulating solutions at the stage when the coal is formed [200-202]. Only preliminary data [203,204] have been given on complex formation by germanium with humic acids, and there are no published data on its complex formation with tannin. This is due to the fact that the individual chemical compounds covered by the general names "tannin" and "humic acids" have been insufficiently studied.

Complexes of Germanium with Hydroxy-Carbonyl Compounds

Coloured or fluorescent complexes with aromatic hydroxyl-containing ligands play an important part in the analytical chemistry of germanium [93] by providing a basis

for photometric methods for its determination. A characteristic feature of these ligands is the presence of a phenolic hydroxyl in the *ortho*- or, less frequently, the *peri*-position relative to a carbonyl (quinonoid) group, or of two phenolic hydroxy-groups *ortho* to one another, together with a group, *para* or *ortho* to one of these, permitting tautomeric conversion of the compound into an *o*-hydroxyquinone, e.g. for derivatives of 3,4-dihydroxyazobenzene:



All compounds of this class can be divided into two types.

A. Compounds already containing an *ortho*- or a *peri*-hydroxy-carbonyl grouping in the molecule.

(1) Triphenylmethane dyes — pyrogallolaurin, pyrogallolsuccinein, catecholphthalein [205-208], Catechol Violet [209], etc.

(2) Xanthen dyes — gallein [205], coerulein [208], and derivatives of 2,3,7-trihydroxy-6-oxoxanthen with aromatic or aliphatic radicals as substituents on the $C_{(9)}$ carbon atom [210-214], including the familiar photometric reagent for germanium 2,3,7-trihydroxy-6-oxo-9-phenylxanthen or phenylfluorone [215-217].

(3) Flavone dyes — 3-hydroxyflavone [3-hydroxy-4-oxo-2-phenylchromen] [218] and its hydroxy-derivatives: 2′,3,4′,5,7-pentahydroxyflavone (morin) [218,219], 3,3′,4′,5,7-pentahydroxyflavone (quercetin), and 3,3′,4′,5,7-pentahydroxyflavone-6-sulphonic acid (quercetinsulphonic acid) [220,221].

(4) Derivatives of 4*H*-pyran, quinoid dyes of vegetable origin (brazilein [205,207] and haematein [205,207,222]).

(5) The tropolone dye purpurogallin [205-208], and also tropolone itself, 3-hydroxytropolone, and 3-aminotropolone [223]. The latter form colourless complexes with germanium.

(6) Hydroxyanthraquinones, containing a hydroxy-group in the *peri*-position to a carbonyl group and reacting with germanium in concentrated sulphuric acid, e.g. quinalizarin, purpurin, 1,2,4,5,6,8-hexahydroxyanthraquinone [39,224,225], the structurally similar monohydroxynaphthacenequinonesulphonic acid [226], and also acetylquinalizarin [227], which, unlike quinalizarin, reacts with germanium in weakly acidic medium.

(7) Colourless compounds reacting with germanium to form complexes which are luminescent under ultraviolet radiation. These compounds contain a hydroxy-group *ortho* to a nuclear carbon atom attached to a side-chain containing a carbonyl group — 2,4-dihydroxyacetophenone [228], 2,4,6-trihydroxyacetophenone, 2,4-dihydroxy-ω-methoxyacetophenone, 2-hydroxy-4-methoxybenzaldehyde, 2,4-dihydroxybenzaldehyde, and salicylaldehyde [229]. A fluorescent compound with germanium is formed also by benzoin [229], which contains a keto–enol group between two phenyl radicals.

(8) Dihydroxy-derivatives of naphthaquinone [230] — spinazarin, spinochromes B1 and M1, etc.

B. Compounds with an arene-*o*-diol structure, capable of tautomeric conversion into *o*-hydroxyquinones.

(1) *o*-Dihydroxyazo-compounds [205-208] — azobenzene-3,4-diol, 3′,4′-dihydroxyazobenzene-4-sulphonic acid, 1-phenylazonaphthalene-2,3-diol, etc.

(2) *o*-Dihydroxy-derivatives of triarylmethanols [205-208] — 3,4-dihydroxytriphenylmethanol, 3,4-dihydroxynaphthyldiphenylmethanol, 4,4′-bisdimethylamino-3″,4″-dihydroxytriphenylmethanol, etc.

(3) Schiff bases from dihydroxy-aldehydes and oximes and phenylhydrazones of the latter [205,207] — 3′,4′-dihydroxybenzylideneaniline, the phenylhydrazone and oxime of protocatechualdehyde, etc.

(4) 3,5-Dinitrocatechol [205,207].

(5) Anthocyanidins containing hydroxy-groups on the $C_{(3')}$ and $C_{(4')}$ atoms — delphinidin and cyanidin [208] — and also the *o*-dihydroxychromenols with similar structures [231].

(6) Dihydroxy-derivatives of 2-oxochromen — 6,7-dihydroxy-4-methyl-2-oxochromen (methylaesculetin) [230] and 7,8-dihydroxy-4-methyl-2-oxochromen [232].

(7) Dihydroxy-derivatives of benzofuran [208] — 6,7-dihydroxy-3-oxobenzofuran, gallorubin, and 3-*p*-dimethylaminobenzylidene-6,7-dihydroxybenzofuran.

(8) Oxazine dyes — gallocyanine and Modern Violet [205-208].

All these compounds react with germanium in acid medium, forming soluble or insoluble coloured or, less frequently, colourless or fluorescent complexes. These complexes have been insufficiently studied and for many of them even the composition has not been determined. Tchakirian and Bévillard [205-207,233,234] suggested that the reaction of *o*-hydroxyquinone compounds of type A with germanium is due to the presence of the *o*-hydroxyquinone group in the molecule, whereas the reactivity of arene-*o*-diol compounds of type B results from preliminary tautomeric conversion to the *o*-hydroxyquinone form. Later, Bévillard [208,235] abandoned this viewpoint and concluded that these compounds react with germanium in the arene-*o*-diol form to give complexes of the hydrogen phenolatogermanate type [179] having the composition H_2GeL_3, and that the quinonoid structures, even if present in the ligand molecule, do not take part in the interaction with germanium.

Kimura et al. [230], who could not establish that reaction takes place between germanium and partly and completely methylated phenylfluorone and 2-hydroxy-1,4-naphthaquinone, came to the same conclusion. Kimura's proof, however, is not convincing, since methylated phenylfluorone in general is unable to form cyclic complexes with metal ions, and for the hydroxynaphthaquinone an equivalent structure is that of 4-hydroxy-1,2-naphthaquinone in which this compound is also unable to form cyclic complexes.

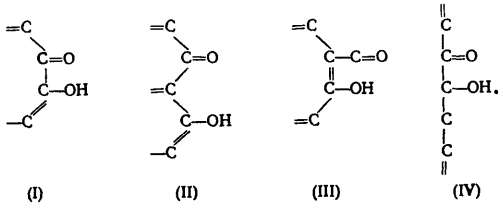
Subsequent studies have established that the complexes of germanium with compounds of type A have a composition different from that of hydrogen phenolatogermanates. Thus for trihydroxyxanthones a Ge : L ratio of 1 : 2 was found [214,236,237]. It was shown that the trihydroxyxanthones containing both groups — *o*-diol and *o*-hydroxyquinonoid — react with germanium [238] and also with zirconium [238], antimony [238], scandium [238], and molybdenum [239] as *o*-hydroxy-carbonyl compounds. Similar proof was obtained for the complexes of germanium with Catechol Violet [240] and purpurogallin [241]. Chloranilic acid, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, which is capable of undergoing tautomeric conversion into 3,6-dichloro-4,5-dihydroxy-1,2-benzoquinone, reacts with germanium in the *o*-hydroxy-

quinonoid form [242], forming three coloured complexes with Ge : L ratios of 1 : 1, 1 : 2, and 1 : 3. Kanno [218,243] established that only those hydroxyflavones which have an unsubstituted hydroxy-group on the $C_{(3)}$ carbon atom are capable of reacting with germanium in acid medium: i.e. the reactive group is the $C_{(3)}-C_{(4)}$ *o*-hydroxy-carbonyl group. Analogous results had been previously obtained in a study of the reaction of hydroxyflavones with zirconium [244-246].

The reactivity of *o*-dihydroxychromenols towards germanium and other metals is attributed to tautomeric conversion of the dyes into anhydro-bases having the structure of *o*-hydroxyquinones [231]. It was finally shown [247] that the *o*-diols 3′,4′-dihydroxyazobenzene-4-sulphonic acid and 3,4-dihydroxynaphthyldiphenylmethanol react with germanium in dilute solutions of strong acids only after conversion into the *o*-hydroxyquinonoid forms, to give complexes GeL and GeL_2 (in the case of the first compound) or only GeL (with the second compound).

The composition GeL has been established for the complexes of germanium with hydroxyanthraquinones, formed in sulphuric acid medium [39].

The groups of atoms which, in the molecules of hydroxy--carbonyl compounds, react with germanium in acid medium can be represented by the fragments: (I) — compounds of type A (1)–(5) and (8), and all compounds of type B in the tautomeric form; (II) — A (6); (III) — A′ (7), *o*-hydroxy--phenones and *o*-hydroxy-aldehydes; and (IV) — A (7), benzoin.



(I) (II) (III) (IV)

The groups (I)–(III) are parts of the conjugated bond systems of aromatic nuclei, and in the coloured compounds they are also parts of the chromophoric conjugation systems. The group (IV) of benzoin is not part of an aromatic ring, but the influence of the conjugation systems of the two phenyl radicals on either side of the group gives it an "aromatic" character. In the reaction with the ions of germanium or other multivalent metal, five-membered [groups (I) and (IV)] or six-membered [groups (II) and (III)] cyclic complexes are formed, in which the metal atom is joined to the oxygen atoms of the ligand by non-equivalent bonds — by an ionic bond or almost ionic covalency to the phenolic oxygen, and by a donor–acceptor bond to the carbonyl oxygen. The complexes in which the metal ion replaces only one hydrogen atom in the ligand molecule during ring formation are more stable than the cyclic complexes formed by the dihydric phenols, whose formation involves the replacement of two hydrogen atoms. According to the law of mass action, the influence of hydrogen ions on the equilibrium for the formation of the complex is proportional to the first power of the concentration in the first case and to the square of the concentration in the second case. The nature of the complex-forming bond in the phenylfluoronates of germanium and other metals was examined by Sano [248].

In the colourless addition compounds formed by germanium tetrahalides with acetylacetone and other β-diketones [249], the ligand is present in the keto–enol form; this is to some extent analogous to the case of the complexes formed by germanium with aromatic *o*-hydroxy-carbonyl ligands.

Nitrogen- and Sulphur-Containing Complexes of Germanium

Apart from the addition products formed by germanium tetrahalides, complexes of germanium with compounds containing nitrogen and sulphur are few in number. It is generally considered that the formation of complexes containing a Ge–N bond is not characteristic of germanium. It has been established, however, that germanium forms a complex with 1,1′-bianthrimide in sulphuric acid [250], analogous to the complex formed by boron with the same reagent, and a complex with ethylenediaminetetraacetic acid (H_4Y) in weakly acidic solutions [251], suitable for quantitative analysis. A complex with H_4Y of composition $GeY.2H_2O$ has been isolated in crystalling form by the action of $GeCl_4$ on hot Na_2H_2Y solution [258].

The naturally occurring sulphides of germanium — argyrodite, germanite, and renierite — and also double sulphides [252] of the type $CuS.GeS_2$ are undoubtedly complex compounds. The potassium and sodium thiogermanates $M_6[Ge_2S_7].9H_2O$ isolated by Schwarz and Giese [253] have the structure of dinuclear complexes. Formation of the dinuclear complex thiogermanate $K_2Ge_2S_5$ is used for the iodometric determination of germanium [172]. Among organic thio-compounds, toluene-3,4-dithiol (dithiol), which forms a complex dithiolate, has been described as a reagent for germanium [254]. Germanium reacts with the thiol analogues of hydroxy-carboxylic acids — mercaptoacetic, mercaptosuccinic, and mercaptopropionic — to form di- and tri--basic complex acids [259], whose ionisation constants have been determined.

Potassium and sodium selenogermanates $M_6[Ge_2Se_7].9H_2O$, analogous to the corresponding thiogermanates, have been prepared [255].

Complex-Forming Germanium Ions.

It is evident that for complexes of bivalent germanium, the complex-forming ion is Ge^{2+}, even if it exists in insignificant quantities only as one of the equilibrium forms. It is much more difficult to reach conclusions regarding the nature of the complex-forming ions of quadrivalent germanium, since our knowledge of the state of quadrivalent germanium in solution is inadequate.

It may be taken as established that in the reactions with polyhydroxy-compounds and dihydric phenols, the complex--forming ion is the metagermanate ion $HGeO_3^-$, since complex formation takes place at germanium concentrations which exclude the formation of polymeric forms either in acidic medium or in alkaline medium, where no germanium cations are formed. This agrees with the situation for the analogous complexes formed by boron and arsenic with polyhydroxy-compounds, where the complex-forming ions are assumed to be the singly charged ions of boric and arsenious acids [256]. It may be assumed that, in the reactions with hydroxyanthraquinones in concentrated sulphuric

acid, the complex-forming ion is a germanium cation, since it has been shown for the analogous reactions of boron [257] that the complex-forming ion is a boron cation. In the same way, it may also be assumed by analogy that germanium cations take part in the reactions with *o*-hydroxy-carbonyl compounds and ethylenediaminetetraacetic acid in acidic medium. It is probable that in all complex-formation reactions in acid medium the complex-forming ions are germanium cations, but there are as yet no data for characterising these cations.

It is evident that a successful quantitative study of the chemistry of germanium complexes is possible only if the forms of the components of the complex-formation equilibrium are known. Thus determination of the basic dissociation constants of GeO_2 and of the ranges of existence of the individual cations is of primary importance in the chemistry of germanium.

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THE DIELS–ALDER REACTION WITH MOLECULAR OXYGEN AS DIENOPHILE

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I. INTRODUCTION

The present review surveys the reactions of conjugated dienes with molecular oxygen to form peroxides.

It has been established that transannular epidioxides are produced by the photosensitised oxidation of alicyclic, aromatic, and heterocyclic homoannular 1,3-dienes. Such dienes undergo the Diels–Alder reaction with maleic anhydride and other dienophiles. Therefore the photooxidation of homoannular 1,3-dienes to transannular epidioxides can be regarded as a photochemical Diels–Alder reaction in which oxygen acts as dienophile.

It has recently been found that homoannular 1,3-dienes are oxidised to transannular epidioxides by molecular oxygen in an excited singlet state. This must be regarded as a diene synthesis with singlet oxygen. It is probable that excited singlet oxygen is the active intermediate also in photosensitised oxidations with molecular oxygen.

The ability of homoannular 1,3-dienes to form transannular epidioxides at low temperatures, and also the ease with which some of the latter rearrange into more stable oxygen compounds or break down again with the liberation of oxygen, suggest that some biological oxidation processes may involve the intermediate formation of transannular epidioxides. This hypothesis has recently been confirmed experimentally.

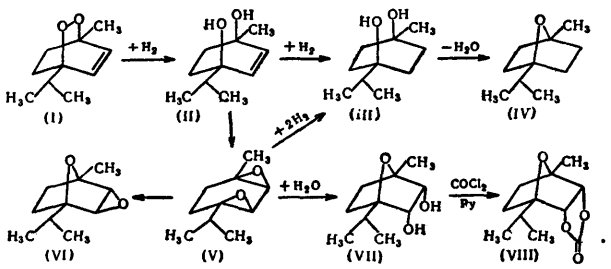
The paper covers the literature published up to 1st March 1965.

II. REACTION OF MOLECULAR OXYGEN WITH ACYCLIC AND ALICYCLIC 1,3-DIENES

1. Ascaridole

In 1908 Gütig[1] isolated an oily substance, having the composition $C_{10}H_{16}O_2$ and boiling at 80–84° (4–5 mm), from chenopodium oil (the essential oil of a species of wormwood, *Chenopodium ambrosioides* var. *anthelminticum*), which possesses an anthelmintic (vermifugal) action. This substance, which is the active principle of chenopodium oil, was termed *ascaridole*. In 1912 Wallach[2,3] established that ascaridole was 1,4-epidioxy-*p*-menth-2-ene (I): catalytic hydrogenation with colloidal palladium gave the previously unknown *p*-menthane-*cis*-1,4-diol (III), dehydration of which with oxalic acid yielded the known 1,4-epoxy-*p*-menthane (IV).

It must be noted that at that time ascaridole was the only known organic compound having a transannular epidioxide structure.



Study of the chemical properties of ascaridole gave interesting results. Catalytic hydrogenation with platinum